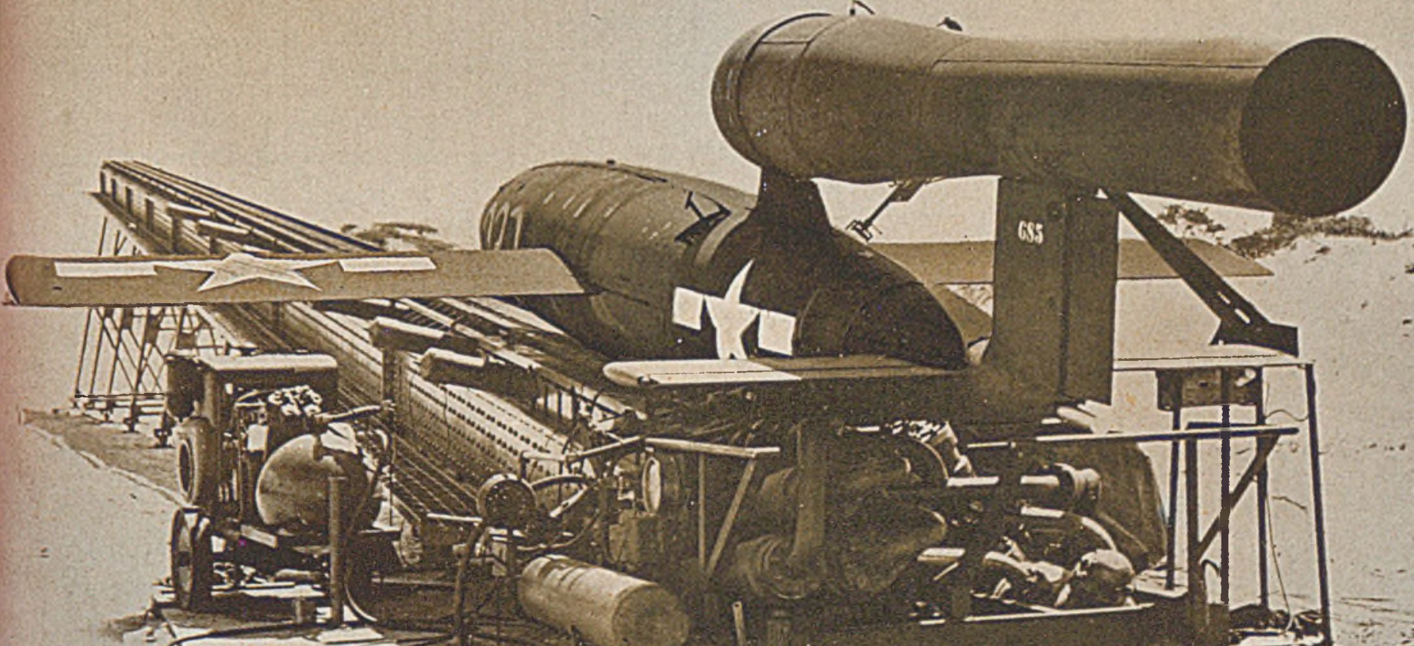
INDUSTRIAL AND ENGINEERING Chemistry



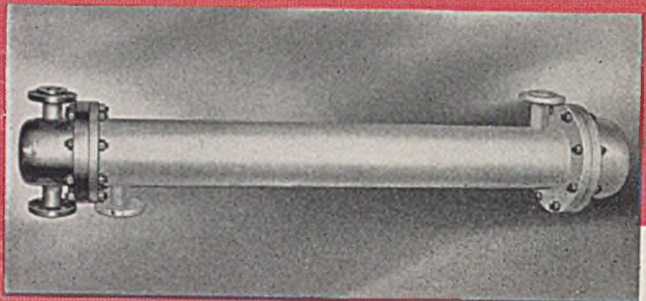
FEBRUARY 1946

NEW! Pfaudle

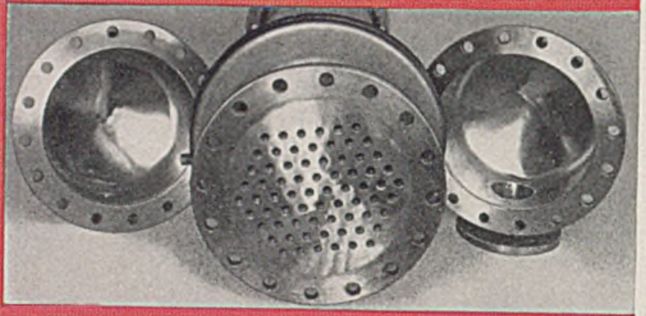
TUBULAR CONDENSE

and

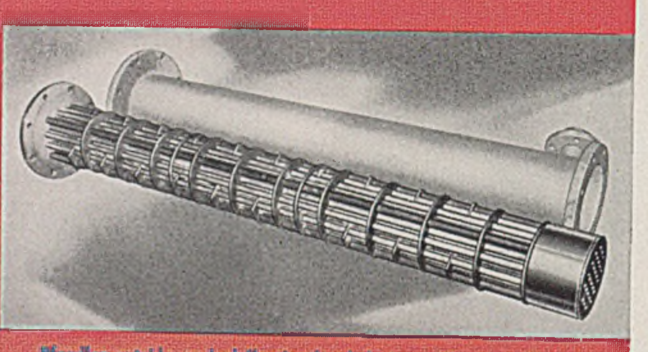
HEAT EXCHANGERS



Pfaudler internal floating head design with removable tube bundle and shell



Pfaudler fixed tube sheet design with non-removable tube bundle



Pfaudler outside packed floating head design with removable tube bundle

New Pfaudler Heat Exchanger Manual No. 837, gives complete specifications as well as:

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INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

VOLUME 38, NUMBER 2 • ISSUED FEBRUARY 15, 1946 • CONSECUTIVE NUMBER 3

• • •

37,600 copies of this issue printed

• • •

We acknowledge with thanks the action of Merco-Nordstrom Valve Company in releasing the front cover of this issue for editorial purposes.

The cover shows an American buzz bomb. Its place there is to call attention to an article in this issue on the research behind one of three powerful chemical mixtures investigated as propellants. For more information see Bellinger and co-authors, page 160, and As We See It, advertising section, page 65.

Departments

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

Technical Articles

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

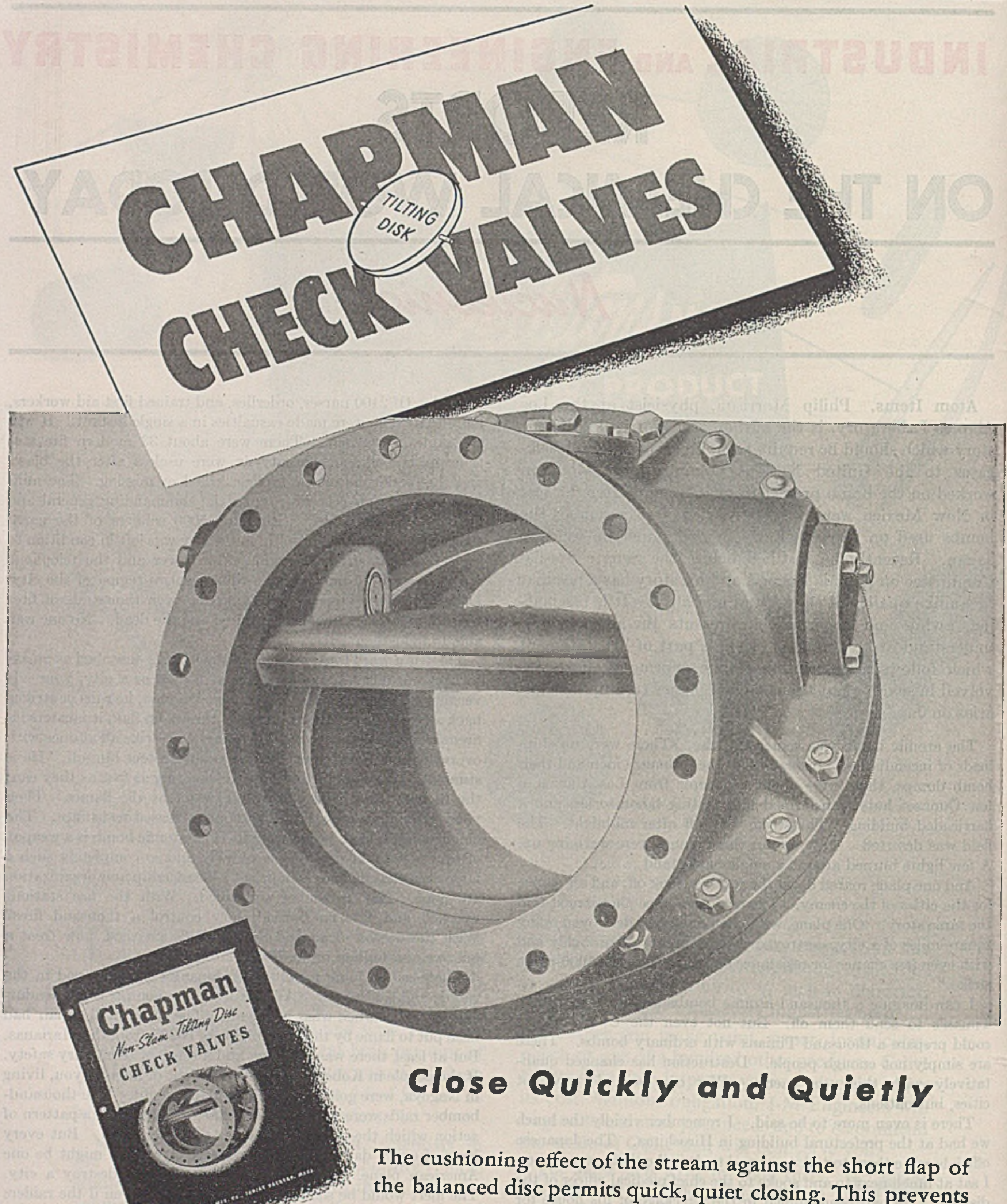
Nucleonics

Atom Items. Philip Morrison, physicist at the Los Alamos Laboratory, is the author of an intriguing horror story which should be required reading, especially for delegates to the United Nations Organization. Morrison worked on the bomb project from 1942, and after the test in New Mexico went to the Marianas to assemble the bombs used on Japan. Early in September he went to Japan. Recently he testified before the Senate Special Committee on Atomic Energy, and his story has a peculiar dreamlike quality of clarity and unreality. It is fascinating, awful, and inspiring; it presents the alternative—understand or be doomed. Here is part of his statement which follows a description of the enormous efforts involved in sending out thousands of planes to drop incendiaries on Japan:

> The atomic bomb was something else. There were no shiploads of incendiaries. Instead of all the ordnance men and their bomb dumps, there were about 25 people from Los Alamos, a few Quonset huts transformed into testing laboratories, and a barricaded building. The strike took off after midnight. The field was deserted. Only two or three planes were warming up. A few lights burned around a single hard-stand . . . . .
>
> And one plane roared down the runway, took off, and set course for the cities of the enemy. The reconnaissance photos next told the same story. One plane, with one bomb, had destroyed many square miles of a city, destroyed them even more thoroughly and with even less chance for resistance or escape than the 1000-plane strike.
>
> I can imagine a thousand atomic bombs and an airport like Tinian's to send them off. But not even the United States could prepare a thousand Tinians with ordinary bombs. There are simply not enough people. Destruction has changed qualitatively with this new energy. War can now destroy not cities, but nations.
>
> There is even more to be said. I remember vividly the lunch we had at the prefectural building in Hiroshima. The Japanese officials came there to talk to us and to describe their experiences. I sat at lunch next to and spoke to the chief medical officer of the district. He had been pinned in the wreckage of his house for several days after the explosion. He lived a little more than a mile from the point of impact, and was still wearing splints. His assistant had been killed, and his assistant's assistant. Of 300 registered physicians, more than 260 were unable to aid the injured. Of 2400 nurses, orderlies, and trained first aid workers, more than 1800 were made casualties in a single instant. It was the same everywhere. There were about 33 modern fire stations in Hiroshima. Twenty-six were useless after the blast, and three-quarters of the firemen killed or missing. The military organization was destroyed; the commanding general and all his staff were killed, with some 5000 soldiers of the garrison of 8000. Not one hospital in the city was left in condition to shelter patients from the rain. The power and the telephone service were both out over the whole central region of the city. Debris filled the streets, and hundreds, even thousands of fires burned unchecked among the injured and the dead. No one was able to fight them . . . . .
>
> There is a word for this kind of attack; it is described as an attack of saturation. If you strike at a man or a city, your adversary protects himself. If you attack a man, he runs or strikes back at you; if you attack a city, it throws up flak, it musters its firemen, it treats the wounded. But if you strike all at once with overwhelming force, your enemy cannot protect himself. He is stunned. The flak batteries are all shooting as fast as they can; the firemen are all busy throwing water at the flames. Then your strike may grow larger without increased resistance. The defenses are said to be saturated. The atomic bomb is a weapon of saturation. It destroys so quickly and so completely such a large area that defense is hopeless. Leadership and organization are gone. Key personnel are killed. With the fire stations wrecked and firemen burned, how control a thousand fires? With the doctors dead and the hospitals smashed, how treat a quarter of a million injured?
>
> There is one more novelty. A Japanese official stood in the rubble and said to us: "All this from one bomb; it is unendurable." We learned what he meant. The cities of all Japan had been put to flame by the great flights of B-29's from the Marianas. But at least there was warning, and a sense of temporary safety. If the people in Kobe went through a night of inferno, you, living in Nagoya, were going to be all right that night. The thousand-bomber raids were not concealed; they even formed a pattern of action which the warwise Japanese could count on. But every hour of every day above any Japanese city there might be one American plane. And one bomber could now destroy a city. The alert would be sounded day and night. Even if the raiders were over Fukuoka, you, in Sendai, a thousand miles north, must still fear death from a single plane. This is unendurable.
>
> When the bomb is detonated in the middle of a city, it is as though a small piece of the sun has been

(Continued on page 8)

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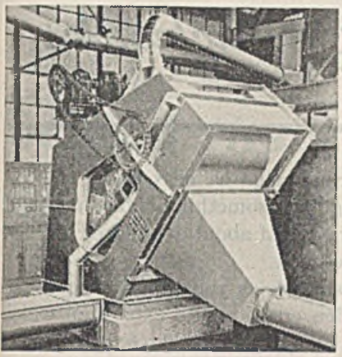

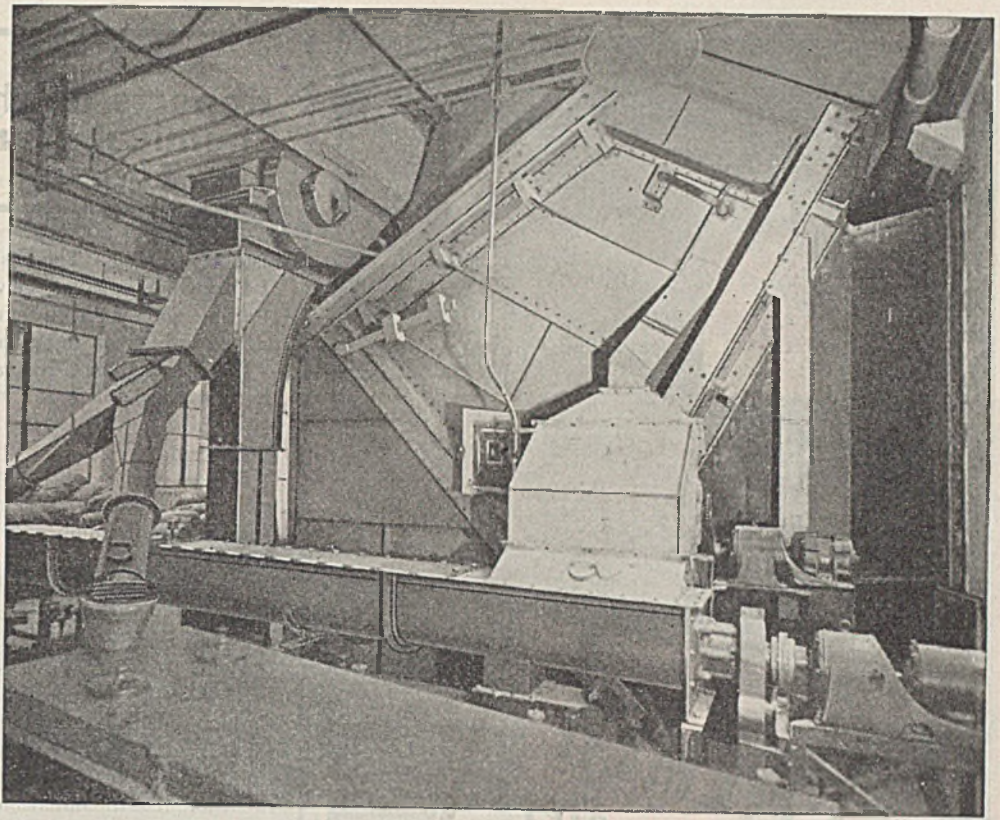

Above: The new Link-Belt Multi-Louvre Dryer-Cooler, first announced o the trade about a year ago. *Right:* Same equipment in use at A. E. Staley Mfg. Co., Decatur, Ill. In foreground s discharge spout through magnetic separator into an L-B screw conveyor. Also shown is an L-B Bulk-Flo elevator with two-way chute to a set of creens. Other types of Link-Belt coneyors are also used throughout this ew plant.

How Staley Uses L-B Multi-Louvre to Dry and Cool Soybean Flakes

Advantages of Multi-Louvre Dryer-Cooler at A. E. Staley Mfg. Co.

Compactness. One Multi-Louvre dryer-cooler serves in place of a number of other units otherwise required. Great saving of floor space.

Cleanliness. Unit is fully enclosed. Any dust is collected in cyclone dust collectors.

Economy, both in first cost of installation and in operation. Low horse power requirements. Also saves floor space for other use.

Freedom from Condensation and subsequent dripping on floors.

Prevention of Balling of material through ondensation.

Elimination of Any Pockets and corners n which the product might lodge and become rancid.

● Seeking an improved method of cooling large flows of spent soybean flakes without having a multiplicity of equipment, the engineers who laid out the A. E. Staley Mfg. Company's large new solvent extraction plant at Decatur, Ill., came to Link-Belt.

Taking into consideration the large cooling capacity required and certain other conditions, a Link-Belt Multi-Louvre Dryer-Cooler was installed, with highly satisfactory results. (For smaller capacity, a Link-Belt Roto-Louvre unit might have been recommended.)

The Multi-Louvre Dryer-Cooler applies the well-known Link-Belt Roto-Louvre principle of operation, and is especially suited to the drying or cooling of materials that do not require long retention periods. It is extremely compact in both small and large capacities, requires but little power for its operation, and effects substantial economies in drying or cooling many materials.

The louvres of the Multi-Louvre unit move the material gently through an air stream to secure uniform results with minimum degradation of the product. When used as a dryer, this method permits relatively high air temperatures to be utilized without danger of overheating or case-hardening the product, clogging, etc.

Get the details on this and other Link-Belt dryers and coolers. Ask your nearest Link-Belt office to have a Materials Handling Engineer call on you.

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DRYERS AND COOLERS
DRYING PROCESS ENGINEERING

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

Nucleonics

instantly created. There is formed what we have called the ball of fire, which is a hot, glowing mass something about one-third of a mile across, with a temperature of about a hundred million degrees Fahrenheit in the center of it.

The effects from this small sun are as you would expect. In the first place, there is a sudden creation and expansion which pushes away, with terrible violence, the air that once occupied this region.

This air, shocked into motion, as we say, moves just like a blast wave from a great explosion of TNT. We often measure the effectiveness of a bomb in tons of TNT equivalent.

This pushing air creates an enormous pressure, even a great distance away. Behind the wave of pressure, which travels rapidly through the air, there come great winds, 500 to 1000 miles per hour, winds which damage and destroy all structures . . . . .

There are two more effects. At the instant of the explosion there is emitted from this small sun not only the great push through the air, the violent blast, which is the violent explosion—there is not only the concentrated heat which you would expect from being close to the sun, there was also a great amount of radiation, like the radiation used by doctors, like the x-ray radiation used for the treatment of cancer . . . . .

Even more striking than the damage to buildings is the great number of casualties. Very few people were in shelters, because there was evidently no large bomber raid. Virtually all the people in the streets within almost a mile were instantly and seriously burned by the great heat of the bomb. These burns covered all the exposed flesh, sometimes even clothing caught fire and burned the wearer fatally.

I remember seeing one man, a patient, who had worn a railway worker's uniform. This uniform, in Japan, is a dark serge with an insigne to designate his grade. This man wore, as insigne, a kind of a cross-shaped emblem over the left breast.

His whole body was burned very badly and blackened, with the exception of the region under this cross. That was because the white clothing passed the heat somewhat less than the dark clothing did. The dark clothing absorbed the heat and caught fire and burned him . . . . .

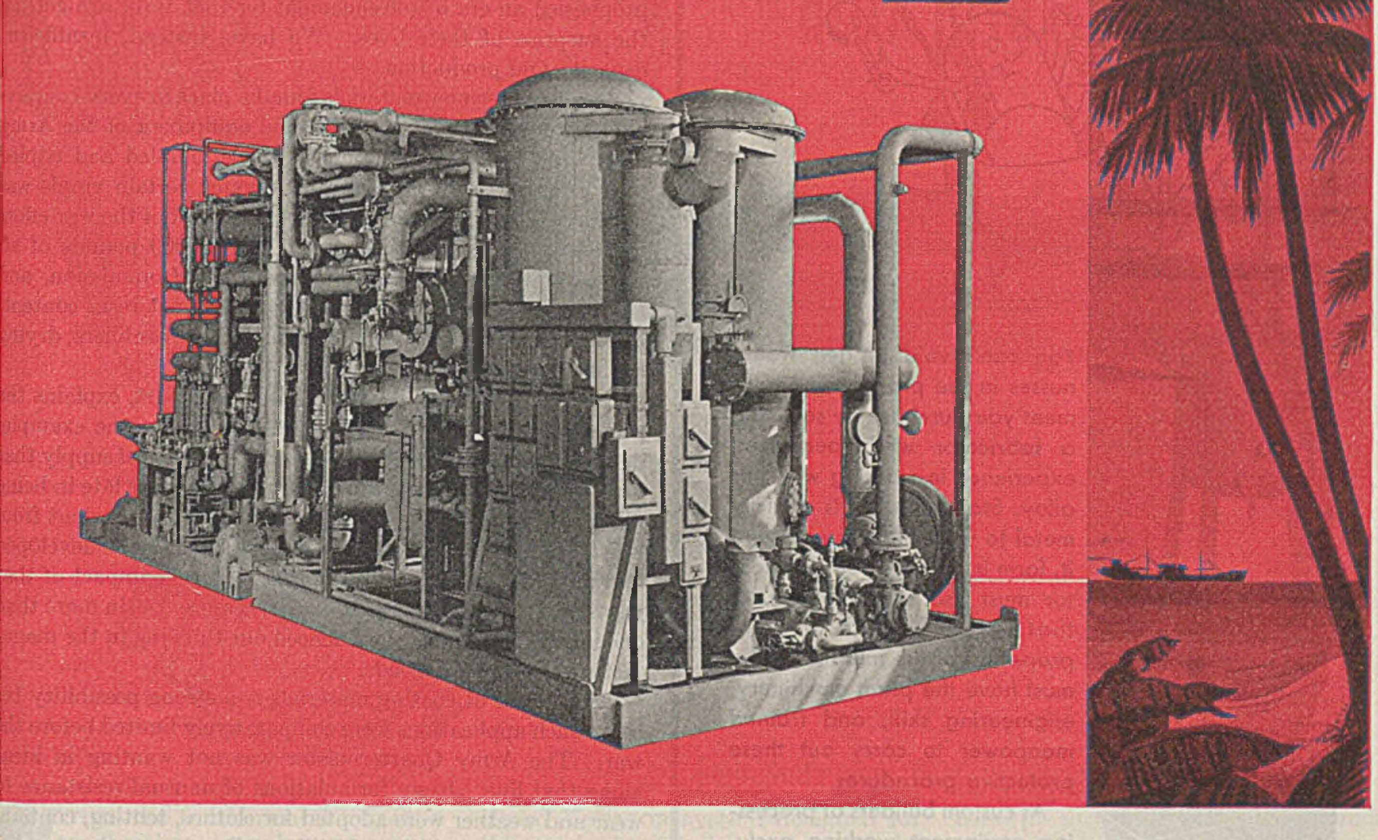
People inside buildings were not burned by the flash, but were for the most part killed or seriously injured by falling walls and beams. Caught in the wreckage of their homes, many were burned to death by the secondary fires. Those fires resulted from combustion material set ablaze after hundreds of stoves had been overturned; this was in addition to the fires started by the bomb itself.

Of these people within a thousand yards of the blast, about one in every house or two—perhaps 5 or 10 per cent—escaped death from blast or from burn. By chance these people were screened from the heat of the bomb by some object too light or too strong to kill them by falling upon them. Many literally crawled out of the wreck of their homes relatively uninjured. But they died anyway. They died from a further effect, the effects of radium-like rays emitted in great number from the bomb at the instant of the explosion. This radiation affects the blood-forming tissues in the bone marrow, and the whole function of the blood is impaired. The blood does not coagulate, but oozes in many spots through the unbroken skin, and internally seeps into the cavities of the body . . . . .

The white corpuscles which fight infection disappear. Infection prospers and the patient dies, usually 2 or 3 weeks after the exposure. I am not a medical man, but like all nuclear physicists I have studied this disease a little. It is a hazard of our profession. With the atomic bomb, it became epidemic.

(*Continued on page 10*)

Behind *the global high-sign*



Girdler's global carbon dioxide plant

ORCHIDS to The Coca-Cola Company for an outstanding morale-building accomplishment in bringing the familiar COKE to Amercans in so many far away places. We are proud of our contribution, in urnishing this "package" carbon dioxide plant, designed and contructed by Girdler for overseas duty with COCA-COLA.

Capable of producing 300 pounds of high-purity liquid carbon dioxide per hour, the plant is only 9 feet wide, 22 feet long, 11 feet high. It was shipped virtually intact, in two sections, ready for use upon arrival at any destination. It has been moved with the Armed Forces from place to place in the Far East and will probably be in Tokyo when you read these lines.

Portable and semi-portable plants of this type have been developed by Girdler in a number of standard designs and capacities.

Girdler offers processes for *gas manufacture, purification, separation, and dehydration.* Consult Girdler about your problems concerning *hydrogen sulphide, carbon monoxide, carbon dioxide, inert and controlled atmospheres, natural gas, refinery gases, liquid hydrocarbons, hydrogen, nitrogen.* Originators of the *Girbotol Process.*

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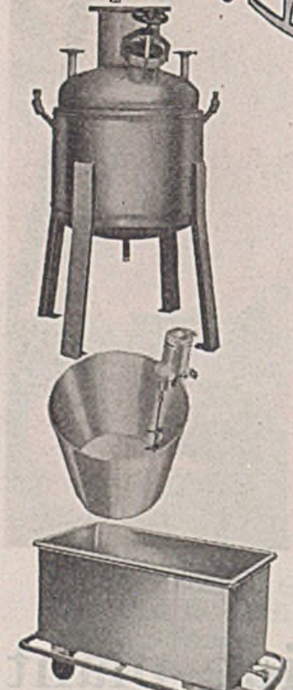

I. & E. C. Reports on the Chemical World Today

Commerce and Industry

Postwar Upset. We were not so certain during the war that plastics manufacturers would be able to find peacetime markets for even half of the potential production which had been built up by heavy military demands. The elder J. P. Morgan's sage observation that no reliable business forecasts could be made for more than three months ahead is now amply borne out in the resins and plastics field, and those who prophesied an era of retrenchment for that trade are getting the surprise of their lives. We have, instead, insufficient capacity and production.

Because these new materials found a place in every conceivable bit of clothing, armament, and equipment of the Army and Navy, resin production had to be doubled and tripled over prewar years. Capacity for making certain vinyls was increased as much as ten times. At the peak of the war effort in 1944 the industry turned out 784,137,000 pounds of all plastic materials, according to the Tariff Commission, and these figures are compiled on the basis of net resin content, meaning that they do not include such things as fillers, drying agents, dyes, or plasticizers.

Reviving normal outlets, for the most part, explains the present urgent plastic requirements. To cite one example, demand for cast phenolics is so greatly in excess of supply that orders for radio cabinets are two to three months late in being filled. But the industry is also benefiting to an extent from hundreds of new military applications which were developed and put into actual use during the war. The impact of that wartime research, much of it under pressure, has in more than one instance profoundly influenced our thinking in the manufacture of consumer goods.

Greater use of coating materials is a strong possibility because such applications were comparatively limited before the war. The Army Quartermaster was not wanting in ideas along that line. Resin formulations of unusual resistance to wear and weather were adopted for clothes, tenting, containers, and various articles of utility. Ponchos made of nylon fabric were coated with vinyl, and gun coverings were produced from polyethylene, one of our newest materials.

"Armor" processed from a heavy textile of glass fibers and polyester contact-type resin, strong enough to stop shell fragments and reduce casualties about 10%, is another of the less publicized military resin applications with many promising possibilities in industry. In this product layers of glass cloth are placed in cross lamination and heat-pressed with resin into an extremely tough, resistant material.

Instead of overcapacity the plastics industry faces a problem of underproduction and, hence, is making expenditures of $102,000,000 to enlarge its facilities during 1946 and 1947. Most of this amount will be spent in erecting or installing facilities for the manufacture of molding materials. Thermoplastic production will get first attention, and by the second quarter of 1946 it is estimated that supplies in this group will be expanded some 150% over that of the last quarter of 1945. Increases of about 10% are contemplated for cellulose ester materials, and new equipment for polystyrene molding powder should increase the output of that material 135% early in 1946.

(Continued on page 12)

This close shave puts profits into processing

WITHIN the fundamental VOTATOR mechanism, revolving scraper blades constantly shave the heat transfer surface clean. The film of material which customarily inhibits heat exchange never gets a chance to accumulate. Combined with continuous flow under pressure, suitable agitation, and closed construction, this gives you the world's fastest, most profitable heat transfer and processing operation for many kinds of viscous liquids.

Aluminum stearate lubricating grease for example. The continuous, closed VOTATOR system designed for this product safely heats the material from room temperature to some 300 degrees in 1½ minutes, cools it again in the same fraction of time.

Variations of the VOTATOR are achieving similar record-breaking, money-making results in the processing of lard, photographic emulsions, margarine, shaving cream, printing ink, textile printing gums, fruit puree, waxes and polishes. If your processing problem falls into one of these categories, plans are ready for a tried and proved VOTATOR installation certain to put production on a more profitable basis.

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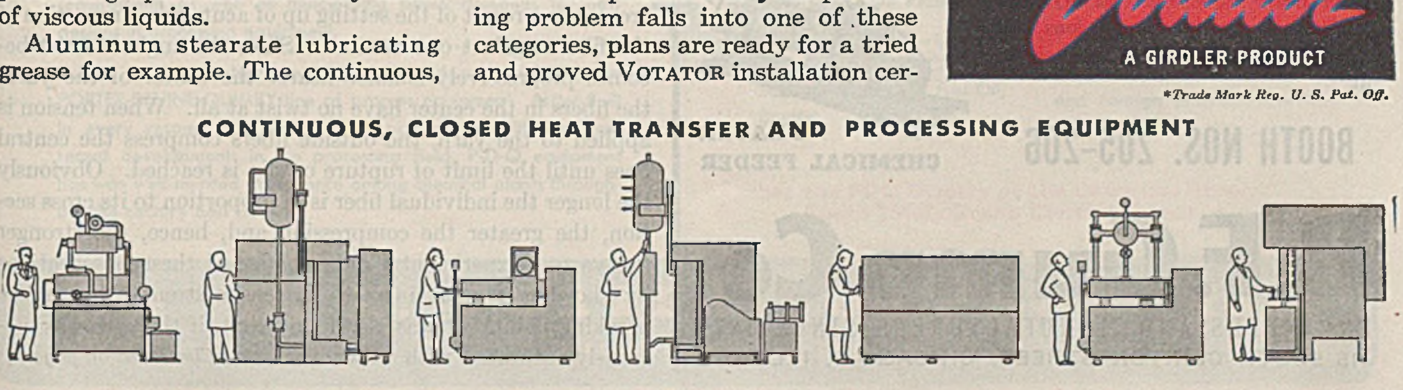


I. & E. C. Reports on the Chemical World Today

Commerce and Industry

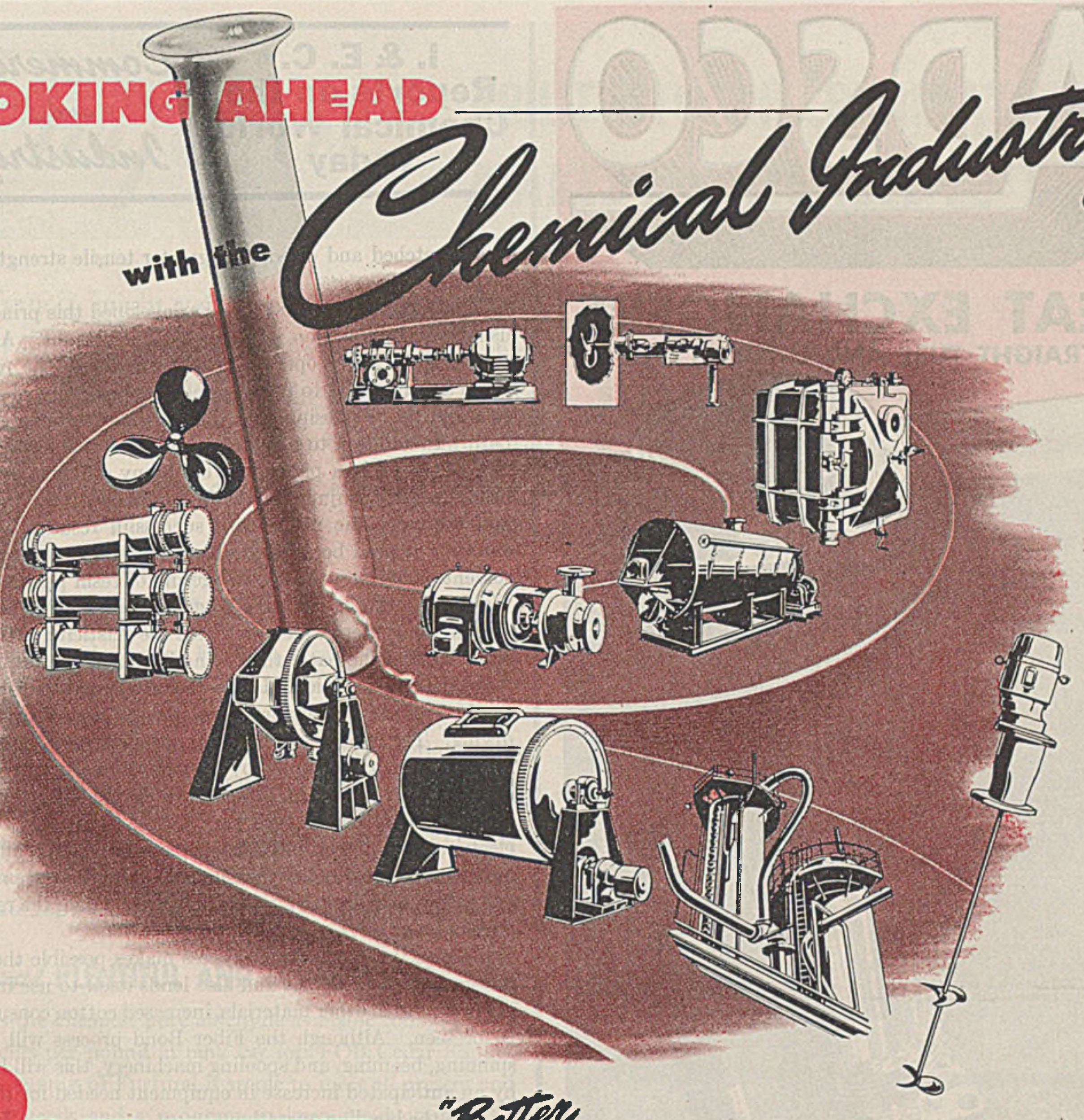
Demands necessitating enlarged output are also reported in acrylic molding powder, ethylcellulose, polythene, and nylon molding material. Substantial increases have already been effected over 1944 in vinylidene chloride, while facilities appear ample in urea and melamine adhesive and laminating products. One manufacturer, however, is extending his processes for melamines.

Resin manufacturers meanwhile are beset with raw material shortages. Supplies of wood flour are insufficient for the manufacture of phenolic molding materials, and considerably more cellulose acetate flake is needed, according to the Plastic Materials Manufacturers Association, Inc. At this writing the most serious strike ever to hit the steel industry threatens to choke off tar acids and other coke-oven and coal-tar chemicals needed by industry. H. S.

New Strength for Cotton. A 60-ton modern tank could be suspended from a cotton rope of one square inch cross section if the full potential strength of cotton could be utilized. The problem of increasing the tensile strength of cotton is that of preventing the slippage of one cotton fiber along another parallel fiber in a yarn or roving. A step has been taken toward the ultimate solution of this problem with the announcement of a new process originated at the Dan River Mills. This will be done by drying and setting a resin-bonding agent in the cotton yarn while it is under tension near the breaking point. Eliminated are the spinning, spooling, beaming, twisting, and cabling steps used in the conventional method of yarn manufacture. In addition the new Fiber Bond method will produce a yarn with a tensile strength 50 to 70% greater than that produced by the present method. Such "tack welding" of one fiber to another will be accomplished in equipment marketed by Walter Kidde & Company, Inc.

Previous approaches to the problem of increasing cotton's tensile strength were directed along two basic lines, biochemical and physical. Essentially biochemical efforts were devoted to the production of plants that would yield cotton of a longer staple by studying the effect of climate and soil upon the characteristics of the fiber. It has been long known that the tensile strength of a group of cotton fibers is increased by giving them a twist, and around this principle the operations of spinning and twisting have been developed. There is a limit, however, to what twisting can do; an optimum angle of twist is soon reached after which the tensile strength decreases as a result of the setting up of acute shearing action of the fibers against one another. Since the angle of twist becomes progressively smaller nearer the center of the yarn, the fibers in the center have no twist at all. When tension is applied to the yarn, the outside fibers compress the central ones until the limit of rupture or slip is reached. Obviously the longer the individual fiber is in proportion to its cross section, the greater the compression and, hence, the stronger the yarn. Experimental data confirmed these observations by showing a great increase in tensile strength before the breaking point. It was also found that, if the yarn was previously saturated with water and *(Continued on page 14)*

LOOKING AHEAD with the Chemical Industry



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How well this is being accomplished is demonstrated by the PORTER-DEVINE-QUIMBY line of process equipment. *Better-Built* in every respect and designed in accordance with the most recent developments in the processing field, P-D-Q equipment has won well-merited acceptance among chemical plants throughout this country and abroad.

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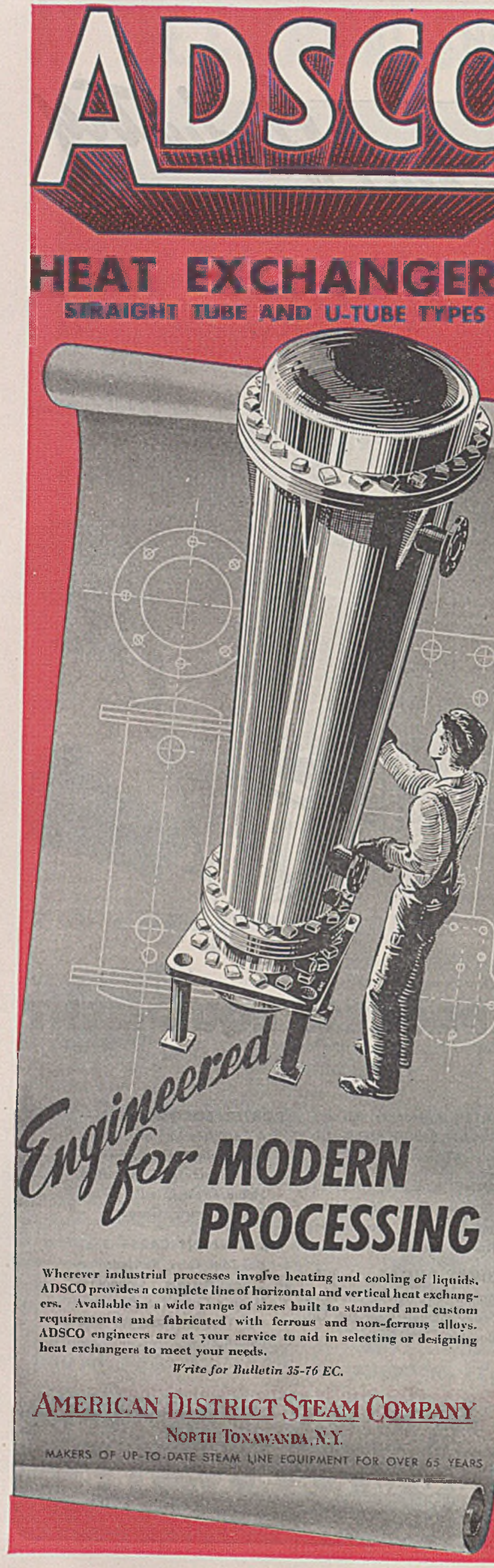


I. & E. C. Reports on the Chemical World Today

Commerce and Industry

then stretched and dried, this greater tensile strength could be preserved.

The Dan River process further developed this principle by using a resin emulsion in water as the saturant. After the conventional sliver operations are completed, the roving is given a slight twist to provide necessary mechanical strength to stand the processing, and then it is led through the resin bath. In addition to furnishing the resin, this bath can also be used to apply a pigment dye. Many different dyes have been used in conjunction with hundreds of thermosetting and thermoplastic resins with successful results. A water emulsion is used because complete solution of the resin in a solvent would prevent the staggering of resin particles along the fiber; on heating, this staggering provides the desired tack-welding effect which preserves the elasticity of the yarn. After leaving the bath, the roving is passed over a roll to remove the excess liquid and collected on a spool which becomes the feed for the second part of the process, that of tensing and drying. The tension can be set at any previously determined figure within close limits by a unique device employing a spring-loaded arm. At present the drying operation is accomplished by passing the yarn over a grooved, two-faced, electrically heated grid which sets the resin, scrapes off foreign matter, and polishes the yarn surface. However, this method of heating and drying may be changed pending the results of development work now being done.

Because the Fiber Bond process makes possible the use of low-grade raw materials and also lends itself to use in blending cotton with other materials, increased cotton consumption is foreseen. Although the Fiber Bond process will obviate spinning, beaming, and spooling machinery, this will be offset by an anticipated increase in equipment needed for the steps prior to the bonding operation. R. L. D.

Sugar, Raw Material. Sugar, cane and beet, is primarily a food which the world consumes to the extent of 35,000,000 tons annually, but it is also a raw material with many strikingly unusual industrial uses. To the dietician, sugar is the carbohydrate which helps in the digestion of other carbohydrates. To the chemist, sugar is a valuable commercial substance found in many compounds. The Sugar Research Foundation, which has sponsored such research, tells us that of all the pure organic chemicals produced in the United States, sugar is quantitatively far in the lead.

The manufacture of sorbitol and mannitol as reduction products from glucose and fructose is familiar. Less known is the fact, determined through research, that sucrose and its hydrolysis products may be used in making phenolic or alkyd type resins. Sugar and its derivatives have actual and potential uses in a long list of other industrial applications which start with acetone and wind up with yeast culture.

Sugar enters the preparation of boiler cleaning flux, cement manufacture, insecticides and fungicides, embalming fluid, mirrors, pharmaceuticals and photographic fluids, calcium glutinate, electrodes, some types of synthetic rubber, tire patches, penicillin, motor fuel, and

(Continued on page 18)

Furfural's ABILITY TO DISCRIMINATE MAKES IT VALUABLE TO YOU

FURFURAL might very well be called the chemical with the high I.Q. That's because it seems to use an inherent intelligence in picking its solutes. These unique selective solvent properties have contributed to economical and efficient production in many fields.

The use of Furfural as a selective solvent is outstanding in:

1. Lubricating Oil Refining
2. Synthetic Rubber
3. Glyceride Oils
4. Wood Rosin

OTHER USES FOR VERSATILE *Furfural*...

Pre-eminent as is the use of Furfural because of its selective solvent properties, this versatile aldehyde is gaining new adherents because of its other properties, too.

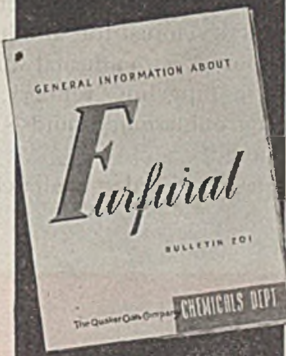
Other uses of Furfural growing in importance continuously, are as a dispersant in resinoid-bonded abrasive wheels, dyes, lacquers, varnish removers, etc.; as a resin former and plasticizer in the manufacture of phenolic and non-phenolic resins; as a fungicide and bactericide, and as a highly reactive intermediate for the production of many organic compounds.

Furfural PLENTIFUL AND ECONOMICAL...

Furfural is the cheapest pure aldehyde available today. It sells for 9½ cents per pound in tank car lots FOB Cedar Rapids, Iowa. The supply of Furfural is ample to meet all present and anticipated needs and a program to keep production facilities ahead of increasing demands is already in operation.

Furfural's PERFORMANCE WARRANTS YOUR INTEREST...

Furfural's performance on so many fronts justifies your investigation of its possibilities for your particular needs. You are invited to call on our Technical Staff to help you in evaluating this chemical for your proposed applications. A little time spent in Furfural exploration now may repay you in shortening time and lessening costs in the manufacture of your product. A sample of Furfural will be sent you when requested on your letterhead.



GENERAL INFORMATION ABOUT
Furfural
BULLETIN 201
The Quaker Oats Company CHEMICALS DEPT.

A New BULLETIN *on* *Furfural*

We have in preparation a series of bulletins on Furfural and the other Furans. The first bulletin in this series, No. 201, is available now. It contains general information on Furfural and is both interesting and up to date. Send for your copy now.

PROPERTIES OF QUAKER FURFURAL

(Furfuraldehyde, C_4H_3O-CHO)

Amber-colored liquid of high stability and unusual purity

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

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

Analysis:

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

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

Standard Containers: 9, 45, 90, and 520 lb. Drums
†Carload of Drums 80 to 88..41,600 to 45,760 lbs.
Tank car 8,000 gal..........78,000 lbs.
Tank car 10,000 gal..........98,000 lbs.
†ODT requires maximum loading
Drums non-returnable

The Quaker Oats Company CHEMICALS DEPT.

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

FURFURAL • FURFURYL ALCOHOL • FUROIC ACID • TETRAHYDROFURFURYL ALCOHOL

The story of THE CAMERON SHAFT-SEAL An Ingersoll-Rand Product for use on Ingersoll-Rand Pumps

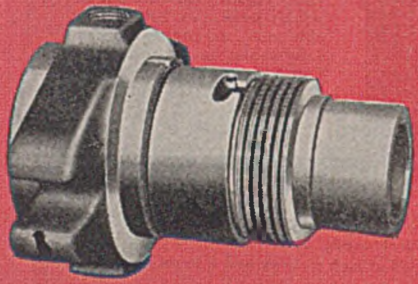
PATENTED

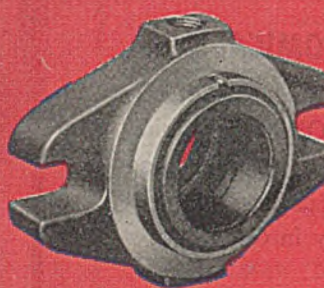
A tough problem, when thoroughly understood, usually proves to have a simple answer. The Cameron Shaft-Seal, a new answer to the old problem of packing a pump, represents the end product of more than 17 years of constant study and development by engineering specialists. We are proud of the reliable simplicity of the Cameron Shaft-Seal. It has been welcomed enthusiastically by pump operators for its versatility of application and wide range of operation. The seal has proved an indispensable aid to fine performance and overall economy in a wide variety of industries using Ingersoll-Rand pumps.

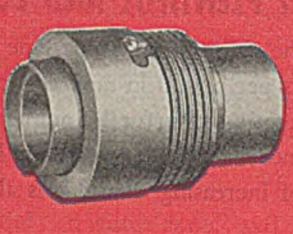
DELIBERATELY DEVELOPED FOR TOUGH STUFFING BOX SERVICE For 50 years engineers have worried over the problem of preventing liquids from leaking out along the shafts of centrifugal pumps. Moreover, the problem grew in seriousness as pumps were used for higher and higher pressures. This seal was developed for, and has its most valuable application on pumps with unusual stuffing box conditions. These exist in pipe line, refinery, and process work where the most troublesome liquids—volatile or corrosive—are encountered.

Cameron Shaft-Seals were designed and immediately installed on pipe-line installations way back in 1928—and they are still in use to this day! Extensive field study and continued research has brought the unit to its present high state of development. Back of this latest design stands the cumulative knowledge of the Ingersoll-Rand engineering laboratories with its more than 70 years of experience.

OPERATING PRINCIPLE The sealing parts of the Shaft-Seal are two rings with perfectly true and flat faces. The stationary seal ring is made of carbon and the rotating seal ring of stainless steel. The rotating seal ring, spinning against the stationary seal ring under sufficient pressure, provides the sealing action and successfully prevents leakage from the pump. The surfaces opposite the seal face are seated against packing rings which prevent escape of fluids around the seal. The packing seats allow sufficient movement so that the seal faces maintain perfect contact and alignment. The extremely low contact pressure between the sealing faces is predetermined and controlled. This accounts for the elimination of a great amount of friction and wear and assures long periods of trouble-free operation.


COMPLETELY ASSEMBLED SHAFT-SEAL


STATIONARY ELEMENT

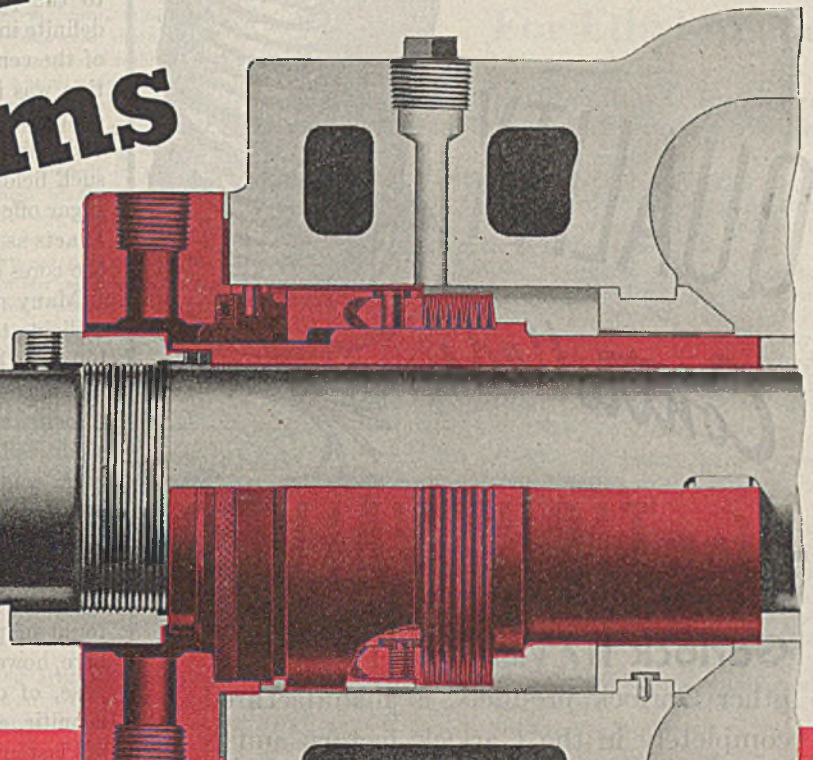

ROTATING ELEMENT

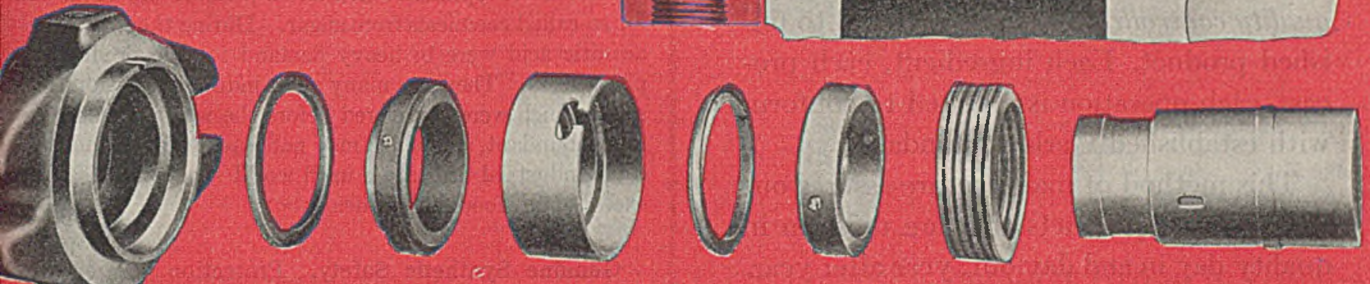
Advantages of Cameron SHAFT-SEAL

- ✓ Eliminates conventional or complicated packing with all its troubles.
- ✓ Simple construction . . . easy to install.
- ✓ Once installed, it requires no further adjustment.
- ✓ Controlled hydraulic balance . . . low contact pressure between the sealing faces . . . satisfactory performance even when handling liquids with poor lubricating qualities.
- ✓ No outside lubrication needed for operation of seal.
- ✓ Both seal rings have flexible mountings which allow them slight freedom of movement to insure proper contact and alignment.
- ✓ Positively driven . . . locking collar keyed to shaft sleeve.
- ✓ Overall economy—cuts down maintenance and slop problems.
- ✓ Seals for volatile liquids have special gland construction to vent escaping gas to atmosphere or to torchline.
- ✓ Suitable for use on pumps having variable loads or stuffing box pressures.

COMPRESSORS • AIR TOOLS • ROCK DRILLS • TURBO BLOWERS

The Answer to
STUFFING-BOX Problems





EIGHT COMPONENT PARTS OF SHAFT-SEAL

An interesting and colorful booklet, "The Answer to your Stuffing-Box Problems," offers a detailed explanation of the Shaft-Seal and its parts, its operation and application.

It's Yours For the Asking

Ingersoll-Rand

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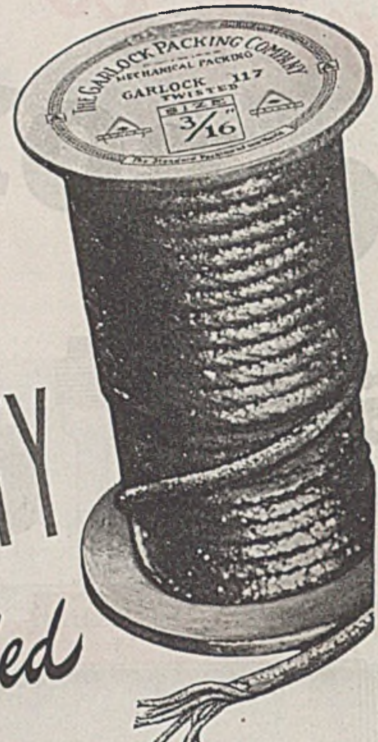
NDENSERS • CENTRIFUGAL PUMPS • OIL AND GAS ENGINES



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

Commerce and Industry

even wieners. Research inaugurated at Mellon Institute led to the preparation of an improved lime-sand mortar. A definite improvement resulted in the handling and plasticity of the cement, and the transverse strength of brick construction was increased. In achieving this result, some 13 pounds of sucrose materials were used per thousand brick.

Sugar products have found important processing roles in such fields as confectionery and pharmacy. In metallurgy, sugar offers distinct advantages in setting up foundry molds. It acts as a binder in making cores, and the material entering the cores can be reclaimed because of its water solubility.

Many materials in industry and commerce are capable of utilizing the property of solubility after they have been combined with glucose and other sugar derivatives. Again, compounds derived from sugar have been found to possess certain insecticidal and fungicidal values, and there are research possibilities here which have not yet been explored thoroughly. Such compounds would differ considerably from the sugary concoctions once employed to attract insects.

The Sugar Research Foundation has determined that levulinic acid is available commercially in moderate quantities at a cost low enough to warrant its consideration as a raw material in plastics manufacture. More research is indicated here, however, as well as for the application, for the same purpose, of other products from sugar and molasses, such as aconitic, citraconic, and itaconic acids.

Plasticizers represent still another possible important outlet for so-called chemicals from sugar. During the war, esters of aconitic acid were in heavy demand for the production of plasticizers. There are many other industrial possibilities for sugar which were uncovered before the war when sugar was more abundant, and which may not reach fruition and practicable industrial utilization until world sugar supplies are in excess of our food requirements. H. S.

Genuine Synthetic Safety. Protection of workers in the Nation's synthetic rubber plants has reached an enviable high and offers a mark for others to shoot at, especially since the safety record of the chemical industry has been slipping lately. Production of the synthetic material is considered dangerous since the reactants are explosive and toxic. Added to management's worries concerning the ordinary accidents which are inevitable in every manufacturing process, was the additional factor that each plant was, potentially, a major target for sabotage efforts. According to government authorities, however, there has been no "proven or suspected cases of sabotage throughout the program". Despite the newness of the processes, the dangers involved were overcome neatly; the safety record supplied by the National Safety Council, and compared to other industries, is:

Industry	Frequency[a]	Severity[a]
Petroleum	12.87	1.30
Chemical	10.07	1.12
Rubber	11.14	0.76
Government synthetic rubber	8.20	0.58

[a] Frequency, as defined by the National Safety Council, is the number of lost-time accidents per million man-hours worked, and severity is the number of days lost per thousand man-hours worked.

ADVERTISEMENT—*This entire page is a paid advertisement.* *Prepared Monthly by U. S. Industrial Chemicals, Inc.*

U.S.I. CHEMICAL NEWS

FEBRUARY ★ A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries ★ 1946

Quick-Dry Varnishes, High Color Retention From 2 U.S.I. Resins

Used with "Soft" Oils to Yield Tough, Quick-Drying Films

Developed during the war, when the cry was for faster bodying in the varnish kettle and faster drying on the production line, two non-phenolic U.S.I. varnish resins are proving of great postwar utility because of the excellent results they produce with the currently available, slow-polymerizing and relatively slow-drying oils.

Arochem 607

Arochem 607 is a high-melting point synthetic resin produced especially for use with linseed, castor and other "soft" oils. It is appreciably better than the usual modified phenolics in four respects: it bodies faster; it yields faster drying vehicles; it gives greater film hardness; it is much superior in color retention and can be used satisfactorily for whites.

In addition to providing the advantages associated with high melting point and large molecular structure resins, Arochem 607 also facilitates processing because of its unusually high solubility in all normal varnish oils. It can be cooked with "soft" oils in the same manner as modified phenolics of corresponding melting points; no special cooking procedures are necessary.

The water and alkali resistance of "607" varnishes are almost equal to those of modified phenolic varnishes; for all but a few special applications, its resistance will be found entirely satisfactory.

Arochem 603

A companion resin to "607," Arochem 603 is a lower priced resin of lower melting point which yields slightly slower bodying and

(*Continued on next page*)

The versatility of Arochem 607 is demonstrated by its many applications in the household. Illustrated here are its uses in rubbing varnishes for furniture, in enamels for V[illegible] blinds, in architectural finishes [illegible] es, and in metal [illegible]

THE MONTH IN COATINGS

Electrostatic paint spraying saves up to 50% in paint, minimizes chipping . . . The "duo-color metal painting system" offers a means of reducing maintenance costs . . . A wall paint blended with DDT proves an effective insect control as long as 16 months after a single coat application . . . Induction heating bakes resin coatings on ferrous metals in a few minutes . . . A number of coatings are developed to increase eye appeal and chemical resistance of plastics . . . An electronic instrument measures paint films deposited on non-magnetic metals . . . Details of certain German processes made available . . . New standards proposed for determining the degree of color change of paints and enamels . . . Use of luminescent pigments booms in textile industry.

New Synthetic Drug Tops Atebrin, Quinine

U.S.I.'s Noval Ketone Vital As Intermediate in Synthesis

A new synthetic drug, said to be superior to both atebrin and quinine in the treatment of malaria, has been developed by U. S. scientists, according to a recent government announcement. The drug, known as "SN 7618," relieves malaria three times as fast as the other two drugs, and produces fewer ill effects. Noval ketone (5-diethylamino-2-pentanone), a product of U.S.I., is an important intermediate in the manufacturing process.

Advantages of "SN 7618"

As a result of research extending over four years, the Board for the Coordination of Malarial Studies found that "SN 7618" is an effective malarial suppressive when administered no more frequently than once weekly in a well-tolerated dose. It will also cause an abrupt termination of the clinical variety of malaria. In addition, it neither discolors the skin nor produces gastro-intestinal irritation—symptoms usually associated with the use of atebrin.

"SN 7618" was the 7,618th drug tested in the four year screening of over fourteen thousand compounds for antimalarial activities.

(*Continued on next page*)

Synthetic Carnauba Wax Production in Sight

It will soon be possible to secure speedy production of synthetic carnauba wax in the U.S., according to a recent government announcement. The synthetic wax – manufactured on the basis of patented German processes now released to American industrialists – is reported to be equal to and, for many purposes, superior to natural wax.

Carnauba wax, now produced principally from the wax palm grown in Brazil, is used in the manufacture of floor wax and polishes, carbon paper, and leather finishes. A new and increasingly important use has been found for it in the preservation of fruit.

Russian Research Uncovers New Uses For Ethyl Acetate

Versatile Chemical Is Employed In Many Novel Organic Syntheses

Ethyl acetate – used principally as a solvent for nitrocellulose and cellulose acetate, and in the production of many pharmaceuticals such as sulfadiazine – offers many new possibilities in organic synthesis, according to papers published in Russian scientific journals during the last five years. This compound has been employed successfully by Russian research chemists in reactions varying from Grignards to the polymerization of vinyl plastics.

New Applications

The following are among the new uses of ethyl acetate reported in the Russian literature:

1. With benzol in the presence of aluminum chloride, ethyl acetate forms 9,10-dimethylanthracene which can readily be oxidized to anthraquinone.
2. Heated with iodine in the presence of aluminum, magnesium, or iron, it produces ethyl iodide.
3. After prolonged heating with 2-mesitylmagnesium bromide, it produces mesitol, mesityl acetate, and the acetate of methyldi-2-mesitylcarbinol.
4. Polyvinyl acetate is prepared by polymerizing vinyl acetate in the presence of ethyl acetate. The solid polymer is obtained by steam-distilling the solvent.
5. With tertiary and secondary butyl magnesium chloride, it forms ethyl butyl ketone and diethyl ketone.
6. It reacts with silicon tetrachloride to form tetra-acetylsilicate, and other silicates and chlorides.

Seminar Group to Discuss Economics of Chemistry

Thirteen specialists from industry will participate in a graduate seminar dealing with economics and cost aspects of chemical industries, it was announced recently. The seminar, which is scheduled to begin early in February, will be held at the Polytechnic Institute of Brooklyn.

Topics to be discussed include: the preparation of economic surveys and appraisals, plant location, cost analysis and estimates, organization and control, and interpretation of financial statements. The course will be offered on Thursday evenings.

Enzyme May Be Remedy For Oak, Ivy Poisoning

The recent discovery that mushroom tyrosinase can render the irritant toxicants of poison ivy and poison oak innocuous adds another plant enzyme to those already known to have the same property. The other enzymes, however, have not been effective *in vivo*. It is hoped by the discoverers that mushroom tyrosinase will have a definite remedial action.

ADVERTISEMENT—*This entire page is a paid advertisement.*

FEBRUARY ★ **U.S.I. CHEMICAL NEWS** ★ 1946

New Synthetic Drug

(Continued from preceding page)

Chemically, "SN 7618" is a member of the 4-aminoquinoline series. It is known as 7-chloro-4-(4-diethylamino-1-methylbutylamino) quinoline. The vital side-chain is added to the basic 4-amino-quinoline group by reaction through noval ketone.

Plans Simplification Of Plastic Nomenclature

To eliminate confusion arising from the lack of uniformity in plastics nomenclature, the Society of Plastics Industries has opened a campaign for proper labeling of plastics. The first step in this program was taken recently with the Society's publication of the "Informative Labeling Guide." This book contains a series of descriptions of various plastics used in consumer goods.

Organic Nitrogen Compounds Made By Direct Amination

A method for producing nitrogen compounds by direct amination of olefins containing more than 3 carbon atoms is described in a recent patent. It accomplishes nitrogen fixation by treating the olefins with ammonia in the presence of a catalyst at temperatures between 400 and 650 degrees F.

Direct nitration offers a simple method for preparing nitriles and amines. By this method, for example, ethylene and propylene can be converted to acetonitrile, acrylonitrile, and ethyl, isopropyl, and n-butyl amines. These compounds are vital in the making of plastics and synthetic rubber.

U.S.I. Announces New Feed Fortifier

Curbay B-G 40 is a new low-cost fermentation product, containing the vitamins of the B-complex, and has a guaranteed riboflavin content of 40 micrograms per gram. This newly announced U.S.I. product is rapidly winning wide acceptance among poultry-and-stock feed formulators.

Quick Dry Varnishes

(Continued from preceding page)

slower drying varnishes. Otherwise, the properties obtainable are quite similar.

Find Many Uses

Many manufacturers are finding these resins ideal for use in quick-drying enamels, porch and deck enamels, vehicles for architectural and industrial finishes, spar varnishes, gloss inks, and other coatings which are in such heavy demand today. Especially, these manufacturers report excellent results in whites because of the pale color and high color retention of these resins.

Specifications

	AROCHEM 607	AROCHEM 603
Acid Number:	25-35	25-35
Melting Point:	155-165°C.	130-140°C.
	(Mercury Method)	
Color:	9-11	9-11
	(G.H. 1933—50% cut in Toluol)	
Solubility:	Complete in petroleum hydrocarbons and the usual varnish oils. Insoluble in alcohol.	

Arochem 607 is a vehicle for a wide variety of white and colored industrial finishes. Parts of toy trains, such as those illustrated here, retain their color longer when coated with varnishes based on this modified phenolic.

Decreases Hosiery Runs

A patent has been issued on a new preparation to inhibit runs in sheer hosiery. The preparation, claimed to have a run load characteristic of 2½ pounds, consists of zinc resinate, ammonia, water, and a mixture of isopropyl alcohol and acetone.

TECHNICAL DEVELOPMENTS

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

A new fungicide, said to be effective against numerous diseases that attack growing plants, has been announced. **(No. 030)**

U S I

Transparent plastic sheets, claimed to be non-electrostatic and shatter-proof, are now available for a variety of applications. They are said to be easily shaped into windows for precision electrical instruments. **(No. 031)**

U S I

A new paint stripper is claimed to be non-destructive to aluminum, zinc and other base metals. It is said to remove synthetic enamels and many other types of tough organic coatings cleanly and rapidly. The product is diluted with warm water. **(No. 032)**

U S I

Heat-screening glass, said to be capable of screening about 90% of infrared, or heat, radiation from light while transmitting 85% of visible radiation is available for many applications ranging from housing to therapeutics. **(No. 033)**

U S I

Silicone oils, which are said to flow at temperatures as low as —121°F., are described as suitable for use in aircraft hydraulic systems, in fine instruments, and as a dielectric fluid in capacitors and transformers. **(No. 034)**

U S I

A new moisture detector, described as being based on an electronic principle, is recommended for detecting leaks. **(No. 035)**

U S I

To remove scale, a new "alkaline pickling" process is offered for application to metal surfaces. The process is said to eliminate pitting and hydrogen embrittlement. **(No. 036)**

U S I

To secure linoleum in place, an adhesive trowelling material stated to be immune to the attacks of water, is claimed to be easily applied to concrete surfaces. **(No. 037)**

U S I

Redyeing olive drab and other shades of wool material for civilian use is said to be accomplished by a simple process. A booklet is available describing the process and the dyes used. **(No. 038)**

U S I

A waterproofing, bonding mortar, claimed to be made by mixing a liquid chemical with cement, is said to be effective for use in stopping leaks, eliminating seepage, and in patching and waterproofing pits and concrete pipes. **(No. 039)**

U S I

A dew point recorder, is claimed to provide virtually continuous record of humidity within a temperature range of —70° to +60°F. **(No. 040)**

U S I

To handle any shaped drum, cradle handles are said to be able to pick up barrels with straight, bilged sides, flat or chimed sides. **(No. 041)**

U S I

U.S. INDUSTRIAL CHEMICALS, INC.

60 EAST 42ND ST., NEW YORK 17, N. Y. (U.S.I.) 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
- Ansol PR

ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Dibutyl Oxalate
- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

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

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

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

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

ACETONE
- Chemically Pure

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

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

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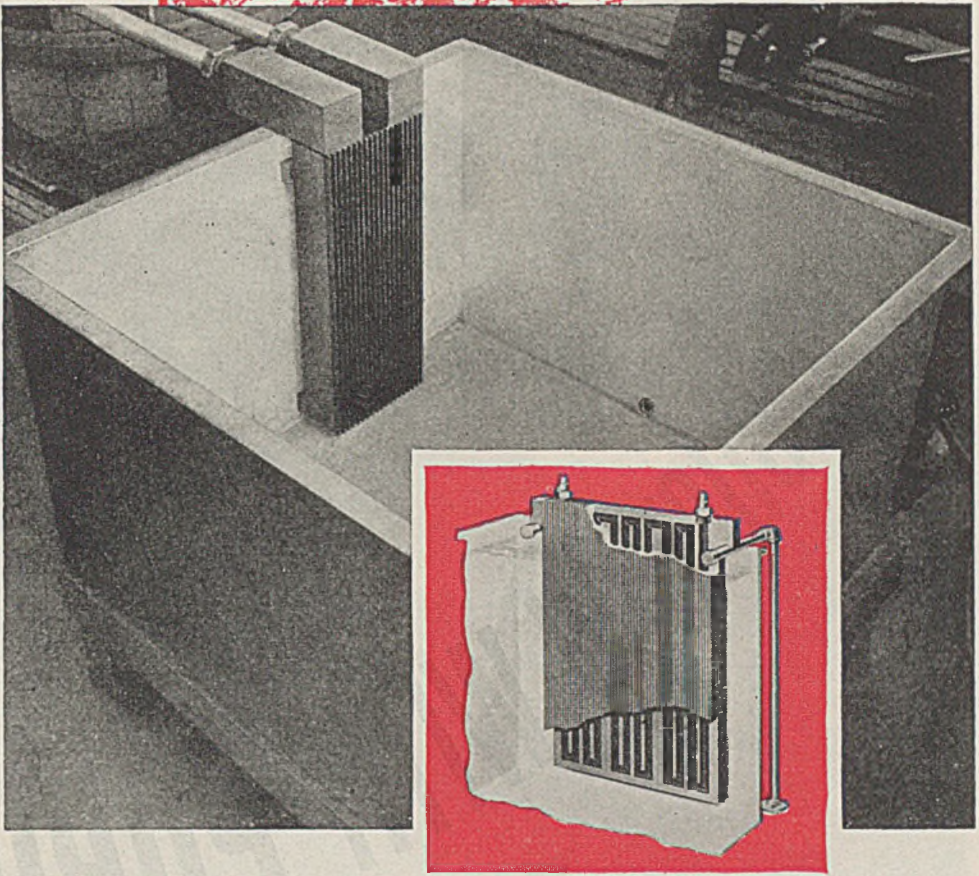


KARBATE
HEAT EXCHANGERS


H
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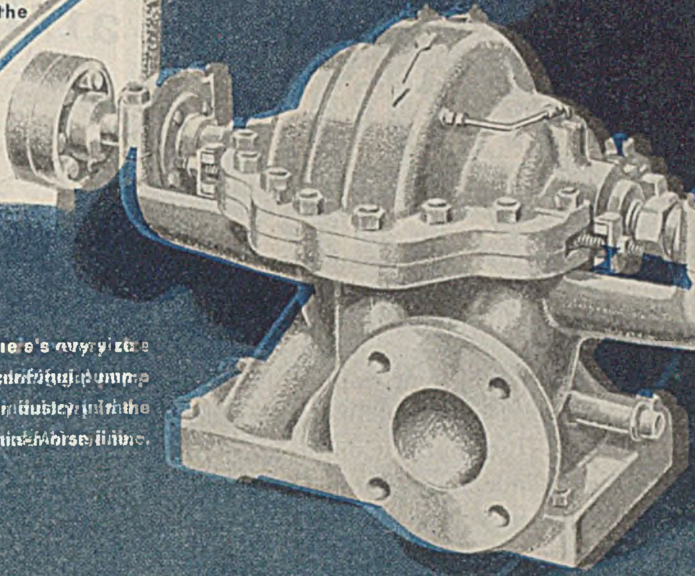
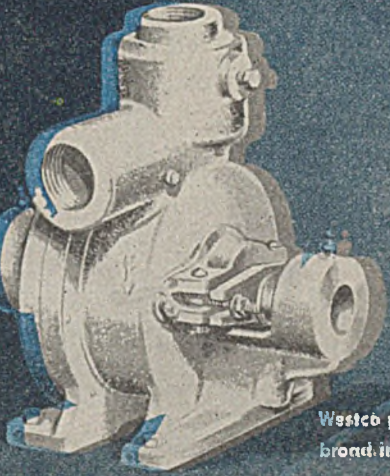
Can ANYONE make a Pump?

Well, there's no law against it—except perhaps the "law of survival." It's a question of what *kind* of pump you want—and how *good* you want it to be. If you want a pump that will squeeze the last fraction of a cent in value out of the monthly power bill, that is designed to the very limits of hydraulic knowledge—built with the fine tools and complete facilities that such precision design requires—you'll want a Fairbanks-Morse pump!



There's every size and type of centrifugal pump used in industry in the Fairbanks-Morse line.

WHEN YOU BUY a Fairbanks-Morse, Pomona or Westco pump, you get a design which is the result of accumulated years of research in not only our own laboratories but those of the universities' scientists whom we have retained.



Westco pumps: precision-built, broad in application.

For all vertical turbine pump work—the Pomona line.

THIS DESIGN and unlimited manufacturing facilities, which only the largest pump manufacturers can offer you, combine to give you pumps superior in performance and reliability.

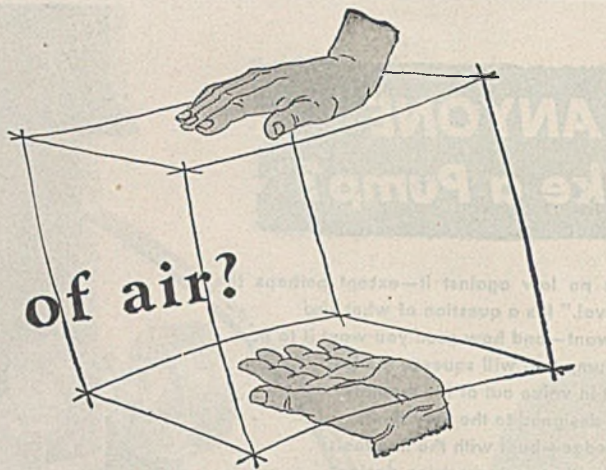
ANYONE CAN MAKE A PUMP—perhaps! But for proved value, skilled service—regardless of the type of pumping requirements or the amount of liquid to be moved—Fairbanks-Morse is an unquestioned leader. Call your nearest Fairbanks-Morse distributor or branch office.

FAIRBANKS-MORSE

A NAME WORTH REMEMBERING

PUMP DIVISION

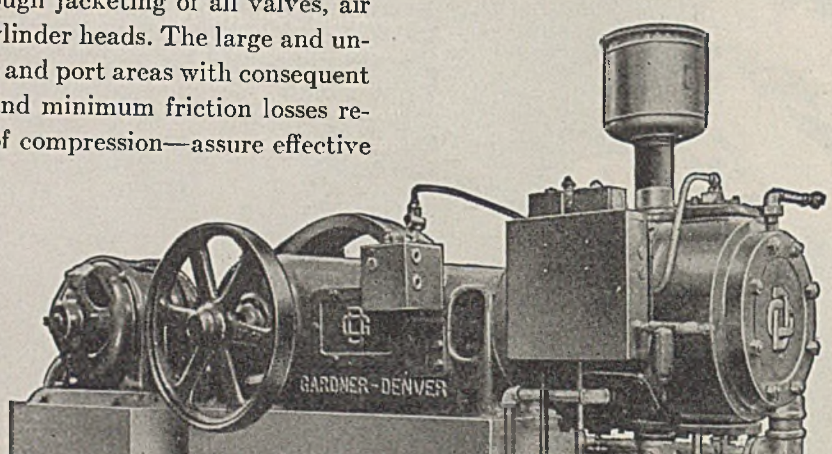
How much will it cost YOU to "squeeze" a foot of air?



Any air compressor will "squeeze" air for you. But how well will that job be done—how much power will it take to compress a cubic foot of air to the pressure you require?

The cylinder design of your compressor has a lot to do with that question. In the Gardner-Denver "RX" Horizontal Compressor, for example, the cylinders are of advanced design to provide higher volumetric efficiency and lower horsepower requirements. The air valves are located radially at each end of the cylinder to permit thorough jacketing of all valves, air passages and cylinder heads. The large and unrestricted valve and port areas with consequent low velocities and minimum friction losses reduce the heat of compression—assure effective lubrication. Add it up—it means *lower cost.*

Better cylinder design is only one of the many outstanding features of the Gardner-Denver "RX" Compressor. Let us tell you why "RX" compressors have made a name for themselves in industry—for full facts, write Gardner-Denver Company, Quincy, Illinois.

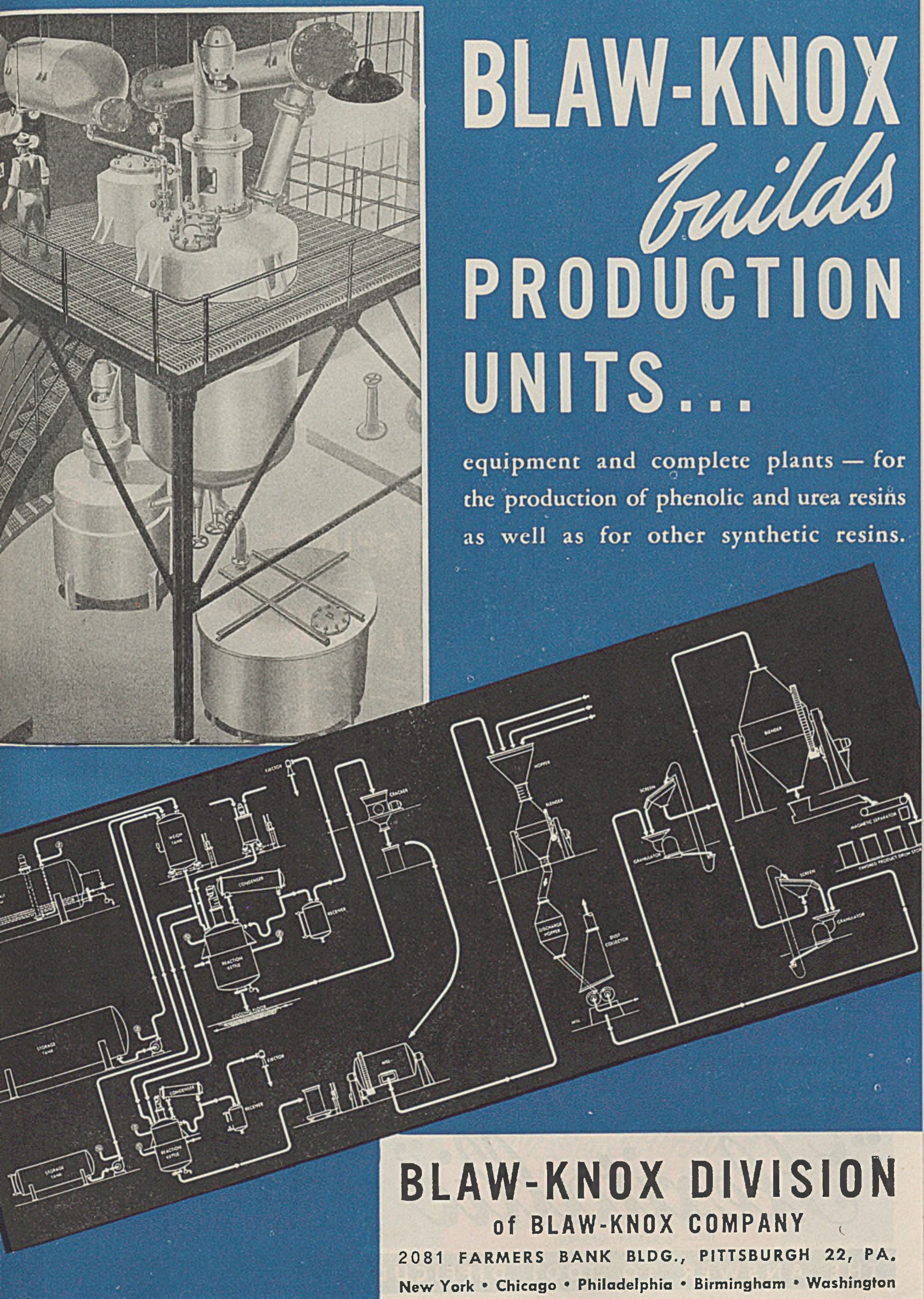


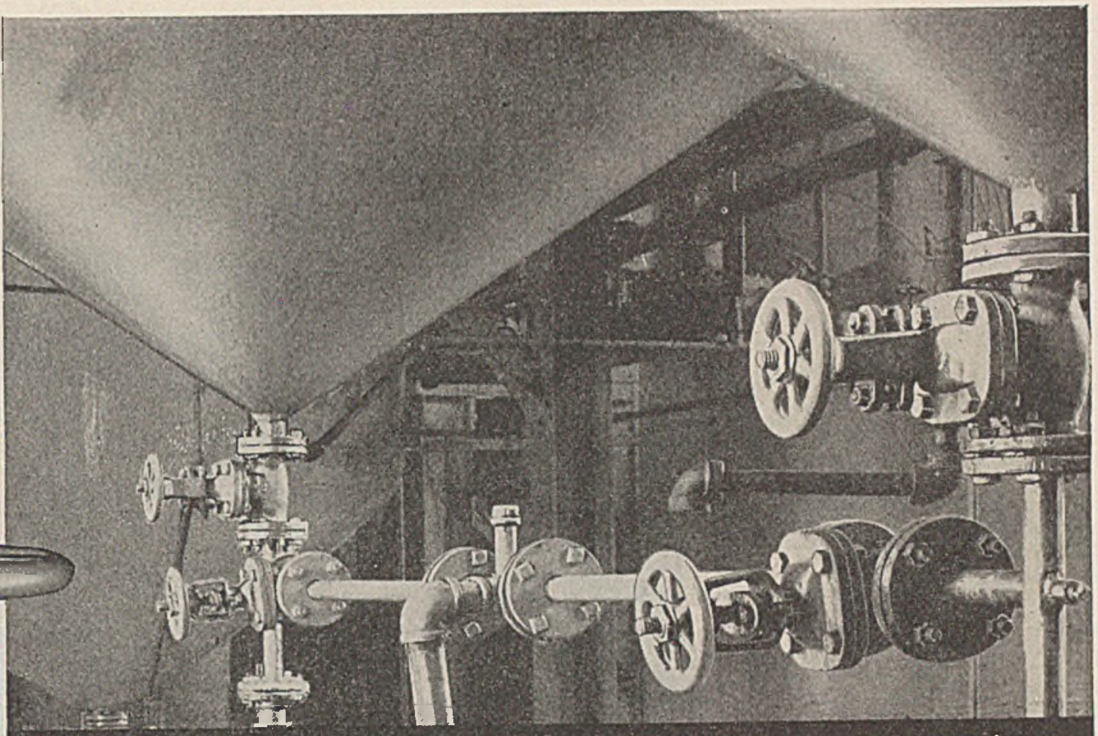
Gardner-Denver "RX" Horizontal Single Stage Compressor—capacities from 89 to 1292 cu. ft. displacement per minute.

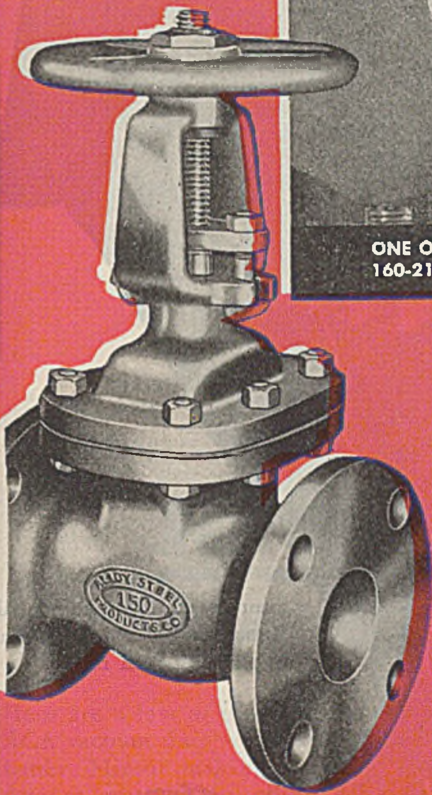
- No compressor is better than its valves—and in the "RX" compressor, Gardner-Denver duo-plate cushioned valves provide high compression efficiencies with lowest power consumption. These valves are "air cushioned" for long life.
- Rugged main frame is completely oil and dust-tight, yet provides easy access to all working parts.
- The entire lubricating system is positive, automatic and foolproof.
- Timken adjustable double row tapered roller bearings on crankshaft provide considerable overload capacity with consequent long life.

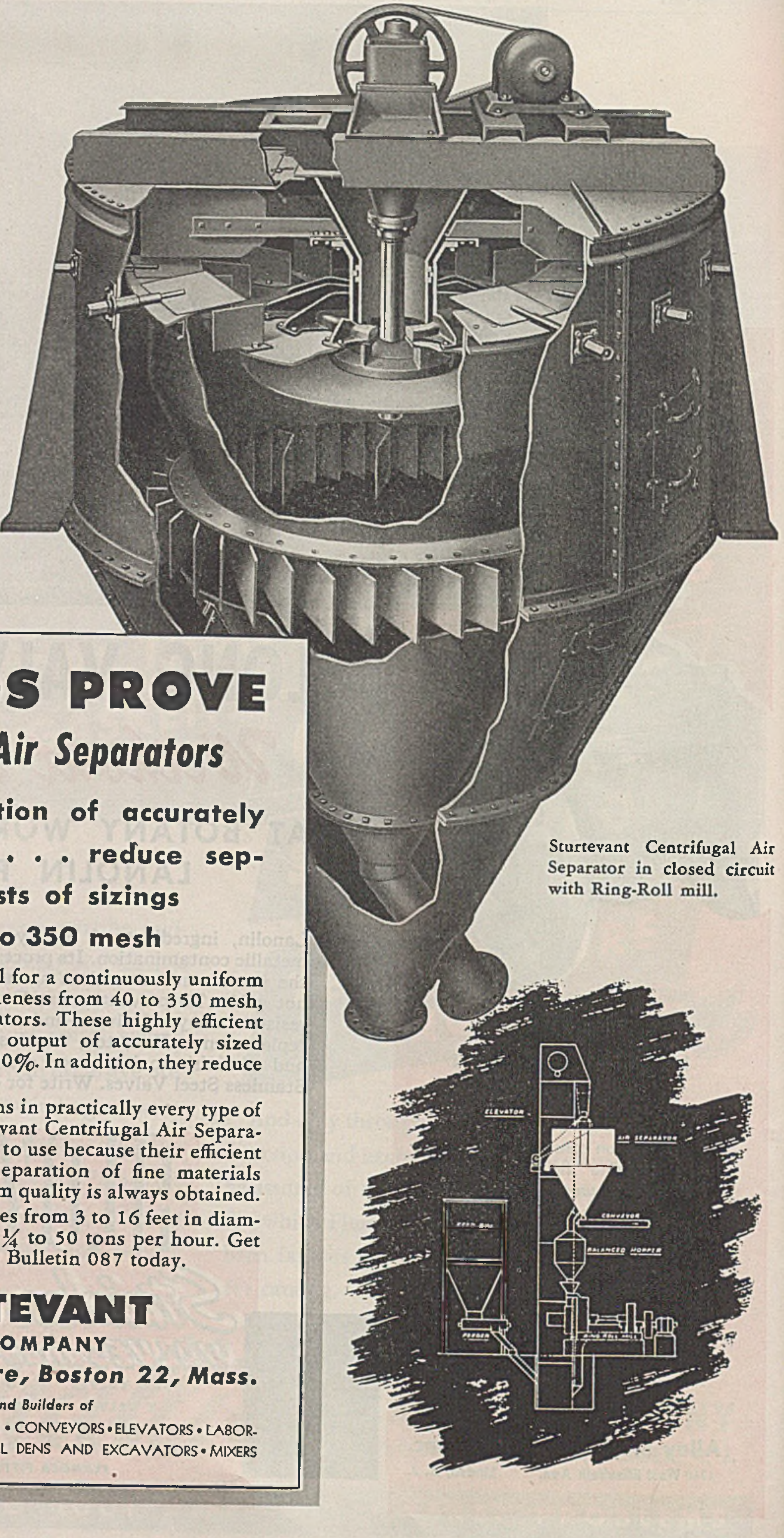
GARDNER-DENVER

Since 1859


EJECTOR
CRACKER
WEIGH TANK
CONDENSER
RECEIVER
REACTION KETTLE
COOLING FLOOR
STORAGE TANK
EJECTOR
MILL
CONDENSER
RECEIVER
REACTION KETTLE
STORAGE TANK
HOPPER
BLENDER
DISCHARGE HOPPER
DUST COLLECTOR
MILL
SCREEN
GRANULATOR
BLENDER
MAGNETIC SEPARATOR
FINISHED PRODUCT DRUM STO
SCREEN
GRANULATOR

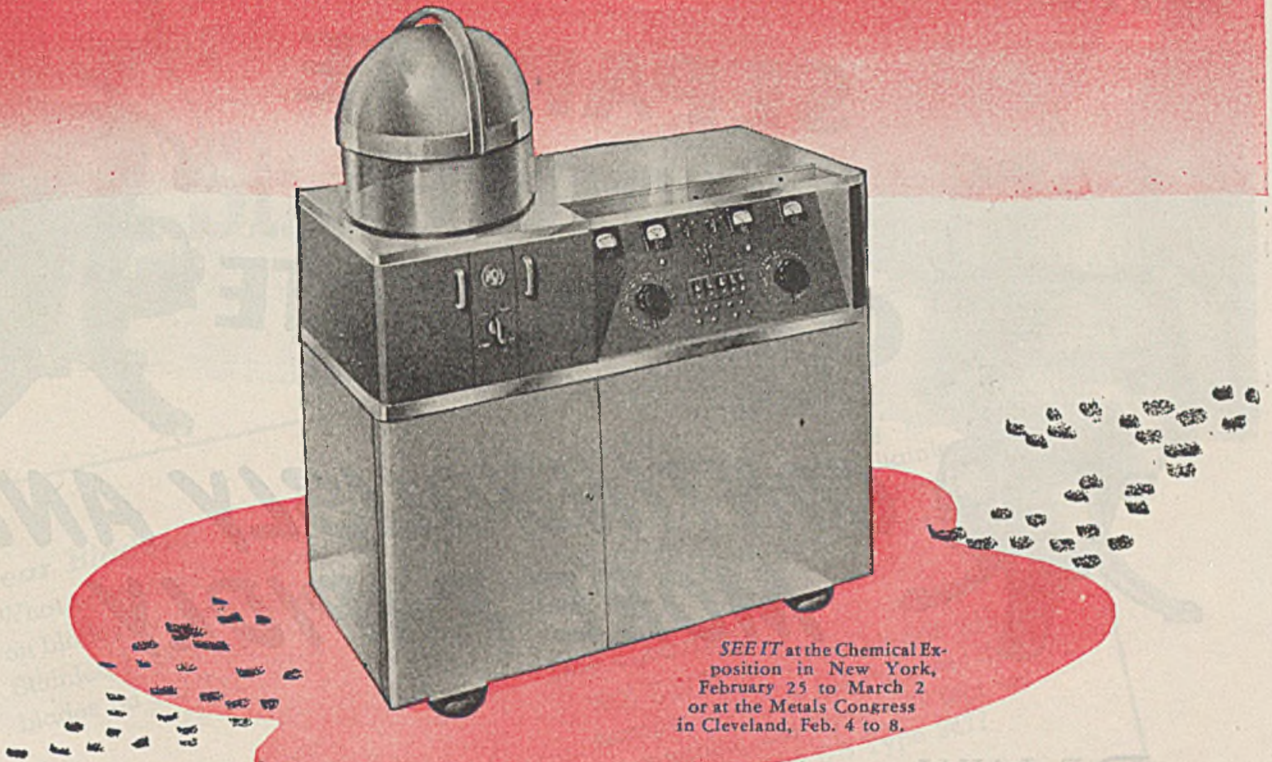



ALLOY STEEL PRODUCTS CO.
150



Sturtevant Centrifugal Air Separator in closed circuit with Ring-Roll mill.

A VERSATILE VACUUM!



SEE IT at the Chemical Exposition in New York, February 25 to March 2 or at the Metals Congress in Cleveland, Feb. 4 to 8.

NEW RCA VACUUM UNIT

speeds many laboratory and factory processes

Here are a few of the jobs that this new, multi-purpose RCA vacuum unit will help you do easier, quicker, and better: Mirror making; lens coating; vacuum or freeze drying; evaporating, condensing, or sputtering of materials on metal or non-metallic surfaces; and experiments where various gases at reduced pressures are required.

The RCA vacuum unit (Type EMV) consists of a vacuum chamber or bell jar, a high-speed pumping system (with simplified valving) to evacuate it, a control system, and meters and gages for reading currents, voltages, and vacuum pressures.

Within the bell jar are nine pairs of terminals.

Six of these are each capable of carrying 50 amperes. They are used to light filaments for the evaporation of metals or other materials. Any number up to six filaments can be used, and connected in series or parallel from outside the vacuum chamber. The power available for these circuits is 5 kva.

Another set of terminals is capable of carrying up to 5000 volts at 80 milliamperes—useful for ionization cleaning and for sputtering metals.

The two remaining pairs of terminals are useful in making measurements in the vacuum chamber while it is being pumped out, and for supplying power to heaters or other equipment within the bell jar.

Provision has been made so that gases, if desired, can be admitted into the vacuum chamber after the air is removed.

This vacuum unit comes equipped with two bell jars: one 18 by 18 inches, the other 18 by 29 inches (height). A vacuum of better than ½ micron (mercury) pressure is rapidly achieved in 7 or 10 minutes depending upon the size of the vacuum chamber used.

A new bulletin is now available describing many of the other features of this device which contribute to its safe, quiet, easy operation. Ask for your copy today. Write: Radio Corporation of America, Dept. 39B, Engineering Products Division, Camden, N. J.

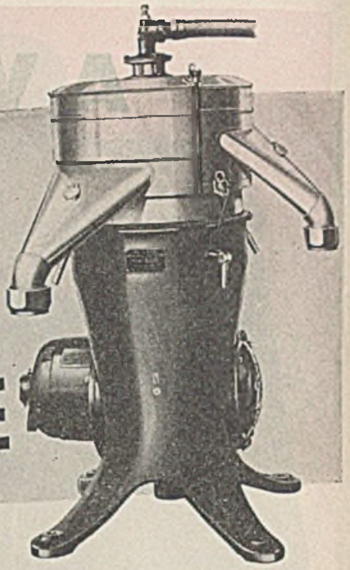
SCIENTIFIC INSTRUMENTS

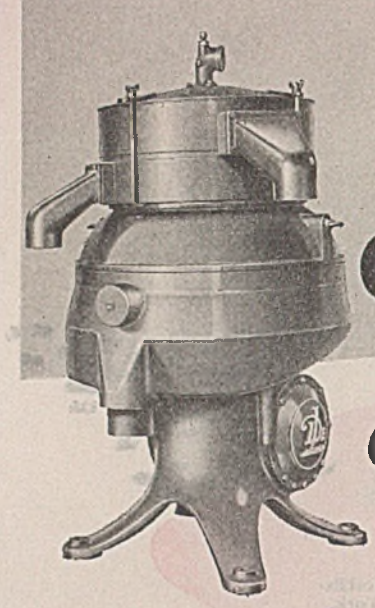
RCA

RADIO CORPORATION of AMERICA

ENGINEERING PRODUCTS DIVISION, CAMDEN, N. J.

WHEN YOU WANT TO SEPARATE CLARIFY CONCENTRATE





CONTINUOUSLY AND MORE RAPIDLY

DE LAVAL centrifugals afford the means of simplifying processes in many different types of plants. They speed up production, they effect savings and often improve the product wherever two liquids of different specific gravities are separated, where removal of small quantities of solid materials is required to clarify a liquid, or where it is desired to remove and continuously discharge somewhat larger quantities of concentrated solids.

De Laval's extensive line of specialized centrifugal separators, clarifiers and concentrators enables the selection of just the right machine to meet the specific problems involved in each plant.

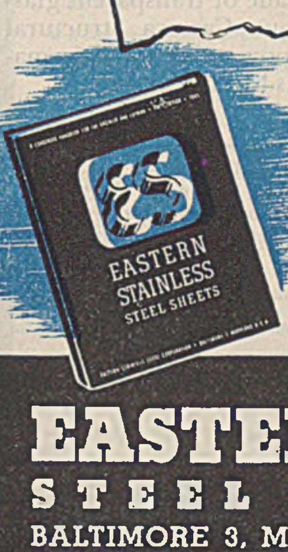
Although your problem may seem at first to be "different," it may be that De Laval experience covering more than 60 years specialization in centrifugal engineering will reduce it to one similar to some application for centrifugal force already known to De Laval engineers. It will certainly pay you to consult De Laval — for such consultation involves no obligation and may lead to quicker, more economical handling of your product.

- De Laval invites you to write for Bulletin 225, sent free.

DE LAVAL

THE DE LAVAL SEPARATOR COMPANY
165 Broadway, New York 6 427 Randolph St., Chicago 6
DE LAVAL PACIFIC CO., 61 Beale St., San Francisco 19
THE DE LAVAL COMPANY, Limited
MONTREAL PETERBOROUGH WINNIPEG VANCOUVER

CENTRIFUGAL PROCESSING SYSTEMS


EASTERN STAINLESS STEEL SHEETS

Glass Tanks mean fewer tank troubles

USE GLASS TANKS BY "PITTSBURGH"

For

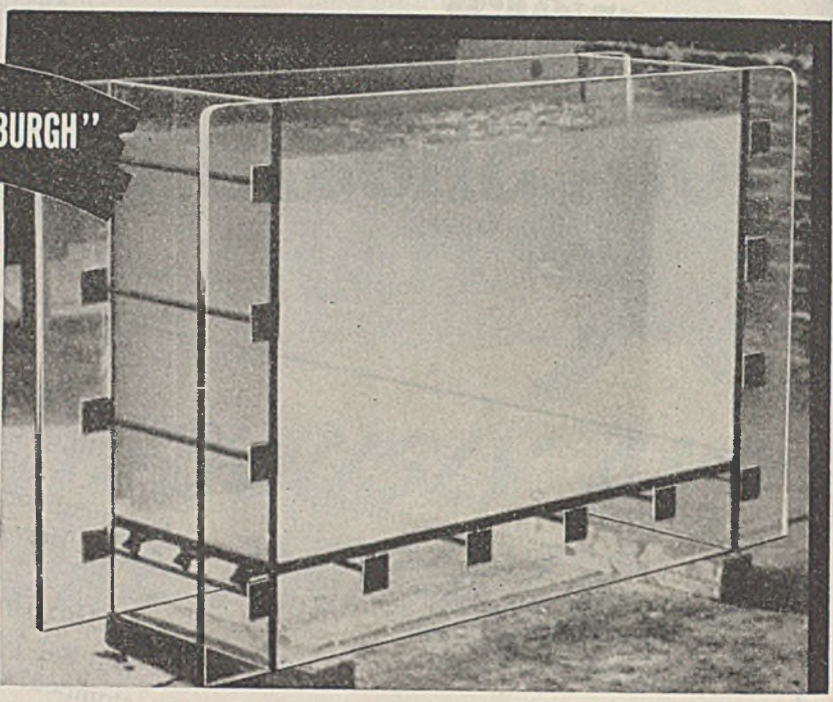
...Electroplating

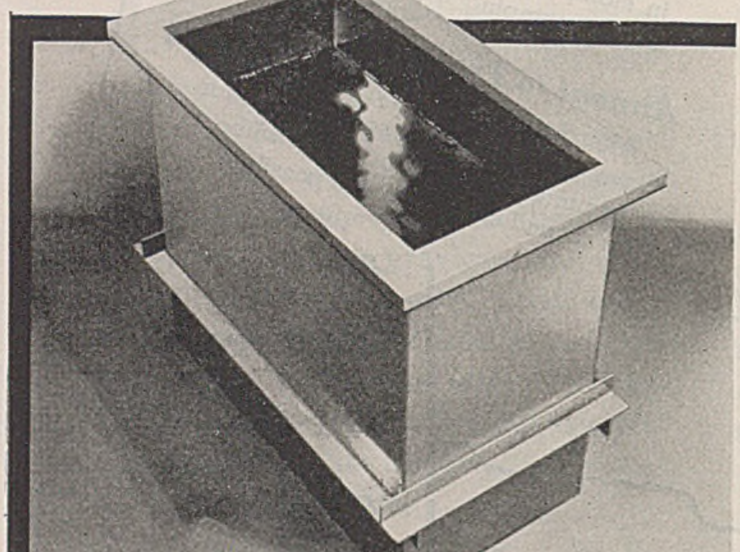
...Compounding Chemicals

...Storing Liquids

...Metal Finishing

...Hard-to-Handle Solutions





THE strength and sturdiness of glass tanks make them practical for any job where you need tanks that are impervious to acids, alkalis, chemicals. Or for jobs when you need tanks that can withstand sharp temperature changes, that are non-porous, non-absorptive, and won't contaminate their contents.

Pittsburgh Glass Tanks are made of specially tempered glass—four times as strong as ordinary glass of the same thickness. They withstand hard usage, give long service.

We will be glad to recommend the kind of glass tanks best suited to your specific working conditions. There is a wide variety of types and sizes available: tanks faced with glass, inside and out; tanks with glass inner facing only; tanks made of transparent glass or of colored, opaque Carrara Structural Glass. Send the coupon today for information about glass tanks by "Pittsburgh."

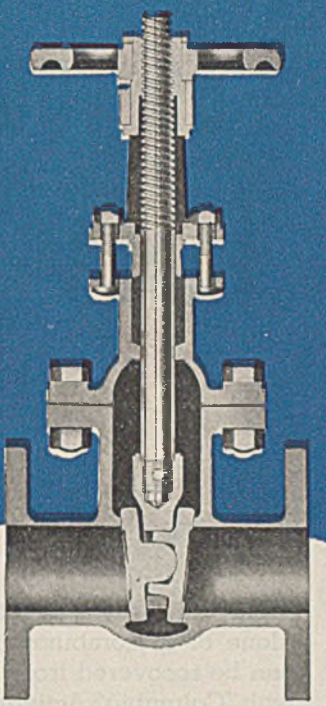
Glass Tanks

BY "PITTSBURGH"

Pittsburgh Plate Glass Company
2042-6 Grant Building, Pittsburgh 19, Pa.
Please send me, without obligation, your free folder giving full details about Glass Tanks by "Pittsburgh."
Name...
Address...
City... State.....................

"PITTSBURGH" stands for Quality Glass and Paint

PITTSBURGH PLATE GLASS COMPANY



Specify "LUSTRACAST" Electrolytic finish. It not only brightens valve appearance, it insures increased corrosion resistance and adds longer life.

COOPER "CERTIFIED" STAINLESS STEEL VALVES

You specify—We certify

Guessing is no longer a factor in determining whether or not the composition of your Stainless Steel valves meets exact specifications — not since we introduced "Certified" Stainless Steel valves.

Now you can be sure you will get exactly what you need. Because, in production, Cooper *registers* the analysis of each heat and stamps each casting with its heat number. Every Cooper unit, therefore, is positively identified. Duplication of analysis in re-orders is simple. And the chance of a mix-up in storage is greatly lessened.

The Cooper valve certification method applies to all parts which come in contact with the fluid being handled. As a Cooper customer you get your certificate on request with each unit specified.

This method of certifying valves is made possible by Cooper's complete foundry service. The metallurgical, engineering and manufacturing processes, including casting, heat-treating, machining and testing are all here. And everything is under one roof for finger-tip control of each production phase of your valve.

The standard types of Cooper "Certified" Stainless Steel valves now available include: Globe, Gate, Y, Check, Needle, Quick-opening. A complete line of stainless steel pipe fittings are also available.

Cooper's up-to-the-minute facilities for casting intricate stainless steel, monel, and nickel parts are unique. If you use such parts our engineers and metallurgists can offer valuable help. For complete data on "Certified" Stainless Steel valves produced in a money-saving manner, drop us a line — today.

THE ONLY ALLOY FOUNDRY WITH ALL THESE FACILITIES

- Laboratory control over raw materials and finished products.
- Dual foundry . . . both hand and machine molding.
- Electric arc and high-frequency-induction melting furnaces.
- Centrifugally-cast castings.
- Heat treating of castings up to six feet.
- X-ray and Gamma-ray inspection.
- Zyglo detection of surface imperfections.
- Precision Castings.
- Machine shop . . . specially equipped for finishing stainless steel.
- Improved cleaning . . . including Lustracast electrolytic finishing which leaves all surfaces bright.
- Castings furnished rough, polished or fully machined . . . one ounce to two tons.
- Development of special alloys to meet unusual requirements.
- Technical consulting service.

THE COOPER ALLOY FOUNDRY CO.
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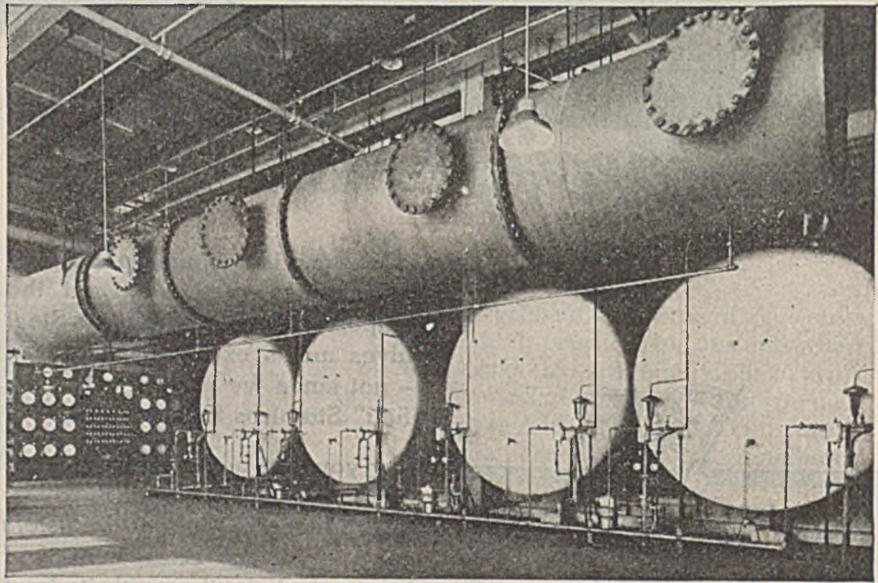
THE Cooper ALLOY FOUNDRY CO.
STAINLESS • MONEL • NICKEL
THE LARGEST EXCLUSIVE STAINLESS STEEL FOUNDRY IN THE COUNTRY

do you vaporize these Solvents?

- ALCOHOLS
- CHLORINATED COMPOUNDS
- ESTERS
- ETHERS
- HYDROCARBONS
- KETONES
- CARBON BISULFIDE



Any of these solvents—alone or in combination—can be recovered from air with "Columbia" Activated Carbon.

Carbide and Carbon Chemicals Corporation supplies complete solvent-recovery systems designed and engineered to recover solvents economically with "Columbia" Activated Carbon. A large indoor installation is pictured at right.

These plants can recover solvent vapors in low concentrations even in the presence of water vapor. Their efficiency is high, often better than 99 per cent of the solvent vapor passed to the adsorbers. However, overall recoveries of solvent used vary with the vaporizing operation and the type of vapor-collecting system. These solvent recovery plants can be completely automatic. The investment is moderate, the recovery expense is only a fraction of the cost of replacing the solvents. For further information write for the booklet, "Solvent Recovery by the 'Columbia' Activated Carbon System" (Form 4410).

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

COLUMBIA
TRADE-MARK
Activated Carbon

Life-Saver for Men and Materials

SOLVENT RECOVERY · CATALYSIS · GAS AND AIR PURIFICATION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SOLID STAINLESS

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If you are identified with any of the above 34 industries, this new and complete Monsanto Catalog should be on your desk . . . It contains 214 pages of valuable, detailed information on more than 400 Monsanto Chemicals and Plastics — a daily guide of definite help to everyone whose thinking is geared to increased production, greater economies, better methods and improved product salability . . . Send for your copy today . . . Fill in and mail the coupon, or write MONSANTO CHEMICAL COMPANY, 1700 South Second Street, St. Louis 4, Missouri.

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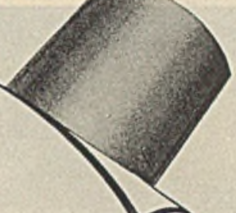
For Prompt Service ON YOUR ORDERS for STAINLESS TUBING



● Whenever you have a problem involving Stainless Tubing, feel free to get in touch with your nearest distributor—listed here. His facilities are there to help you get the best service possible. When you want information about 100% hydrostatically tested Carpenter Welded Stainless Tubing—get in touch with the nearest office shown here.

ALBANY, NEW YORK
Anti-Corrosive Metal Products, Inc.
Castleton 2511
ATLANTA, GEORGIA
J. M. Tull Metal & Supply Co.—Walnut 3525
BALTIMORE, MARYLAND
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BERKELEY, CALIFORNIA
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Cherry-Burrell Corp.—Dearborn 7900
C. A. Roberts Co.—Haymarket 6330
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Service Steel Co.—Wabash 2750
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Prospect 8365
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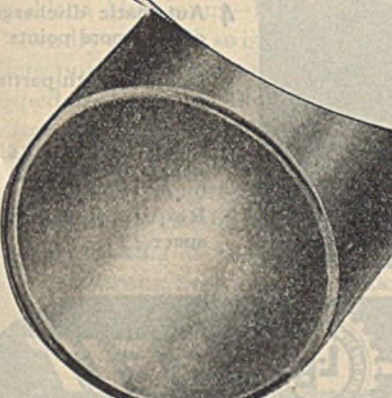
Standard Tube Co., Ltd.—Woodstock 1975



ASK FOR THIS NEW SLIDE CHART OF TECHNICAL DATA

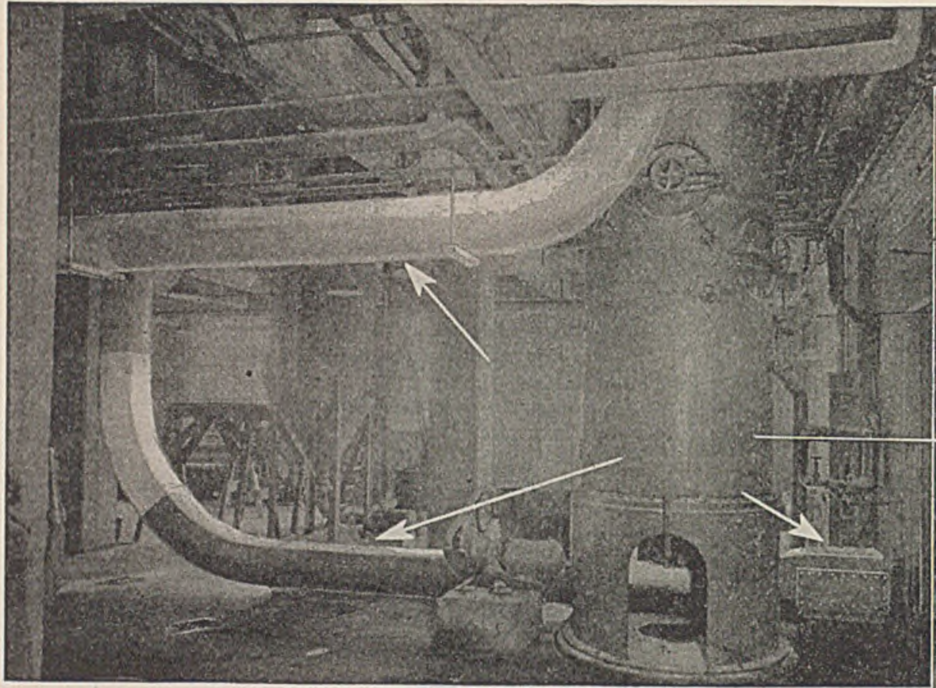
In convenient form, this slide chart gives you useful information on: • Mass Velocity Constants (V_m) • Velocity Constants (V_1) • Cross Sectional Areas of Tubes • Sq. Ft. Internal Surface per Lineal Foot of Tube • Physical Properties of Stainless Tubing. A note on your company letterhead will start your Stainless Tubing Slide Chart on its way. Write for your copy today.

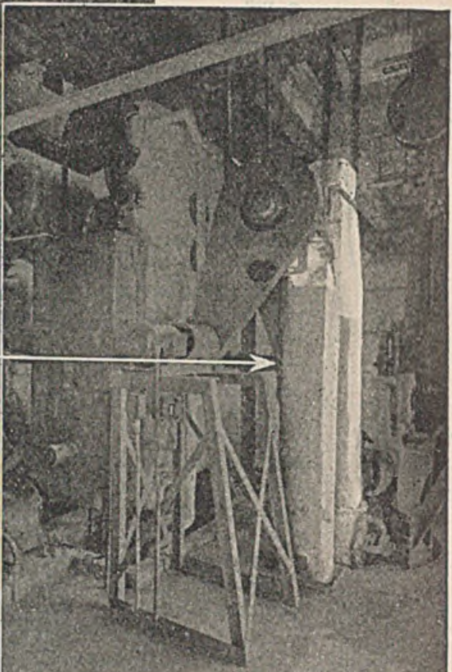
THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division
Kenilworth, New Jersey

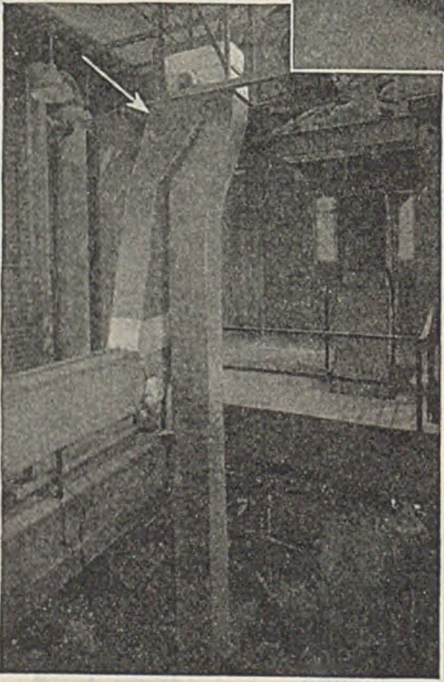
Carpenter
WELDED
STAINLESS TUBING

LINK-BELT *Bulk-Flo*

Brings New Efficiency and Economy to a great Soybean Oil Extraction Plant







● The illustrations on this page furnish vivid proof of Link-Belt Bulk-Flo's adaptability to unusual moving and handling problems in a wide range of industries. In this giant Midwestern soybean oil extraction plant, two L-path Bulk-Flo conveyors are handling spent soybean flakes between processing operations, and are performing their functions with maximum efficiency—at minimum cost.

Shown in the picture above is the conveyor leading from the direct dryer (right) on the first floor to a bridge conveyor on the fourth floor, a vertical lift of 54 feet. In the same photograph, the Bulk-Flo under the ceiling conveys spent soybean flakes from an indirect dryer to a second-floor direct dryer. Photograph at upper right shows the drive and vertical leg of Bulk-Flo used to move flakes from indirect dryer to direct dryer; picture at lower right shows top of vertical leg extending from first floor to the bridge conveyor on the fourth floor.

This installation is typical of Bulk-Flo's practical value in moving flowable, granular, crushed, ground or other materials of a noncorrosive, nonabrasive nature under any regular or special conditions. Bulk-Flo operates vertically, horizontally, around curves or corners, and on any slant. Write for illustrated Book No. 2075—or ask a Link-Belt Materials Handling Engineer for suggestions on your specific problem.

Note these Bulk-Flo Features:

1. Suitable for wide range of capacities.
2. Slow-speed operation.
3. Automatic loading (without feeders) at one or several points.
4. Automatic discharge at one or more points.
5. Operates with partial or full load.
6. Dust-tight casing; no annoying up-draft.
7. Requires minimum space.

10,196

LINK-BELT COMPANY

Chicago 8, Indianapolis 6, Philadelphia 40, Atlanta, Dallas 1,
Minneapolis 5, San Francisco 24, Los Angeles 33, Seattle 4,
Toronto 8. Offices in Principal Cities.

LINK-BELT
THE SYMBOL OF QUALITY · LINK-BELT COMPANY · LB
Bulk-Flo
ELEVATOR-CONVEYOR-FEEDER

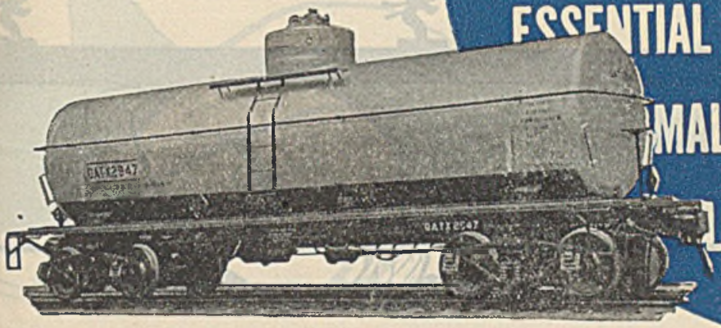
15 GALLONS *OR* A TANK CAR FULL

ship it in an Alcoa Aluminum Container

This barrel is made in 7¾, 15½ and 31-gallon capacities.

This drum is available in 30, 55 and 110-gallon capacities.

NITRIC ACID • ACETIC ACID • HYDROGEN PEROXIDE • ACETALDEHYDE • BENZALDEHYDE • GLYCERYL PHOSPHATE • METHYL SALICYLATE • PARALDEHYDE • PHENOL • ESSENTIAL OILS • ACETIC ANHYDRIDE • MALDEHYDE • BUTYRIC ACID • LACQUERS • OILS



Tank cars of Alcoa Aluminum, built to AAR and ICC specifications, are carrying many materials.

Designed for air transport, this drum weighs about half as much as standard Alcoa Aluminum drums.

You're making a high-quality product. Keep it that way by delivering it in Alcoa Aluminum—barrels, drums or tank cars. Just as aluminum is "friendly to food", so is it friendly to many chemicals and compounds.

The purity of your products is preserved when they are stored or shipped in aluminum alloy containers recommended by Alcoa. Color is unchanged, taste and odor unaffected. And, because aluminum, itself, is not attacked by these materials, these containers are long-lived.

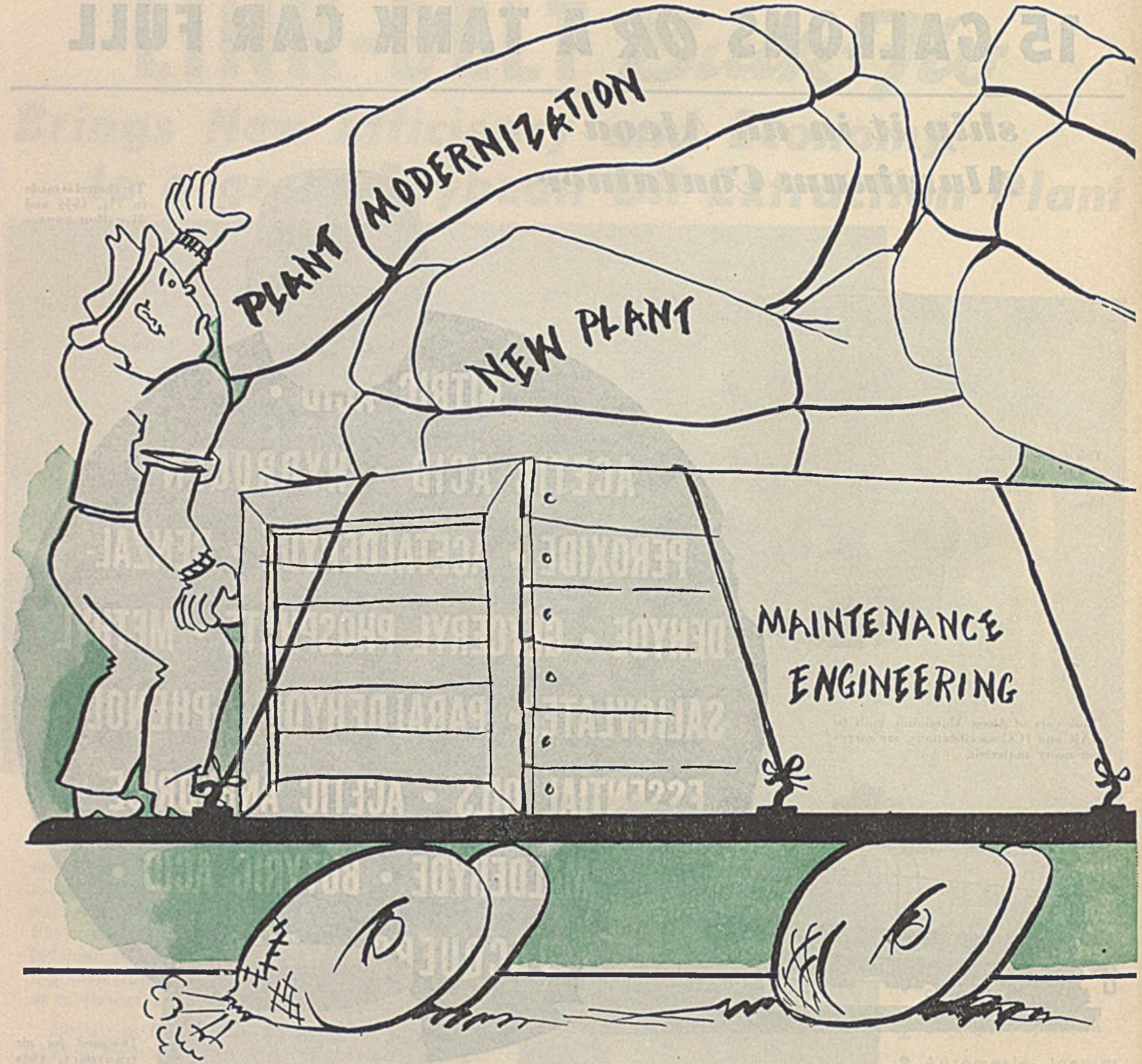
The lighter weight of Alcoa Aluminum containers cuts handling costs all along the line. Standard cleaning methods have been developed, making it easy to get these containers ready for re-use. They are strong and durable, making maintenance costs negligible.

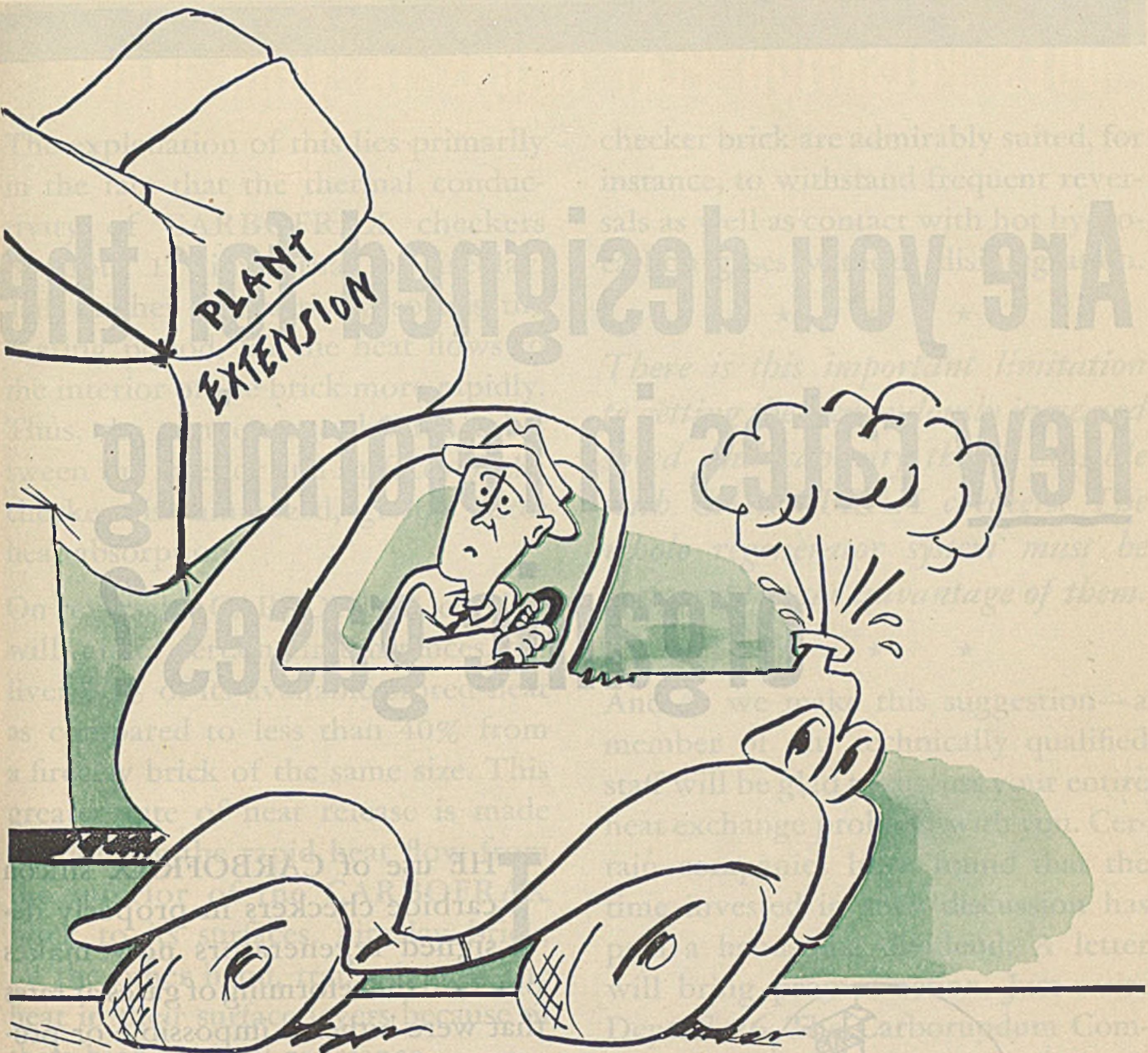
May we quote on your container requirements? ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh 19, Penna.

ALCOA FIRST IN ALUMINUM

REG. T. M.

ALCOA ALUMINUM


PLANT MODERNIZATION
NEW PLANT
MAINTENANCE ENGINEERING



. . . We can handle the overload

The engineering departments of most petroleum refining, petro-chemical or chemical companies are streamlined for normal needs . . . for maintenance and a nominal amount of auxiliary construction.

But sudden "peaks" can be serious. The added responsibilities of a major conversion or new-plant construction project may overload a regular engineering department unnecessarily. Overloads can quickly accumulate to unwieldy proportions. And assembling, qualifying and integrating an extra force for the occasion is not easy, especially in these days of professional manpower shortage.

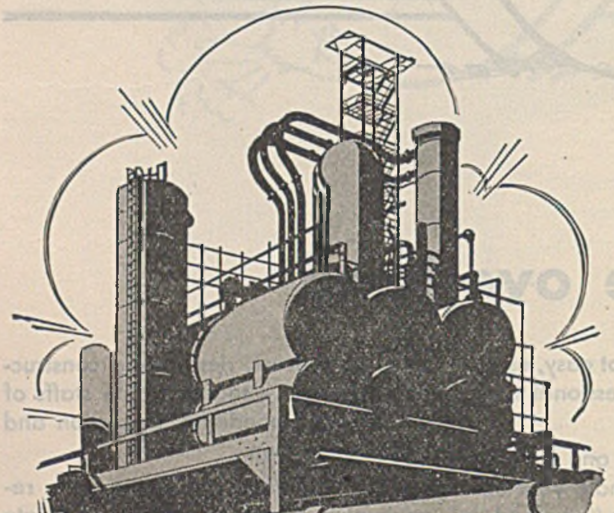
Much can be gained, and nothing lost, in letting Badger handle your engineering and construction "overloads" —either under sole Badger responsibility or with the supervision and cooperation of your own staff.

Badger—a large, flexible, and long-experienced organization—has "all the tools." Badger's sustained flow of assignments enables us to maintain permanently a complete, widely trained force of process, design and construction engineers—together with staffs of purchasing, expediting, inspection and construction men.

Plant additions, processing units, re-equipment, modernizations, or complete new plants of any size—Badger can take them "in stride," with minimum dislocation of your current routine, with over-all economy, and with the assurance that the job will be brought through to early completion and successful operation.

We invite discussions—now.

Are you designed for the new rates in reforming organic gases?



THE use of CARBOFRAX silicon carbide checkers in properly designed regenerators now makes practical the reforming of gases at rates that were hitherto impossible or prohibitively costly.

Under the same set of conditions, CARBOFRAX checkers will absorb in 2 min. 20 sec., the same amount of heat as a fireclay split of the same dimensions will absorb in 22 min. 52 sec. Tests have shown that in cracking and reforming organic gases, CARBOFRAX checkers transmit heat at rates between 20 and 50 BTU/hr./sq. ft./F° difference.

The explanation of this lies primarily in the fact that the thermal conductivity of CARBOFRAX checkers is about 11 times that of fireclay. This higher conductivity speeds the heating period, for the heat flows to the interior of the brick more rapidly. Thus, the temperature difference between the interior and surfaces of the checkers is minimized, giving faster heat absorption.

On reversal a CARBOFRAX checker will, under certain circumstances, deliver 90% of its available stored heat as compared to less than 40% from a fireclay brick of the same size. This greater rate of heat release is made possible by the rapid heat flow from the interior of the CARBOFRAX brick to its surfaces. Fireclay brick, on the other hand, transmit only the heat in their surface layers because of their high thermal resistance.

In addition, CARBOFRAX thin checker brick are admirably suited, for instance, to withstand frequent reversals as well as contact with hot hydrocarbon gases without disintegration.

★ ★ ★

There is this important limitation to getting the tremendously increased speed and capacity that's possible with CARBOFRAX checkers. The whole regenerator system must be designed to take advantage of them.

★ ★ ★

And so we make this suggestion—a member of our technically qualified staff will be glad to discuss your entire heat exchange problem with you. Certain companies have found that the time invested in such discussion has paid a handsome dividend. A letter will bring prompt action. Just write Dept. E-26, The Carborundum Company, Refractories Division, Perth Amboy, New Jersey.

SUPER REFRACTORIES

BY CARBORUNDUM

TRADE MARK

CARBORUNDUM

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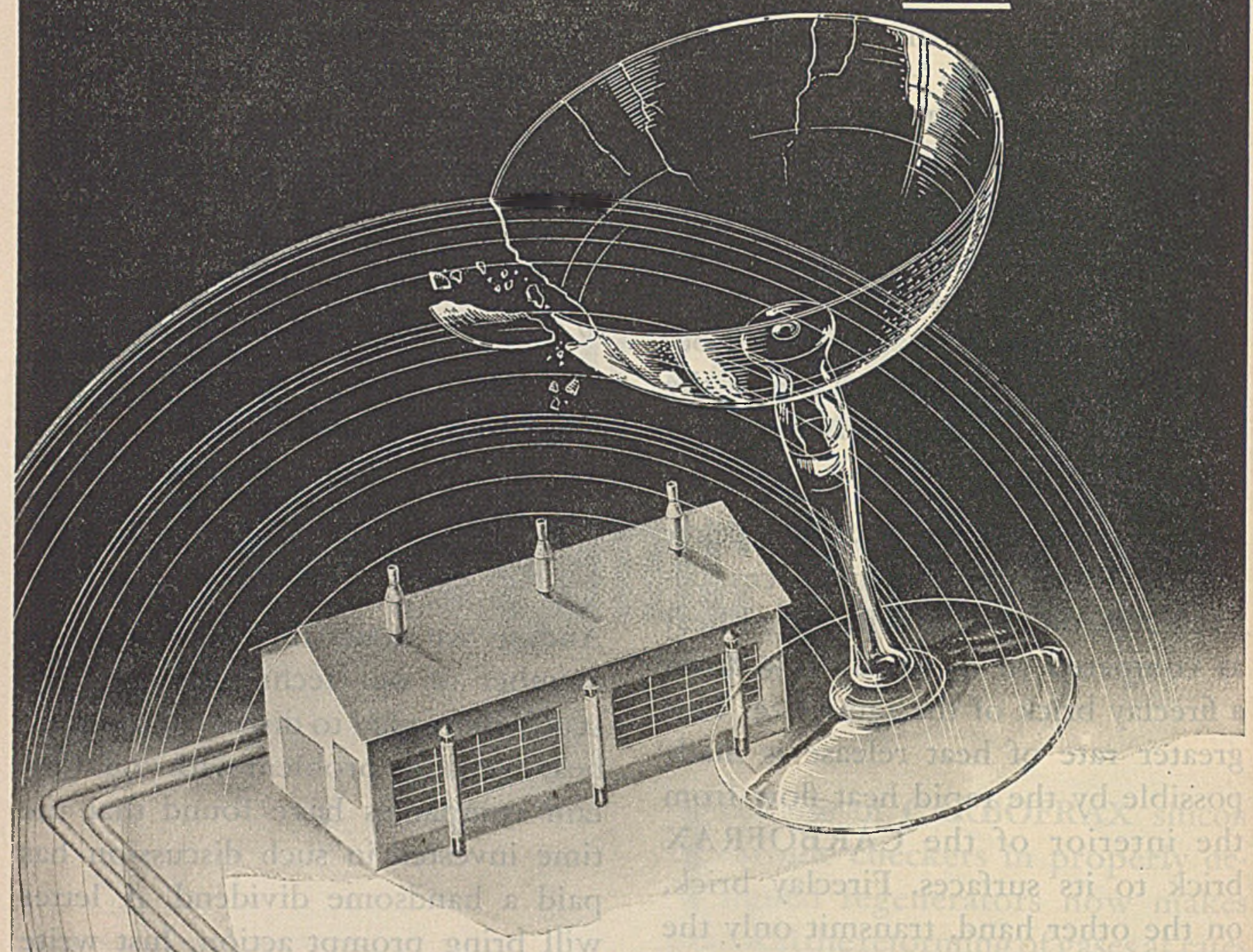
DOES PULSATION PLAY TRICKS IN YOUR PLANT?



Shatter a champagne glass at ten paces just by the sound of your voice? Sounds incredible! But, Caruso could do it. His vocal chords, by setting up air waves of sufficient pitch and intensity, produced vibrations in the glass severe enough to shatter it. Although Caruso's feat is rare, the effects of air waves are not. They are constantly playing havoc with objects far more durable and more expensive than champagne glasses.

For example, there is the phenomenon which recently occurred in the Compressor Plant of a large Eastern Gas Company. Here the compressor house and an auxiliary building were constructed parallel to each other, 24 feet apart. When the plant was put into operation, the main engine air intakes... installed between these two buildings... created so great an air surge as to cause both buildings to vibrate dangerously. A FLUOR Pulsation Dampener was installed in each air intake line. By reducing the air surge substantially, all vibration due to that cause was eliminated.

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

SINCE 1890

FLUOR PULSATION DAMPENER

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

ENGINEERS • MANUFACTURERS • CONSTRUCTORS

Enduro Pays in many ways

High strength and long life are two qualities of Republic ENDURO Stainless Steel which pay profitable long-term dividends in chemical and other processing applications.

Containing approximately 115 tons of ENDURO, the ammonia oxidation towers shown below were erected in 1926. Today, after twenty years of continuous service, they are reported to be, structurally, as sound as when they were installed.

Hundreds of other long-time ENDURO installations afford additional proof of the long, trouble-free service which ENDURO provides.

For complete information about these and the many other reasons why it pays to specify Republic ENDURO Stainless Steel in your equipment, write directly to:

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

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

Typical of the many processing applications for Republic ENDURO Stainless Steel are these ammonia oxidation towers. Others include autoclaves, condensers, conveyors, evaporators, heat exchangers, valves, vats, tanks and many types of equipment.

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


CHEMICAL
HEAT TREATING
PLASTICS
CERAMICS
Simplicity
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Just what are ROTAMETERS?

▶Rotameters are an extremely simple and accurate instrument for measuring rate of flow. They have only one moving part—a rotor which moves up and down in a tapered tube. Schutte & Koerting, having a background of 65 years' experience in designing and manufacturing tapered tube jet devices, produced the first rotameter in this country more than 15 years ago.

• When you install an S-K Rotameter, you benefit in many ways from the practical experience of both local and factory engineers that has gone into its development. You can be sure you have the right meter for the job to be done. And service, from the initial inquiry to successful installation, is designed for customer convenience. Our local engineers have had years of experience in your territory.

• Detailed information about S-K Rotameters can be obtained by writing for Bulletin 18-R which completely illustrates and describes the different types of S-K Rotameters, including accessories, and discusses the factors which help you to select the correct Rotameter for specific applications.

If you need help on an immediate flow metering problem, telephone or write to the nearest S-K representative for engineering assistance.

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Pyramid — 1-1303

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1526 Blake St., Denver
Main — 1869

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Walnut — 5192

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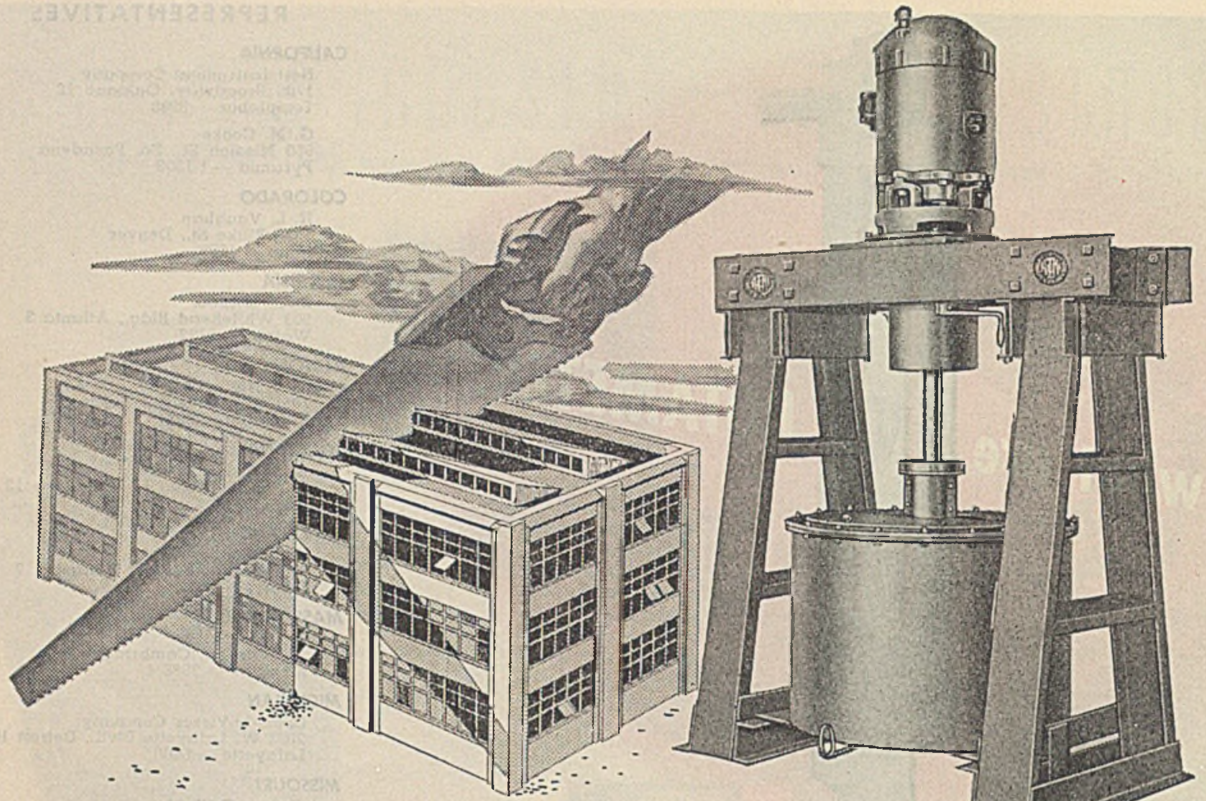


BETTER RESULTS IN A SMALLER SPACE

SEDIMENTATION: *AT&M Centrifugal Gives Higher Recovery*. Day after day, in new fields and old, centrifuging is bringing fresh proof of its ability to deliver better results faster—and in smaller space than less modern equipment requires. "Better results", moreover, include end-product-improvement, for in very many instances AT&M Centrifugals turn out a product of higher quality than former methods could achieve.

In separating oil and water from protein content, for example, a processor of fish meal is now using an AT&M Centrifugal. The high speed of this machine produces a dryer cake for final drying-out and results in much higher recovery of the valuable solids and oils.

CLARIFICATION: *AT&M Centrifugal Saves Materials and Manpower*. The many new, successful uses of centrifuging indicate practically unlimited scope for future applications. Not only where time and space are all-important, but also in cases where old techniques are ineffective, AT&M Centrifugals are solving production problems. As time goes on they will be used increasingly to lower costs and broaden sales horizons.

To recover an expensive grinding compound from oil, AT&M designed a special clarifying basket to centrifuge the oil, taking out the solids and recycling the grinding fluid in one swift operation. Results: End of a threatened shortage of materials and release of customer's manpower for other duties.

Consider Centrifuging for

extraction . . . filtration . . . dehydration . . . precipitation . . . impregnation . . . coating. See AT&M's 4-page catalog in CHEMICAL ENGINEERING CATALOG.

Consider AT&M for

capable engineering service — no charge for study and recommendation. Centrifugals and baskets in all machinable metals and coatings. Strict confidence preserved. AMERICAN TOOL & MACHINE COMPANY, 1421 Hyde Park Ave., Boston 36, Mass., 30C Church Street, New York 7, N. Y.

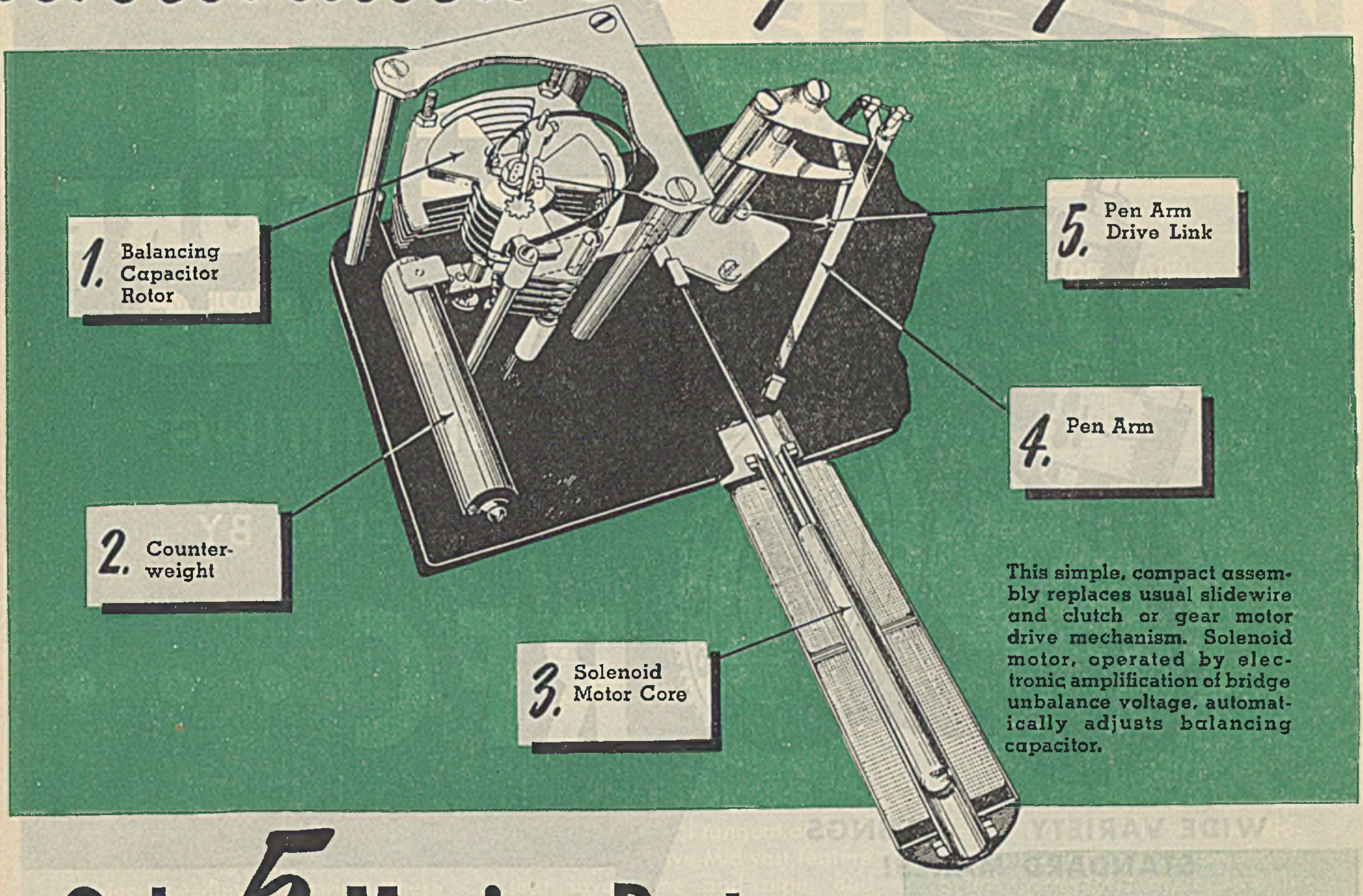
SAVE TIME, SPACE AND COSTS WITH

A.T. *and* M.

CENTRIFUGING

3-5-11

Unrivalled Simplicity—



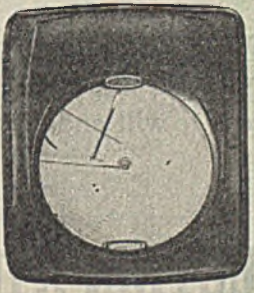
This simple, compact assembly replaces usual slidewire and clutch or gear motor drive mechanism. Solenoid motor, operated by electronic amplification of bridge unbalance voltage, automatically adjusts balancing capacitor.

Only 5 Moving Parts in DYNALOG* Instruments!

Here at last are industrial bridge-type instruments specifically designed as *electronic instruments,* not merely supplemented by electronic improvements. That's why Foxboro's *DYNALOG* temperature and pressure instruments are *the first* to offer the full simplification and high performance made possible by electronic principles.

In *DYNALOG* Instruments, moving parts are reduced to only *five.* Sensitivity is so stepped-up that *narrow* scales are recorded with high accuracy previously possible only on wide scales. And balancing speed is cut to 3 seconds for full-scale pen travel.

If your process responds directly to faster or more accurate measurements, call in a Foxboro Engineer. *DYNALOG* Recorders and Multi-Point Indicators are available for temperature and high-pressure uses. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U. S. A.



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ADVANCED CHARACTERISTICS OF *DYNALOG* INSTRUMENTS

1. HIGH SENSITIVITY—Positive balancing action on unbalance voltages of less than 15 microvolts. Bridge output voltages electronically amplified up to 1,000,000 times to control balancing drive motor.

2. HIGH BALANCING SPEED—3 seconds for full-scale travel of pen or pointer. Balancing drive motor with high power (at least 10 times as much as pressure-spring instruments.)

3. HIGH ACCURACY—Calibration accuracy ¼ of 1% of scale for all ranges . . . a direct result of Live-Balance drive. Full power is available, even at minute unbalances.

4. GREATER SIMPLICITY—Entire balancing mechanism contains only 5 moving parts! Electronic circuits employ only standard, easily-replaceable tubes. There's nothing to clean, lubricate, adjust, or take up!

FOXBORO
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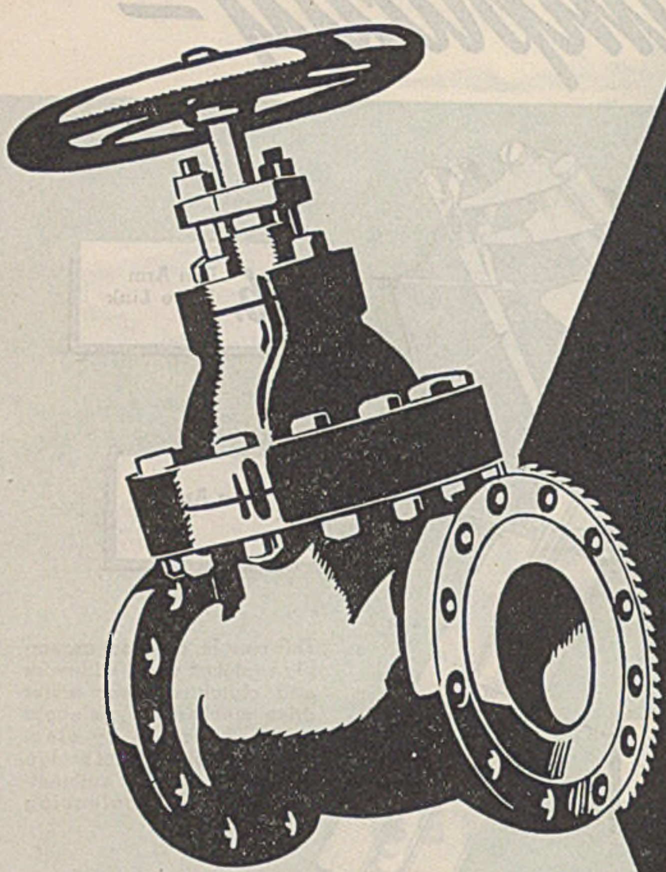

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HIGH PRESSURE VALVES AND FITTINGS OFFERED BY RFC . . .

WIDE VARIETY OF FITTINGS STANDARD MAKES!

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VETERANS: To help you exercise your priority, special veteran service facilities are now available at our offices.

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Write, wire or phone your requests to the nearest RFC agency listed below for more detailed information. Credit terms can be arranged. If your local office does not have all the materials you need, it will endeavor to locate them from other offices throughout the country.

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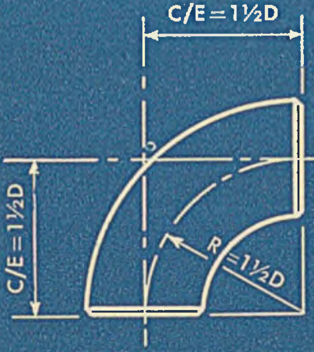
177-1

ONLY MIDWEST OFFERS A COMPLETE SELECTION OF 90° WELDING ELBOWS

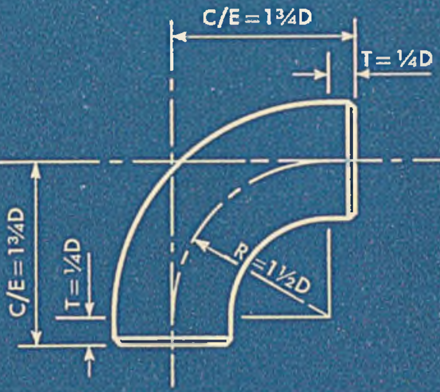
① LONG RADIUS AMERICAN STANDARD



SIZES: 3/4" TO 12", INCLUSIVE

All dimensions conform to the American Standard for Steel Butt-Welding Fittings ASA B16.9. Unless order specifies otherwise, these "ASA Elbows" will be furnished.

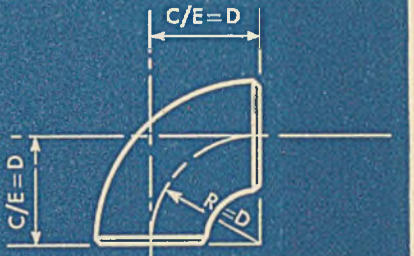
② LONG RADIUS LONG TANGENT



SIZES: 2" TO 20", INCLUSIVE

Same radius as "ASA Elbows" but with long integral tangent on each end—an exclusive Midwest feature that saves time and pipe, and sometimes eliminates an extra weld.

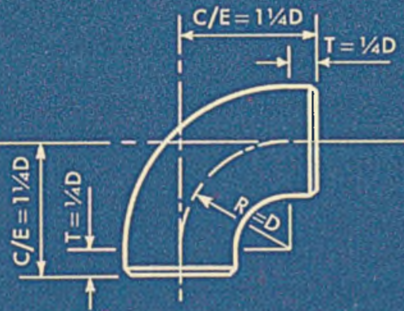
③ SHORT RADIUS



SIZES: 1" TO 12", INCLUSIVE

Where space limitations prevent the use of "ASA Elbows" or Midwest "Long Tangent" Elbows shown at left, these short turn elbows without tangents are recommended.

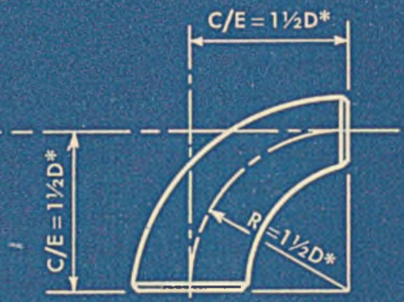
④ SHORT RADIUS LONG TANGENT



SIZES: 14" TO 24", INCLUSIVE

These OD sizes are short radius but have the exclusive Midwest long tangents that save pipe and make it possible to line up the fitting and pipe more quickly and accurately.

⑤ LONG RADIUS REDUCING



SIZES: 2" TO 12"*, INCLUSIVE

Only Midwest makes the reducing welding elbow which takes the place of a straight elbow and a reducer. It eliminates one weld, cuts installation cost, and reduces pressure drop.

MIDWEST WELDING FITTINGS IMPROVE DESIGN AND REDUCE PIPING COSTS

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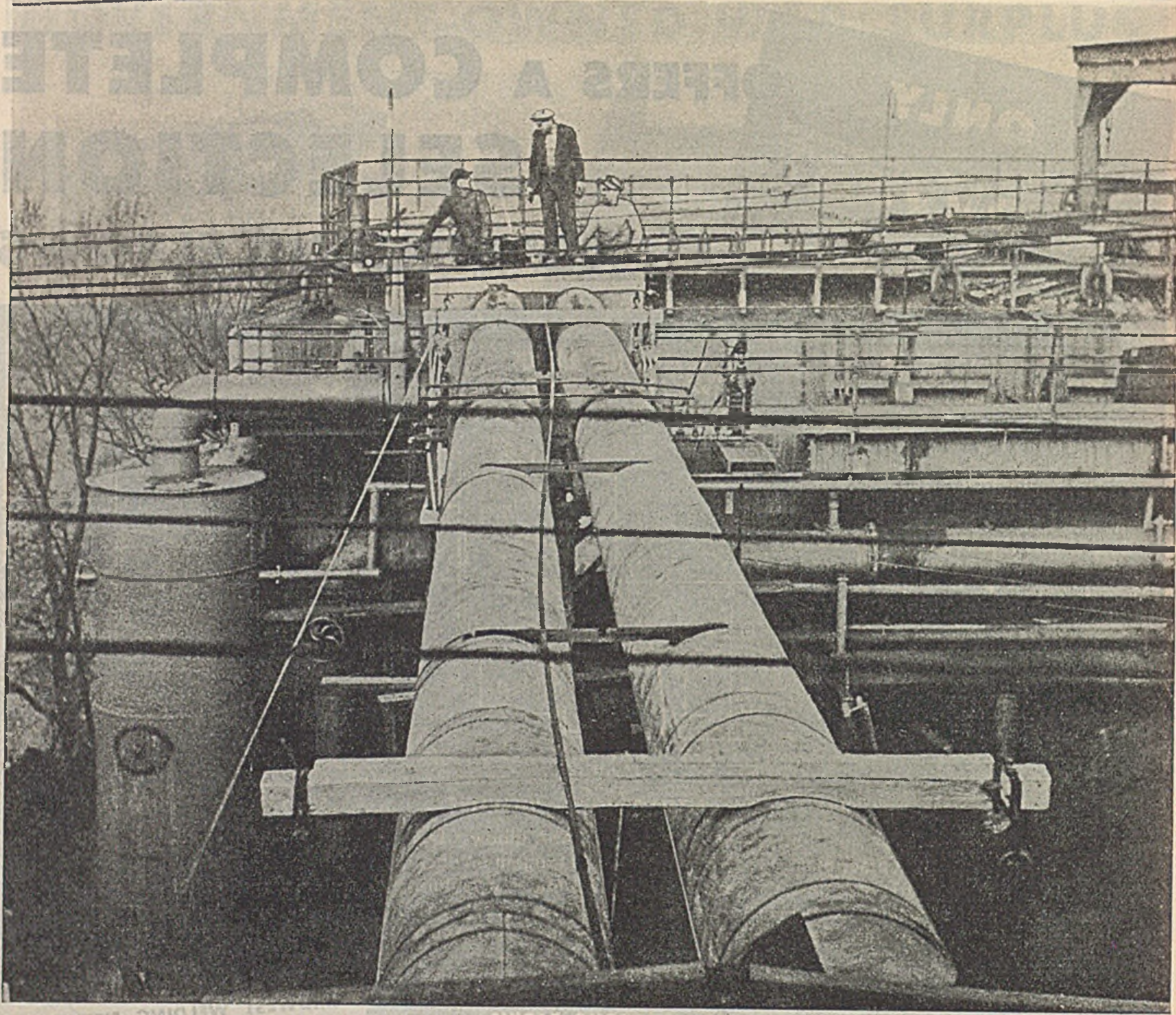
SYMBOLS:
C/E = Center-to-End Dimension
D = Normal Pipe Size
R = Radius
T = Length of Tangent
*D = Dimension is Larger Pipe Size



HOW FIBERGLAS* BEAT THE WEATHERMAN

Predictions of "continued cold" can mean serious trouble—unless pipes are adequately insulated. Fiberglas Industrial Insulation, furnished in forms to meet every interior and exterior requirement, is helping industry avoid the costly effects of weather changes and extremes.

During a natural gas shortage, a West Virginia concern built its own gas-producing unit. Efficient operation was aided by the application of Fiberglas insulating blankets, pipe covering and insulating cement. Moisture condensation in two 18-inch gas lines, which had caused severe pressure drops, was eliminated by insulating more than a mile of lines with Fiberglas pipe insulation. And this same highly efficient thermal insulation, installed on outside water lines, prevented freezing.

The illustrated booklet, "Fiberglas Insulations for Industry", will give you complete information about all of the forms of Fiberglas Industrial Insulation materials. Write for your copy today. Find out how this better material can help you "beat the weatherman" and save money. *Owens-Corning Fiberglas Corporation, 1951 Nicholas Bldg., Toledo 1, Ohio.*

In Canada, Fiberglas Canada Limited., Oshawa, Ontario.

FIBERGLAS

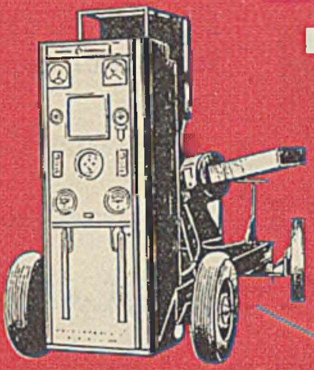
*T. M. Reg. U. S. Pat. Off.

OTHER FIBERGLAS PRODUCTS: ELECTRICAL INSULATION MATERIALS • DUST-STOP* AIR FILTERS • FIBERGLAS YARNS AND CLOTHS • FIBROUS GLASS MATS

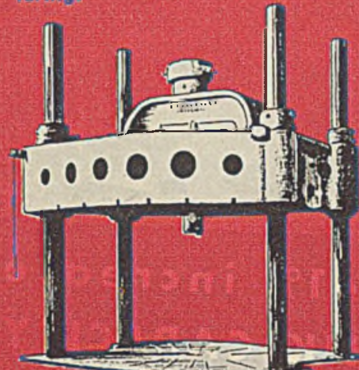
UNEXCELLED FACILITIES FOR THE COMPLETE FABRICATION OF ANY TYPE EQUIPMENT—FROM ANY METAL OR ALLOY

—up to 6 inches in thickness

—and to the most exacting specifications



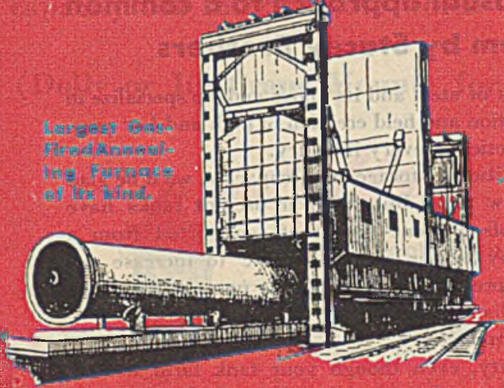
Modern X-Ray and Gamma-Ray Equipment for precision manufacturing.



2000 Tons Pressure Plate Forming Press.

Turn to Struthers Wells—when your equipment calls for "out-of-the ordinary" fabricating or engineering ability either in size, intricate design or for any specialized service.

Our engineers will cooperate with you anytime, any place.



Largest Gas-Fired Annealing Furnace of its kind.

Two Large Welding Shops —172 Welding Machines —Manipulators.

Craftsmanship to meet all A.S.M.E. or A.P.I. Codes.

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PROCESS EQUIPMENT DIVISION
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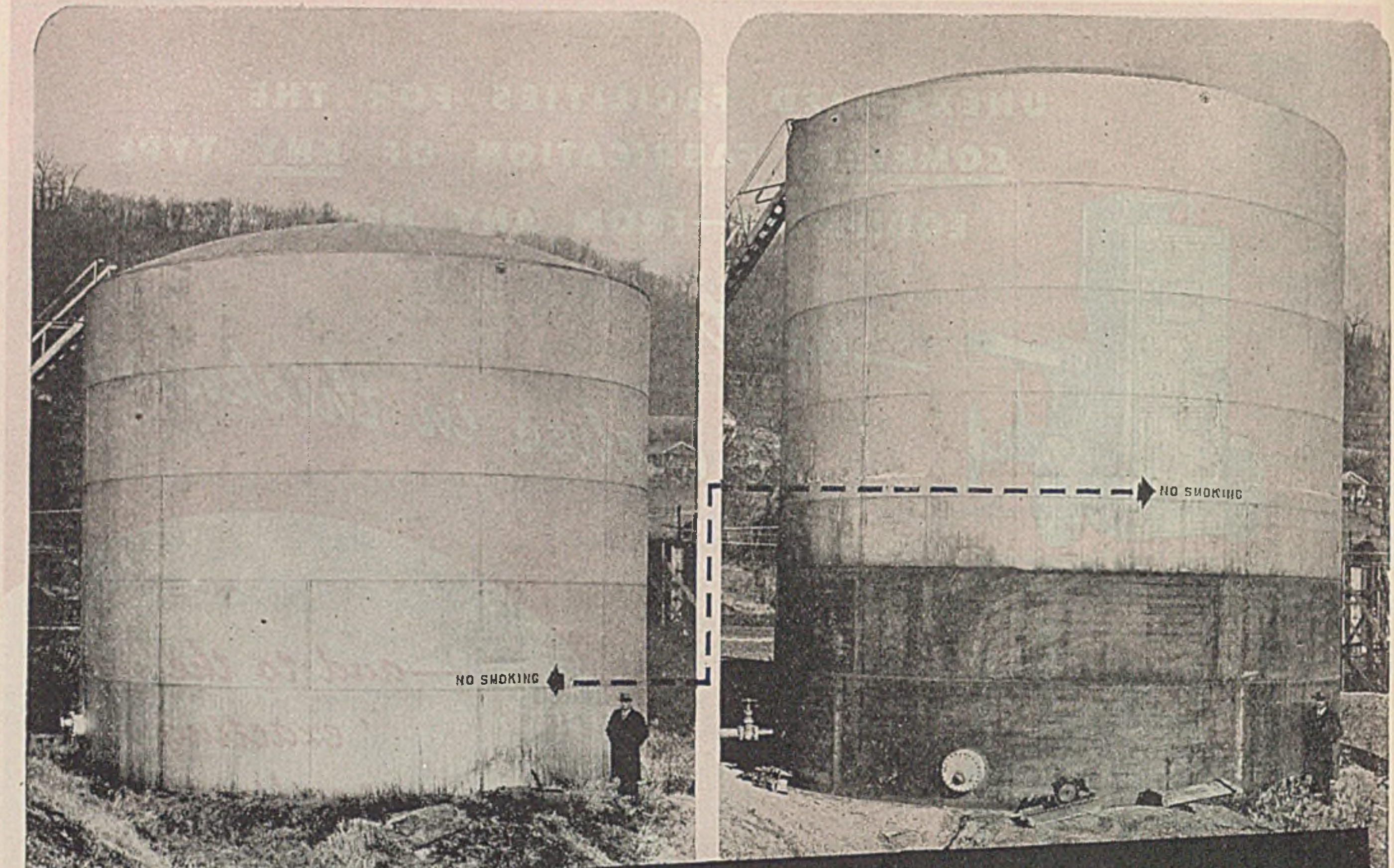
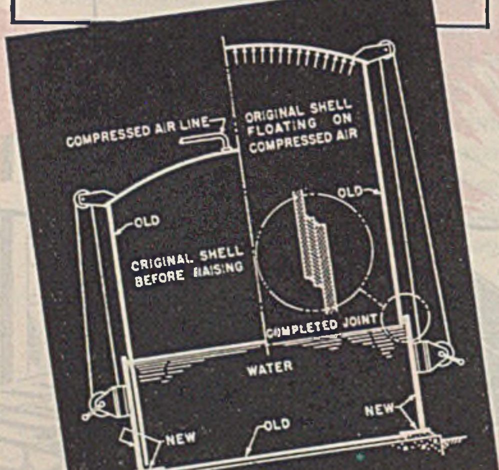

NO SMOKING
NO SMOKING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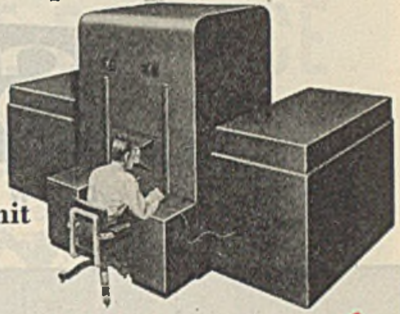
OLD
ORIGINAL SHELL BEFORE RAISING
COMPLETED JOINT
WATER
NEW
OLD
NEW

wherever and whenever x-ray is called upon . . .

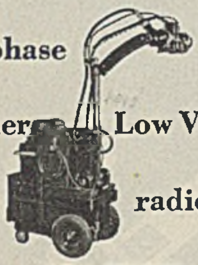
fluoroscopy

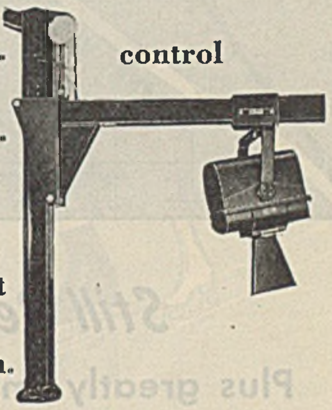
In the rapidly expanding field of light-metal fluoroscopy, Picker offers apparatus for either small-scale or quantity-production continuous inspection. "Pixray 85" is a compact, self-contained unit performing either fluoroscopy or radiography for limited requirements. The Picker "Master" Radiographic-Fluoroscopic Unit is designed for semi-automatic mass-production inspection.



radiography

Picker X-Ray offers a very wide range of equipment to cover every phase of industrial radiographic application. The compact Picker Low Voltage Unit (5 to 50 KV) is ideal for check-and-control radiography of light metals, plastics, low-density materials. Picker 150 KV Unit (Mobile or Stationary) provides ample capacity for intermediate work. Picker 250 KV Unit (Dolly or Jib Crane Mount) for heavy-duty inspection.





diffraction

X-ray diffraction analyses quickly provide otherwise unavailable data of immense significance in research studies, and in product-and-process control and improvement. Picker X-Ray Diffraction Apparatus is compact, self-contained and offers every convenience and facility for rapid and accurate determinations.

Technical Bulletins are available for any or all of the above apparatus (please request them on your letterhead). Or, for further information, get in touch with your local Picker representative. There are branches in principal cities of U.S.A. and Canada.

industrial PICKER X-ray

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NEW and IMPROVED

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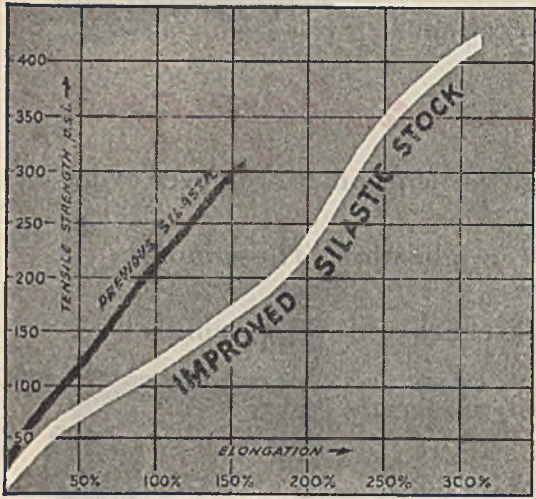
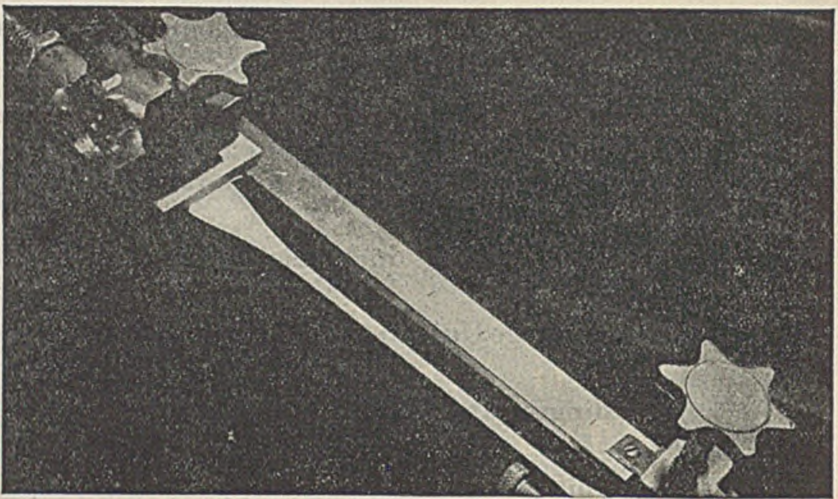
DOW CORNING SILICONE RUBBER





Still Resilient at 500°F. • Flexible at −70°F.

Plus greatly improved TENSILE STRENGTH—up from 200-330 to 280-500 p.s.i.
ELONGATION—up from 70-115% to 150-300%

Silastic* makes history—*again!*

Big new improvements in this unique silicone rubber surpass even the previous history-making Silastic achievements! The *NEW AND IMPROVED SILASTIC* is ready—*NOW*—for many more difficult jobs at extreme high and low temperatures. It offers radically improved physical properties, excellent dielectric values, and resistance to oxidation and ozone.

Earlier stocks supplied urgent wartime demands for elastic materials serviceable above and below temperature limits of natural and organic synthetic rubbers. New stocks perform even better—both at extreme and moderate temperatures.

Look to Silastic for insulating lead wire and appliance cords; for gaskets subjected to severe service conditions; for insulating heating elements and resistor coils; for coating glass fabrics.

*TRADE MARK, DOW CORNING CORPORATION.

New Silastic Stocks Available For
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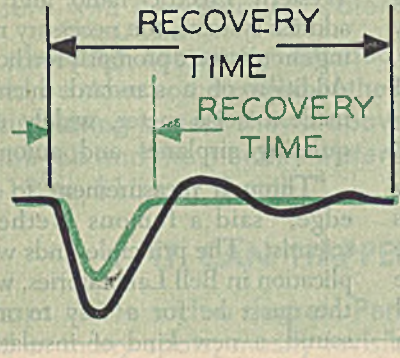
FIRST IN SILICONES

Pal up with a good skater... leave the rest to INSTINCTIVE BALANCE

It's easy to skate after you catch on to the few simple strokes and the rhythm. Just leave everything to INSTINCTIVE BALANCE. Even before you are aware of any threat to your balance, your instinct starts an automatic correction. Because it's INSTINCTIVE, not just mechanical, this correction includes just the right amount of additional action to restore balance quickly and smoothly enough to avoid a real upset.

That's the difference HYPER-RESET makes in process control – the difference between mere alertness of an instrument to a condition of upset, and a combination of that alertness *plus* response to the RATE of disturbance. It's the difference between a control system that measures a disturbance as it develops, and a system that *also* produces an additional, precisely determined corrective action derived from the *rate* of disturbance.



These superimposed characteristic curves of a typical process show how great a difference HYPER-RESET makes. The black curve shows the best possible stabilization of this process without HYPER-RESET. The green curve illustrates how the HYPER-RESET in Foxboro's Stabilog Controller minimizes the upset and quickly restores stability to the process.

On many of the toughest control applications, HYPER-RESET stabilizes a process in as little as one-fourth the usual time. Write for detailed discussion and suggestions for applying this advanced control principle to your process. The Foxboro Company, 40 Neponset Avenue, Foxboro, Massachusetts, U. S. A. Branches in principal cities.

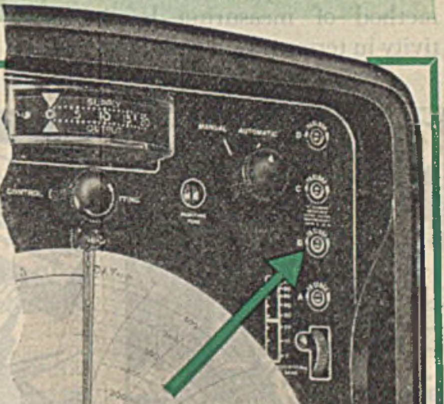
Why HYPER-RESET Saves a Needless, Extra Adjustment

With a HYPER-RESET Stabilog Controller, *only one adjustment* is required for accurate selection of both the reset rate and the rate-sensitive, extra-corrective function.

It has been well established that the response characteristics of a process determine how much correction can be applied, and how fast. It is the time characteristic which determines the reset adjustment. And it is this self-same time characteristic which also establishes the amount of rate-sensitive action required!

Both research and field experience have demonstrated that the rate-sensitive adjustment, as well as the reset, must be matched to the process; and that a definite relationship exists between any given reset value and the corresponding rate-sensitive value for best recovery.

These two values are combined as a *single adjustment* in the Foxboro HYPER-RESET Stabilog Controller.



FOXBORO Stabilog **Control**

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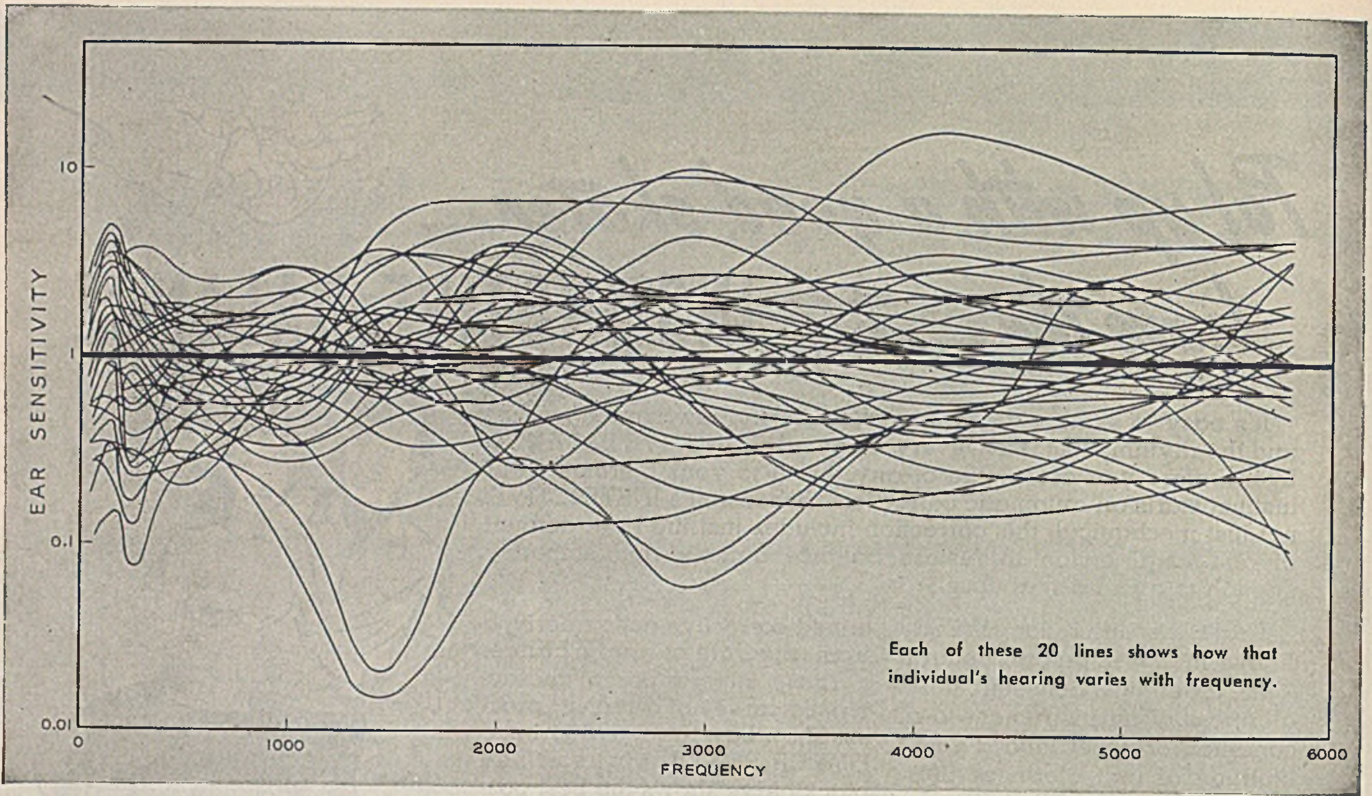


Each of these 20 lines shows how that individual's hearing varies with frequency.

To measure is to know

Twenty-five years ago, one standard of sound power was the ticking of a watch, another was the clicking of two coins; and the measure was how far away the tick or the click could be heard. That test was made in measuring people's hearing, a field of interest to the Bell System scientists because the ear is the end-point of every talking circuit.

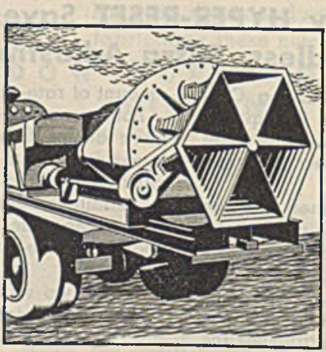
Accustomed to exact measurements, Bell scientists proceeded to develop a method of measuring hearing-sensitivity in terms which could be precisely defined and reproduced. After plotting hundreds of runs like those above, they decided on a particular sound intensity, representing an average "threshold of hearing," as a starting point.

The sounds delivered by a telephone line had previously been evaluated by listeners who compared their loudness with that of a standard source. There were wide variations in ears, as the chart shows, so the engineers replaced them by electrical instruments. When later their associates developed the Western Electric radio and public address systems, the necessary measuring circuits were promptly forthcoming. Addition of a standard microphone made a noise meter, widely used in quieting airplanes and automobiles.

"Through measurement to knowledge," said a famous Netherlands scientist. The principle finds wide application in Bell Laboratories, whether the quest be for a way to measure sound, a new kind of insulation, or more economical telephone service.

Hearing was first measured reliably by engineers in the Bell Telephone Laboratories

For good reception, program loudness must stay within certain limits. Volume-meters help to hold it there

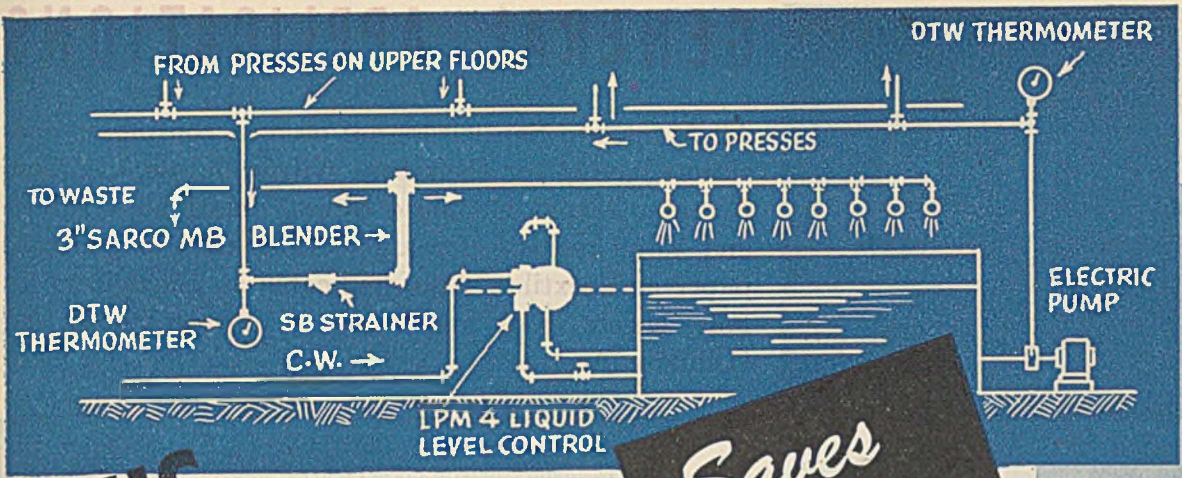


From the throat of this mighty air-raid siren comes the loudest sustained sound ever produced

Visible Speech, result of telephone research, turns sound into "pictures" that the deaf can read

BELL TELEPHONE LABORATORIES

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



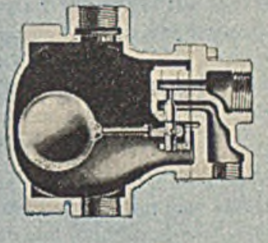
THIS SARCO HOOK-UP..

Saves $500 a month

The Sarco Blender is an automatic three-way valve that recirculates and controls temperatures.

A large plastics plant in New York uses a great number of hydraulic presses, which formerly were cooled by a 3-inch city water main running at full pressure with the returning water at 80 degrees.

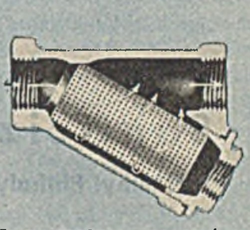
The plumbing contractor decided that something drastic and permanent should be done so he called in the Sarco representative, who recommended the circulating system shown above. Three little inexpensive Sarco products did the job and the monthly water bill of more than $500 has been reduced to $12 to $15 per month.



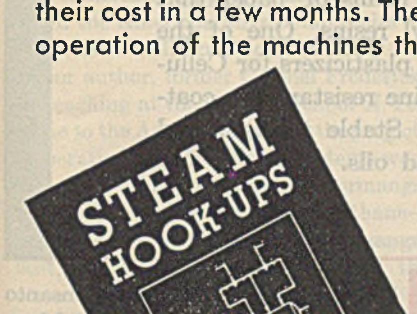
The Sarco liquid level controls are as simple as a float trap.

IT CAN HAPPEN IN YOUR PLANT!

Perhaps not to such a degree. Perhaps it's only a small loss of water multiplied at many spots, mostly invisible. But the Sarco devices used for recirculation and temperature control of tanks, engine jackets, brine coils, condensers, etc., cost so little that even a trickle of wasted water will pay their cost in a few months. The big saving is in the more efficient and reliable operation of the machines they control.



Sarco strainers are used to protect equipment, to clean river water, and strain oil, syrups, etc.



Many ways to save are shown in the Sarco Hook-Up Book and Sarco Catalogs. Many others applying specifically to your plant are available through the Sarco representative near you.

106

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MONSANTO PLASTICIZERS

(Phthalyl Glycollates)

GENERAL APPLICATIONS

All Monsanto Santicizers are used in coating compositions having for their base Nitrocellulose, Cellulose Acetate, Mixed Cellulose esters, chlorinated rubber and Vinyl resins — for applications to wood, metals, paper and textiles. Also applicable as plasticizers for foils, sheets, rods and tubes of Nitrocellulose and Cellulose Acetate.

Santicizer E-15*

(Ethyl Phthalyl Ethyl Glycollate)

A practically colorless liquid, used in making molding powders from Cellulose Acetate, Cellulose Acetate butyrate, and Cellulose Acetopropionate. Stable to light and heat — resistant to fats and oils.

Santicizer B-16*

(Butyl Phthalyl Butyl Glycollate)

A practically colorless liquid, used to improve the adhesion of chlorinated rubber coatings—also as a plasticizer for Polyvinyl Chloride used in making hose through which beverages are passed. A satisfactory medium for grinding pigments used in lacquers. Stable to light and heat — resistant to fats and oils.

Santicizer M-17*

(Methyl Phthalyl Ethyl Glycollate)

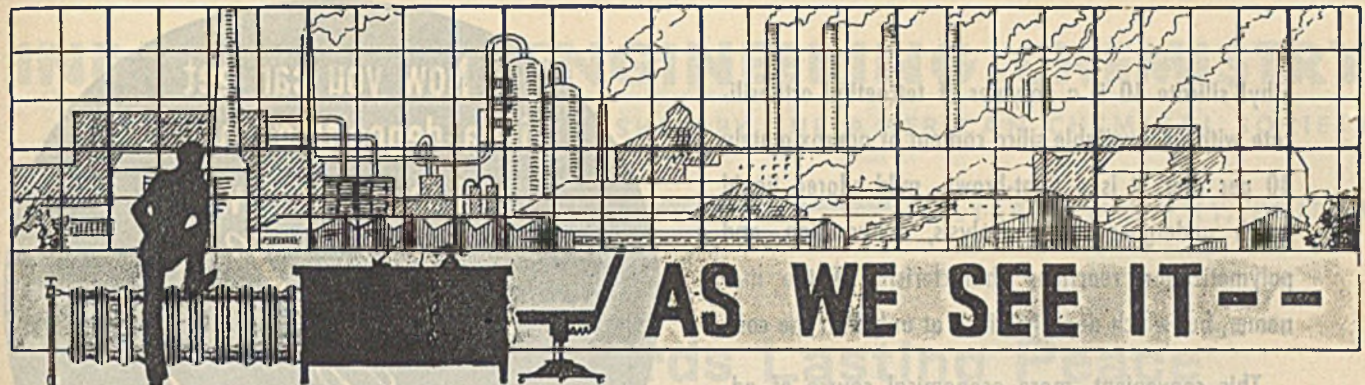
A practically colorless liquid, used for the same applications as Santicizer E-15 — also in making container closures of vinyl resins or paper that has been coated with vinyl resins. One of the least volatile of the solvent plasticizers for Cellulose Acetate. Imparts gasoline resistance to coatings and molded products. Stable to light and heat — resistant to fats and oils.

MONSANTO CHEMICALS

SERVING INDUSTRY . . . WHICH SERVES MANKIND

For further information on Monsanto Santicizers, call at the nearest Monsanto office, or write to: MONSANTO CHEMICAL COMPANY, 1700 South Second Street, St. Louis 4, Missouri. District Offices: New York, Chicago, Boston, Detroit, Charlotte, Birmingham, Los Angeles, San Francisco, Seattle, Montreal, Toronto.

*Reg. U. S. Pat. Off.



AS WE SEE IT--

Number Forty. Adventures of a Perkin Medalist might well be the theme of this issue, for the first three articles are all from the recent ceremonies at New York where Francis Cowles Frary, director of research of the Aluminum Company of America, was made the Fortieth Perkin Medalist. By strange coincidence I. & E. C. began its series of Perkin Medal articles in 1911 when Charles Martin Hall received the honor. Now, thirty-five years later, another genius in the aluminum field receives the same richly deserved acclaim. First, James G. Vail, vice president of the Philadelphia Quartz Company, gives us the personal side of the medalist. The influences on Frary of family and education, and the effect of his personal vagaries on his associates are traced in warm fashion. Webster N. Jones, director of the College of Engineering at Carnegie Institute of Technology, writes on the technical achievements of Frary, depicting the character of the work which led the medal committee to choose him. Jones points out that the interests of the medalist have been varied; they range from the designing of a phosgene plant for the Army during the last war to microstructure of wet negatives. The portion of his work on aluminum metal deals with an enormous number of subjects—from laboratory studies to the use of the metal in construction work and its applications in the chemical industry. In his medal address, Adventures with Alumina, Frary points out that inorganic chemistry has numerous mysteries. As an example, he shows that aluminum oxide is a genuine unknown. The unanswered questions exceed by far the proved data on this material which is so basic to the aluminum industry.

Operation Fred. The cover this month presents an American "robomb", or in the nomenclature of the Army, the JB-2. Reason for this is an article from the Chemical Warfare Service on chemical propellants. When the Germans had perfected the flying bomb to the point of use, it became the job of chemists and engineers in America to make a domestic version of the weapon, and to investigate propellants which would have enough kick to speed the American buzz bomb on its way. The paper Chemical Propellants tells part of the story of the investigation. The senior author, former Colonel Frederick Bellinger, now returned to teaching at the Georgia School of Technology, loaned his first name to the Army as a code for the project—which was called, aptly, "Operation Fred". Three systems were investigated by the six authors: hydrogen peroxide–permanganate, red fuming nitric acid–aniline, and mononitromethane–catalyst. For practical purposes the system peroxide–permanganate was found to be the best, and it is reported here in part; the second installment will come next month. These articles are printed because chemical propellants open up a new field which may become economically important, and further, because they include a wealth of data on highly concentrated peroxide. As more wartime chemical research is made available to the public, we hope to continue our policy of publishing it promptly.

New Products, Old Industry. Wood carbonization is an ancient industry, with which synthetic chemistry and modern industry have not dealt gently. But the same factors which have caused the obsolescence of large portions of the destructive distillation field are now coming to its rescue. Goos and Reiter describe a portion of this change in their current article, New Products from Wood Carbonization. Knowing that tars and oils are a good portion of the carbonization by-products (12.2% to be exact), the authors have attempted over a number of years not only to separate and identify the complex mixtures, but to reduce the separation procedure to plant practice. This has been accomplished for some materials, and plant operations are ready to begin. Flow charts show the procedures, and, as illustrative examples of the new technique, descriptions are given of the isolation of acetol acetate (not previously reported as a constituent of pyroligneous liquors), the isolation of butyric acid, and the recovery of maltol, which is present only in the amount of 0.03% in the starting substance.

Enthalpy, Entropy, & Co. Studies of the thermodynamic properties of carbon dioxide are of interest to engineers in the chemical and power fields. From the Georgia School of Technology comes an extensive group of charts and tables on the specific volume, enthalpy, and entropy of this gas. There are ten pages of tables on the properties of the superheated gas. A footnote tells of the availability of large specific volume and temperature-entropy charts. Portions of both of these are reproduced in the article, Thermodynamic Properties of Gases.

DDT's. Entomology's mystery powder, DDT, is emphasized in two articles. Though the insect specialists may debate on the wisdom of using the material and long argue the effect of DDT on Nature's balance, the chemistry of the subject is rapidly going forward. In the first paper the U. S. Bureau of Entomology and Plant Quarantine publicizes the results of empirical research on the solubility of the insecticide in various kerosenes. Strangely enough there is a decided difference in the solubility, depending on the source; naphthenic kerosenes dissolve more DDT than paraffinic-base solvents. The second article is from the Chemical Warfare Service on a new method of making the compound. At present the commercial practice is to condense chlorobenzene with chloral in the presence of a large excess of sulfuric acid. The authors propose the manufacture of DDT by reacting chlorosulfonic acid with chloral hydrate and chlorobenzene. Laboratory and pilot plant methods are described along with an estimated cost. Although the production price is higher than for the conventional methods as calculated by the authors, they feel that their method holds several advantages for the small manufacturer.

Pure Hydrocarbons, No. 2. Griswold and Van Berg continue, in this issue, a description of the Distex process and its applications to the processing of mixed hydrocarbons. This time it is the production of a pure heptane from a natural gas. First the Distex process was used to separate the hydrocarbon mixture into paraffinic, naphthenic, and aromatic portions. The pure heptane was then fractionated from the paraffinic portion.

F. S. Van Antwerpen

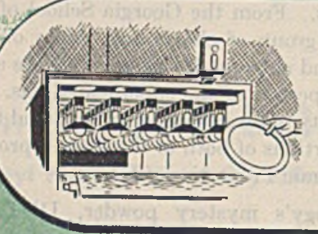
Now you can get silica-depositing solutions at lower cost with *ethyl silicate 40*

Ethyl silicate 40 is a polymer of tetraethyl orthosilicate with an available silica content of approximately 40 per cent. It is a light-brown, mild-odored liquid which undergoes the hydrolysis, dehydration, and polymerization reactions characteristic of the monomer, but which deposits silica at only half the cost.

This convenient, more economical source of adhesive silica is now available in drums and in tank cars. A few suggested applications are illustrated below:

BUILDING PRESERVATIVES

Ethyl silicate 40 solutions are useful for preserving architectural and artistic stonework. The hydrolyzed ester arrests spalling and cracking due to weathering.

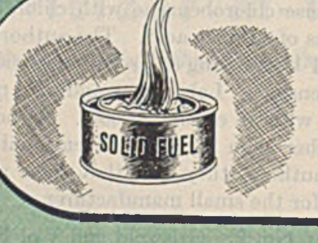


HEAT-RESISTANT SURFACE COATINGS

Ethyl silicate 40 paints are extremely resistant to high temperatures and to most chemicals. They are particularly useful for infrared lamps, asbestos blocks, and other surfaces where lack of flexibility is not a deterrent.

REFRACTORY BINDER

Ethyl silicate 40 is an important binder for refractory materials such as alumina, powdered silica, zirconia, and graphite.



STABLE GELS

Ethyl silicate 40 is a versatile gelling agent for many liquids including ethanol, isopropanol, and acetone. The gels are tough, elastic, and stable.

For information on the use of ethyl silicate 40, write for Form 6221.

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

Progress towards Lasting Peace

WE TRUST and pray that January 24, 1946, will become one of the world's most historic dates, for on that day the United Nations created a commission to control atomic energy. In its first decisive action on a world issue, the General Assembly of 51 nations has created an organization which, in the words of Secretary of State James F. Byrnes, is vitally necessary to save the world from an atomic armaments race—a race in armaments that if continued uncontrolled may destroy the civilization we hope to save.

The problem of working out the detailed plans for controlling atomic energy so that our new source of power is employed solely for the betterment of mankind is now assigned to 12 members of the Security Council—the United States, Canada, Russia, Britain, France, China, Australia, the Netherlands, Poland, Egypt, Brazil, and Mexico. Not a moment should be lost in the appointment of members of the commission so that the agency can be organized promptly when UNO establishes headquarters in the United States. It is no secret that already serious disagreements on other matters of international importance threaten the UNO structure, and that a speedy and satisfactory answer to the atomic energy problem will give great impetus to a deep desire to find adequate solutions to all questions now before that body.

Meanwhile Congress faces the task of establishing a policy for the domestic control of atomic energy. Again there is need for speed, but not undue haste. The McMahon Committee has formulated a bill after several weeks of painstaking research and, as these lines are being written, is engaged in holding hearings on the measure. The bill and the more important portions of the testimony are reproduced in the February 10 issue of *Chemical and Engineering News.*

We must not forget that other countries view with alarm and a certain amount of suspicion the fact that we continue to manufacture and stockpile atom bombs and fissionable material. They realize also that intensive research in nuclear energy continues under the direction of our armed forces. A sound national policy on control in this country will help to allay the fears and suspicions of the rest of the world and will assist the international commission in its task of providing a fully acceptable control plan at the international level.

Surprisingly, a large segment of the American public appears to have shaken off the mental reactions so universally prevalent when the news of the bombing of Hiroshima dramatically proclaimed the dawn of a new and revolutionary era. Problems attending reconversion, the struggle between labor and management, inflation, lack of adequate housing facilities, rapid demobilization of our armed forces, and a hundred and one other domestic questions have pushed the atomic bomb and its dreadful implication of a direct threat to the future welfare of humanity into the background. Yet, by comparison, these problems are definitely of secondary importance.

Strange as it may seem, America and the world in general appear to need further demonstration of what a third world war would be like in an age of atomic power. Possibly the planned bombing project "Operations Crossroads" not only will serve to supply certain military and naval data but will add still further convincing evidence that another world war means the end of civilization; perhaps it will provide sufficient additional evidence to turn men's thoughts from war for all time. Let us solemnly hope that what happens at Bikini Atoll in the Marshalls this spring will be witnessed not only by American Army and Navy officials, but by representatives of every nation on earth and that the story will be indelibly impressed on the minds of every man, woman, and child now alive, and suitably recorded for future generations.

The American Chemical Society appreciates that it shares in the responsibility of interpreting correctly what should be the future course of a world in which the use of atomic energy can lead either to untold benefits or complete annihilation. The Society will sponsor a nuclear energy exhibit at the 20th Exposition of Chemical Industries to be held at the Grand Central Palace in New York during the week of February 25, and will also show the display at the Atlantic City meeting of the Society in April, at the National Chemical Exposition of the Chicago Section of the Society in that city in September, and possibly in other key cities during 1946. It is a huge undertaking but a most important one. The American public must be aroused from its lethargy. Knowledge as well as science is power!

THE PERKIN MEDAL

Presented to Francis C. Frary

in recognition

of outstanding achievement in applied chemistry

▶ ▶ ▶ The fortieth recipient of the Perkin Medal is Francis Cowles Frary, director of research of the Aluminum Company of America. In 1856 William Henry Perkin discovered Perkin's purple or mauve and thereby initiated the synthesis of dyestuffs. This, in turn, became the foundation of the vastly important synthetic organic chemical industry, beginning the utilization of coal tar. Sir William was also the first to synthesize the perfume coumarin, and he actually engaged in the manufacture of dyestuffs until 1874. He had many friends and admirers in the United States, and it is customary for those who were present when the first Perkin Medal was awarded to him in 1906 to wear the same or a replica of the mauve tie which made its appearance on that occasion.

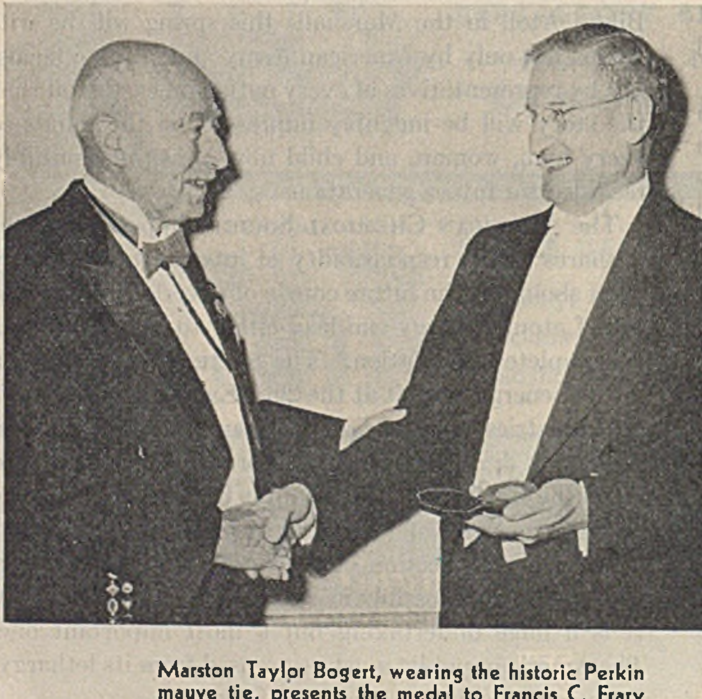
The presentation for 1946 was made after a dinner given at the Hotel Commodore, New York, January 11. The chairman of the American Section of the Society of Chemical Industry, Francis J. Curtis, who is vice president of Monsanto Chemical Company, presided. James G. Vail, vice president and director of research of Philadelphia Quartz Company, spoke on the personal side of the medalist, and Webster N. Jones, director of the College of Engineering, Carnegie Institute of Technology, discussed his scientific achievements. Marston T. Bogert, Emeritus Professor of Chemistry of Columbia University, presented the medal, as has been the custom since 1930 when he graciously made the award to Herbert H. Dow, at that time president of the Dow Chemical Company. After accepting the medal, Francis Frary described some of the complexities of inorganic chemistry met in the manufacture of various types of alumina.

Marston Bogert wore the celebrated mauve tie; and one other "wearer of the purple" was present on this occasion—August Merz of Calco Chemical Company.

The Perkin Medal was founded in 1906 in commemoration of the fiftieth anniversary of the coal-tar color industry. The award may be made to any chemist residing in the United States of America for work which he has done at any time during his career, whether this work proved successful at the time of execution or publication, or whether it became valuable in subsequent development of the industry. The medalist is chosen by a committee representing the Society of Chemical Industry, the American Chemical Society, the Electrochemical Society, the American Institute of Chemical Engineers, and the Société de Chimie Industrielle.

Perkin Medal:sts

1906	Sir William H. Perkin	1927	John E. Teeple
1908	J. B. F. Herreshoff	1928	Irving Langmuir
1909	Arno Behr	1929	E. C. Sullivan
1910	E. G. Acheson	1930	Herbert H. Dow
1911	Charles M. Hall	1931	Arthur D. Little
1912	Herman Frasch	1932	Charles F. Burgess
1913	James Gayley	1933	George Oenslager
1914	John W. Hyatt	1934	Colin G. Fink
1915	Edward Weston	1935	George O. Curme, Jr.
1916	Leo H. Baekeland	1936	Warren K. Lewis
1917	Ernst Twitchell	1937	Thomas Midgley, Jr.
1918	Auguste J. Rossi	1938	Frank J. Tone
1919	F. G. Cottrell	1939	Walter S. Landis
1920	Charles F. Chandler	1940	Charles M. A. Stine
1921	Willis R. Whitney	1941	John V. N. Dorr
1922	William M. Burton	1942	Martin H. Ittner
1923	Milton C. Whitaker	1943	Robert E. Wilson
1924	Frederick M. Becket	1944	Gaston F. DuBois
1925	Hugh K. Moore	1945	Elmer K. Bolton
1926	R. B. Moore	1946	Francis C. Frary



Marston Taylor Bogert, wearing the historic Perkin mauve tie, presents the medal to Francis C. Frary

Personal Side of Francis C. Frary

JAMES G. VAIL

IT IS a pleasant duty to introduce a valued friend to other friends, but it is also a responsibility. The present circumstances suggest some consideration of the nature of the occasion and the purpose to be served by presenting the personal characteristics of the medalist. It poses the deep philosophical question of ends and means. If what I have to say should have no other effect than to inflate the ego of the person we have assembled to honor, it would be a disservice to him and to you. If, on the other hand, an evaluation of those elements of character and experience which have led to achievements of special merit could guide or encourage other wayfarers in the field of science to more worthy attainment, the effort will be justified. The slave who rode behind his master in the triumphal procession to remind him amid thunderous applause, "Scipio, thou art but a man", performed an important office. This service, like certain trusted household remedies, should be kept handy. Happily there is no need for such medicine in the presence of an inherently modest man. A recommendation is often more convincing to an employer if it reflects the positive elements of a person's character with a critical awareness of his limitations. This is immensely more difficult than flattery but more likely to be useful.

Francis Cowles Frary is a curious person. All of us are born curious, but as Romain Rolland put it in Jean Christophe: "Most men die about the age of thirty." Francis Frary did not; this means that he never reached a point at which he was satisfied with his knowledge of the world around him or led into the temptation to assume that it had not much to teach him. He began, like the rest of us, by discovering his toes, but as he grew in wisdom and in stature we find him at an early age copperplating the key to the kitchen door with the aid of a battery of his own devising. The bright red color of that plated key is a landmark in his memory after fifty years, perhaps exceeding the satisfaction of many important later results on which the world would set a higher value.

As a sophomore in high school it was photography which gripped his curious mind. He searched the literature, made his own blueprint and other papers, improved on the published formulas with the most meager equipment—patent medicine bottles, the kitchen sink, and the closet devoted in the summertime to the storage of the wood-burning stove which heated the family living room in winter. The discovery of this period was that chemistry was to be his lifework.

The quality of curiosity was early associated with the idea of discipline. This may have been natural to a boy growing up in a family which had moved into the new country of the upper Mississippi to make its way, but when curiosity drew attention to an outcropping of ore, Frary expected as a matter of course to have to dig for the values.

A homely incident suggests his philosophy of discipline. When daughter Faith was a little girl, Mrs. Frary refused a request with the comment, "You may do that when you have reached the age of discretion." She ran to her father and asked him what that meant; Francis explained, "That means when you are so old that you will not want to." But the relationship never lacked tenderness or understanding, for the same young lady remarked after a session in the garden with her father, "The dear old thing, he was out there talking to me just as if I were grown up." Or again when he tactfully helped to settle a childish problem, "Father seems to have ideas." "Out of the mouths of babes" sometimes comes insight.

The concept of discipline sometimes bore heavily on son John who, at the age of twelve, after being held relentlessly to his school work, on one occasion protested, "Well, I know that Father is a big success, but if you ask me he has missed a lot of fun." It takes maturity to know the joy of sustained effort.

In his presidential address before the American Electrochemical Society in 1930 we have a presentation of Frary's philosophy of research which is of interest in terms of self-portraiture: "A characteristic which is a vital part of a man's personality. . . . is the presence of that combination of imagination and curiosity which may make research the most fascinating adventure into the unknown"; he goes on to say that without this only a "routine success" is possible.

Passing from the picture of Frary the curious man, let us see him as the energetic man. It takes more than ordinary vitality to accomplish the amount of labor which Francis Frary has done. It is not possible to tell how much of this vitality is congenital and how much results from the sustained application of will power, but the forty-nine titles cited to the Perkin Medal committee for the purposes of this award represent an enormous amount of work. Perhaps intellectual toil and physical stamina are more interdependent than we ordinarily assume. However that may be, Francis Frary has dynamic qualities of both body and mind. At the University of Minnesota there is a treasured memory of his speeding several steps at a stride on the way from his classroom in the basement to his laboratory on the third floor. They say that his electrochemical education developed his muscles as well as his intellect. Or yet more precious, perhaps even slightly scandalous at the time, there is a photograph taken in 1903 to preserve for posterity the manly chests and muscular curves of the fifty strongest men in the university. In the middle of this sits our hero as the strongest of the strong, reminiscent of Michael Angelo's statue of Moses but without the beard. Frary was a member of the gymnastic squad that won the national intercollegiate championship in 1903, when both Harvard and Columbia went down before them.

The application of energy develops heat, often in the wrong place without the lubrication of tact and that great reducer of hypertension, a sense of humor. One day Frary was checking some laboratory purchase requisitions and, noting the absence of certain essential data, he telephoned the man who had signed the form and called his attention to the error. The man thought the call was coming from a clerk in the accounting division so when the voice said, "You should find such errors yourself", the man replied, "What do you think we keep *you* down there for?" The answer came, "Well, I guess there's something to that, this is Frary speaking."

Francis Frary has a prodigious capacity for absorbing detailed information along new lines. Once he found his knowledge of pipe fitting inadequate, got hold of a Crane Company catalog, and ended with a competence that would do credit to a piping or plumbing specialist.

One of the anecdotal gems of Aluminum Research Laboratories illustrates how Frary gets down to fundamentals in his study of any question. For many years he has been much interested in the physiological effects of ingested fluoride compounds. On one occasion there were received at the laboratories the bones of a cow which had had an excessively heavy fluoride diet. The cow had been killed and the disassembled skeleton sent in. From a pile of these bones Frary proceeded to assemble one side of the skeleton. He did this on his hands and knees on the floor. The job took the better part of a day, but when he had completed it, he was an authority on the skeletons of cattle suffering from acute fluorosis.

His long record of directed energy has resulted in a mind unusually well furnished. Two more sentences from the address on research may be noted here: "Language training is very desirable, particularly modern languages, not only for their practical usefulness but for their influence on the man's command of his own mother tongue." Or again, "Too many men miss great opportunities because they narrow their interests and become absorbed in their own line of work, losing chances for achievement by failure to know what is going on around them." These advices spring from his own experience. He learned German to work as a student under Nernst, French by study at home as a cultural project with Mrs. Frary; and three business errands to Norway were used to give him a fluent reading knowledge of Norwegian. It all takes energy.

These achievements command our respect in a quantitative way, but the root of the matter is qualitative and the right expression of it more elusive. Laurence Hope, from an Arab source, wrote: "Men should be judged not by their tint of skin, the Gods they serve, the vintage that they drink, nor by the way they fight or love or sin, but by the quality of thought they think."

It seems superfluous to make a case for Frary as an intelligent man. It is already in the record. But the family treasures a story of an event which occurred shortly after they went to Pittsburgh. Francis, with his mind concentrated on higher things, drove against traffic into a one-way street. A policeman, of giant frame, whistled him down and bellowed, "What do you think you're doing?" Francis meekly responded, "I didn't think", to which the minion of the law proclaimed, "Well, it's time you learned to think." Countercurrent studies have since been restricted to the controlled conditions of laboratory and plant.

An unusually capacious and accurate memory is one of Frary's great assets. As an expert witness in patent trials where he was often on the stand for several days, one of the attorneys would say, "Now, Doctor, yesterday you said thus and so", and Frary would say, "No, I did not. What I did say was this", and he would proceed to repeat word for word what he had said 24 or 48 hours before. On several occasions this was checked by following the typed record of his testimony; he repeated whole paragraphs verbatim as if he too were reading the record.

To describe the hard, incisive, logical, imaginative thinking by which he arrived at technical success would be an inadequate tribute. There is another aspect necessary to complete the picture. When Frary received the Acheson Award from the Electrochemical Society, he used the cash grant to set up a revolving loan fund for assisting employees of the laboratory to advance their education, a tangible evidence of his interest in their welfare. All along the way there has been a warm human quality which endeared him to his friends. To make a scriptural reference, he can rejoice with those who rejoice and weep with those who weep. The sensitive man who gains the affection of his children by understanding, who is ready to lend a sympathetic ear to the unfortunate or put his personal interests aside to lend a helping hand, has found a pearl of great price. The company of those who know our friend in this character will never be assembled. He alone knows who they are, and it would be against his code to tell.

One of the resources which the typical research man of our time has lost is the close knowledge of that rich mine of beautiful English and deep experience of life set forth in the King James version of our Bible. Not once but many times have I seen scriptural references lost on scientific men, but Frary is one of the few who can be depended upon to know them. He has never been too busy to lead a group of boys in Sunday school, to keep in touch with them when they were far away; nor has the pressure of an urgent business life diverted him from keeping his Sundays for rest, recreation, and search for spiritual reality.

Frary comes of New England Puritan stock which held high standards of culture and of discipline even if they sometimes dealt roughly with the Quakers or other irritant elements. His mother was one of the early graduates of Mount Holyoke College under Mary Lyons' pioneering leadership about 1877. Rural life in Massachusetts in those days may have lacked material comforts but it put a high value on character. The Frary family tree contains on both maternal and paternal branches an unusual number of teachers. His father regretted that the pressure of making a living kept him from a teaching career, but he took great satisfaction when each of his three children in turn received the Ph.D. degree. Frary not only began his professional career as a teacher at the University of Minnesota, but after devoting himself to industrial life, his relation with associates has often been that of the teacher—stimulating, inspiring, as well as imparting knowledge. He was once heard to suggest that teaching is habit forming like coffee. He has had the teacher's thrill of seeing young minds unfold, of watching the awakening of interest, followed by the development of initiative in the search for knowledge. He has recognized the difference between techniques and facts which can be taught, and the deeper motivation which has to come from the inside out.

Although Francis Lee Frary, his father, was not professionally a teacher, Francis C. acknowledges an asset gained by the direct teaching of his father. During school vacations the son helped in the paternal wholesale grocery business and there he learned the art of double-entry bookkeeping. This early acquired knowledge of the accurate use of data has often stood him in good stead. The Frary predilection toward teaching has been a beneficent influence from another angle. The combination of a rigorously honest mind and a naturally shy disposition makes human contacts more difficult for him than for some of the strong extroverts we know. Teaching has been the balancing discipline and has made the human contact natural.

As family man some evidence is already before you. He grew up in Spartan simplicity with a high sense of duty but in a happy home, and when through church interests shared, he discovered Alice Hall Wingate and married her in 1908, the strong gentleness of his character bore happy fruit. Mrs. Frary testifies that, despite the enormous pressure under which he has often worked, the sacred areas of home and church relations have never been invaded. He is fortunate too in having a life partner who understands and supports him in all his doings, even to the provision of vast quantities of fresh fruit of which he is inordinately fond (his nearest approach to intemperance). We bow to Mrs. Frary as an important contributor to the success we celebrate here.

Finally let us consider the open mind and quote from the essay on research: "The research worker must not let his preconceived ideas, uttered or unexpressed, or a desire to please his superiors by approving their pet theories, interfere with the accuracy or thoroughness of his work. Neither must he be afraid to face the facts even when they are disconcerting." Frary has lived from a primitive period of industrial research to the day of the atomic bomb. With all of us he stands on the threshold of a new epoch. Faced with the alternatives of annihilation by the discoveries of science or the radical reconstruction of the concept of human relations, what do we see in his life which applies to this unprecedented crisis? An open mind is not a mind without settled points of reference but a mind that can boldly face the evidence; if it can welcome the unexpected, even the disconcerting aspects of truth, and make constructive use of them, it is not far from greatness. If we are to escape the disastrous assumption that multiplied violence is the way to human well-being, it will be by a synthesis and coordination of two great avenues of the search for truth (1) a research approach to the physical world, (2) the same bold objective treatment of the study of ways to develop the goodness that is in people and the paths to their cooperation. Science has made of the world one neighborhood so that all people are our neighbors. The soundest teaching about neighbors and how to deal with them is to be found in the New Testament, which Frary knows so well. It is my personal belief that the answer to the crisis of our time must come from people who, like Frary, represent an intimate association with the metric values of physical science and the less tangible but supremely important nonmetric values which determine the behavior of human beings in their relation to one another. So it is with great hope that I take the measure of this man and commend his record to the rising generation, not implying that it is perfect but because it contains so much that is worthy of emulation.

Achievements of the Medalist

WEBSTER N. JONES

TWICE within our lifetime the Perkin Medal has been bestowed on scientists whose professional careers have been devoted to the study of aluminum. In 1911 Charles Martin Hall, a founder of the Aluminum Company of America, was recognized by the Perkin committee for his discovery of an electrolytic process by which aluminum could be separated from its oxide. Now in 1946, when America's aluminum industry has turned from supplying an indispensable war material to assume leadership in peacetime economy, Francis Cowles Frary has been chosen to receive the award. The research for which these two scientists were recognized has been of the utmost significance in the amazing development of the aluminum industry.

It is interesting to contemplate what influence the discovery of aluminum might have had on the early career of Francis Frary. He was born in Minneapolis at the time when Charles Martin Hall, a college student, was laboring with the baffling problem of separating aluminum, the most abundant metal in the earth's crust, from its ores; during his boyhood Hall's discovery and the subsequent rapid growth of the aluminum industry vied as a topic of dinner-table conversation with Wilhelm Konrad Roentgen's discovery of x-ray and the work of Pierre and Marie Curie in the field of radium.

Although the early 1900's were days of scientific progress, it was the unusual parent who urged his son to follow a career in science. When young Frary showed an early interest in chemistry, however, he was encouraged by both his mother and father, who set aside the basement of their home for his laboratory. Francis received further support from his parents when he decided that he wished to become a chemist. He chose the University of Minnesota for his undergraduate work and remained there for graduate study.

Germany was advancing rapidly in chemical research at the time Francis received the master's degree from Minnesota, and with the born scientist's wish to acquire knowledge firsthand, he went to the Technische Hochschule in Berlin to study German progress in electrochemistry. When he returned to America after a year's travel and experience abroad, his alma mater appointed him to the chemistry instructional staff. He was awarded the doctorate in 1912 and continued his work at the University.

In addition to his heavy teaching duties at Minnesota, Professor Frary was a productive research worker and an inspiration to his students. He usually took the stairs three at a time, instead of the university elevators which could not carry him fast enough from one activity to another. He worked night and day as well. This boundless energy and enthusiasm, backed by his scientific ability, brought results. In spite of his teaching obligations, he was successful in producing the technically important hard alloys of lead with calcium, barium, and strontium by electrolysis from fused salt electrolytes. These alloys were later to find important application, particularly during the first World War, when the supply of other lead-hardening elements was cut off.

Frary's proficiency and the breadth of his interests in analytical chemistry and in electrochemistry were also evidenced by his early publications. At Minnesota he contributed such papers as "Rapid Analysis by Electrolysis without Rotating Electrodes", "Rapid Determination of Zinc by Electrolysis", "Use of a Mercury Cathode in the Determination of Metals", "Electrodeposition of Gold and Silver", and "Uber einen neuen Apparat für elektrolytische Schnellmethoden". One of his first enthusiasms was photography, and many of his papers were on such topics as "Direct Positives in the Camera by Thiourea and Its Compounds", "Microstructure of Wet Negatives", "Contributions of the Chemist to the Photographic Industry", "Reducing Power of Photographic Developers as Measured by Their Single Potentials", and "Reaction between Alkalies and Metol and Hydrochinone in Photographic Developers".

Frary's achievements, especially his discovery of a novel and safe method of producing phosphorus sesquisulfide, attracted widespread attention. It was only natural that industry should be impressed and should compete for his services, and The Oldbury Electrochemical Company enticed him to leave teaching for industry. With this company he had great success in applying his knowledge to electrochemical products and became an authority on the production and handling of phosgene, soon to be in great demand for use in chemical warfare.

Just before America entered the first World War, the management of the Aluminum Company decided to establish an organized research laboratory so that the many fundamental problems confronting the aluminum industry could be given full attention. The company canvassed the field thoroughly to find a director capable of developing its research program. Since Frary was a leader in chemistry, chemical engineering, and metallurgy, and a man with breadth of vision, high ethical standards, and deep human interest, he qualified in every way for the position offered him, which he continues to fill so admirably today.

Before Francis Frary could assume his duties with the Aluminum Company, America was at war and was confronted with the new threat of poison gas. Here was an opportunity for him to apply his knowledge of phosgene. At the urgent request of the Government, his services were loaned by the company, and he was assigned by the Army to design and to build a phosgene plant at Edgewood Arsenal.

Not until December, 1918, after the end of the war, was Major Frary free to undertake his new duties with the Aluminum Company of America. He saw in the company's widespread interests a broad field for research, and he attacked the multitude of problems in aluminum with skill and vigor. Under his direction, investigations ranged from the beneficiation of bauxite, the production of pure alumina, and the electrolytic production of aluminum, to the melting, alloying, casting, and working of aluminum into the numerous forms of commerce. Included were problems such as those involved in the structural use of aluminum alloys and their behavior in many environments, together with occasional forays into the electrothermal refining of bauxite and the electrothermal production of aluminum.

Frary's interests have been broad, and his detailed knowledge of a wide range of subjects has amazed his friends. He has contributed generously to the literature on such varied subjects as "Aluminum Alloys of High Strength", "Electrolytic Refining of Pure Aluminum", "Future Developments in the Light Metals", "Aluminum and Its Alloys", "Progress in the Electrochemical Industries", "Aluminum in the Chemical Industry", "Aluminum as a Material for Building Construction", "Aluminum—How and Why. The Development and Commercial Production of a New Construction Material", and "Aluminum Chemical Equipment". He has expressed views on "Research as a Vocation" and on "Logical Divisions of a Research Organization". He has written an excellent book the "Laboratory Manual of Glassblowing" and is coauthor of a two-volume work on "The Aluminum Industry".

To those of us who know Francis Frary well, his most likable characteristics are his modesty and his generosity. He claims credit for only a few of the many contributions which emanate from the Research Laboratory; he always gives credit where credit is due. One compliment can be paid him without fear of contradiction: There has never been a more harmoniously knitted, integrated, and effective organization of management and research than is to be found under his direction in the laboratories of the Aluminum Company of America. This must be very gratifying to Frary, who has been able to impart his own spirit of loyalty to the members of his research staff.

The outstanding achievements of the Aluminum Research Laboratories have been an incentive to research in our country. Heat-treated aluminum alloy castings were developed and used here for many years before they were adopted elsewhere. The early duralumin alloy was difficult to forge. However, through research effort, more forgeable alloys were discovered, and the know-how thus obtained has resulted in the ability to forge harder and stronger alloys. During the war years just closed, millions of pounds of forgings were made for propellers, crankcases, and pistons for aircraft engines.

In the production of aluminum, impurities such as iron and silicon in the alumina or in the carbon anodes are electrolytically reduced and go into the metal. The problem of obtaining aluminum of the highest purity was solved by electrolytically refining aluminum in a bath of fused salts. By this novel and ingenious process 99.99% pure aluminum was produced in quantity. With metal of this purity available, the determination of the fundamental relationships in aluminum alloy systems, without the presence of contaminating impurities, was made possible. Such information was most valuable in the development of modern aluminum alloys.

The principal product of the aluminum industry is, of course, metallic aluminum, and the most spectacular performances of aluminum have been in the alloy field. The well-known alloy duralumin was discovered in Germany before the first World War; except for Zeppelin construction, it found little use in that conflict. However, the potential applications of the strong alloys of aluminum in the structural field and in the airplane industry were foreseen by Frary and his associates, and the research efforts of the laboratories were directed accordingly, despite the fact that as late as 1928 only 1.7% of the aluminum produced went into planes. By 1937, just two years before the outbreak of the second World War, 25% of the outlay for research went into investigations to increase the usefulness of aluminum in aircraft, although only 5.8% of the metal made went into planes.

A new alloy (24S), developed in the 1930's, possessed higher strength and was the principal aircraft material of the second World War. Before the end of the war, another new alloy (75S) was in production. This alloy furnishes over 50% higher yield strength than was available in any alloy in use at the beginning of the war. All new designs of military planes were based on it.

Another research development, the Alclad products, was indispensable in the construction of transport and military aircraft. The Alclad sheet is a duplex metal product which combines a thin surface layer of high-purity aluminum or alloy with a strong alloy core. The surface layer of aluminum affords protection against corrosion, and the core supplies the structural strength. The Alclad structure has been extended to the production of brazing sheet, in which a low-melting brazing alloy and a suitable core metal are combined to enable the practical manufacture of complex parts, such as intercoolers for aircraft.

During the war nearly 70% of Alcoa's production was devoted to the manufacture of aircraft. Production in the United States rose from six thousand planes in 1938 to eighty-six thousand in 1943. Three quarters of the weight of the average war plane was aluminum, and Alcoa produced over 90% of the domestic primary aluminum used.

In contrast to what happened with other strategic war materials, the Aluminum Company foresaw its responsibilities in war production and made certain that there would be no shortage of aluminum for essential military purposes. While aluminum research was being subsidized directly or indirectly by European countries as part of their program of military security, in this country Alcoa carried on its own research at its own expense. One of the important contributions of the Research Laboratories was the process devised to utilize low-grade domestic bauxite when South American supplies were cut off by enemy submarines.

The war years brought on a phenomenal expansion of the aluminum industry in this country. In order to meet gigantic military requirements, prewar capacity was increased nearly 700%. This Herculean task was accomplished with record-breaking speed. Alcoa began its plant expansion three years before our government-financed program started, and was later asked to assume responsibility for the major share of the government building program and for the operation of the many new plants.

The Aluminum Company's support of and sympathetic attitude toward research have made possible these astonishing results. Over the years millions of dollars have been reinvested—plowed back—to bring about a better understanding of aluminum, to develop improved alloys, and to discover new uses. Alcoa's amazing war record could have been made only by a thoroughly integrated company in which research was permitted to function at its optimum. By the same token, we now need peacetime progress in the promotion of pure and applied science for the development of new and enlarged uses of aluminum through a continuation of the efforts of Francis Frary and his associates, backed by a company with willing resources.

All of America should profit from the example set us by the Aluminum Company. However, I am not sure that we have learned our first lesson, the lesson that American industry must be kept free. We may have already forgotten that superior industrial management in America was responsible for the rapid equipping of our armed forces. We may have completely overlooked the fact that Americans have always been able to plan, to venture, to produce, and to sell, and that superiority has thus been won. It can be lost, as well, with every move that is made to stifle and to curb free enterprise.

What a compliment to Francis Frary and to the company he serves that such a high tribute is being paid him tonight! If either the man or the organization had been unsuccessful, both could have worked on unnoticed and unpraised. Along with the others whose names have made Perkin Medal history, Francis C. Frary exemplifies creative genius, capacity for hard work, and the urge to serve mankind. In no other country of the world has a scientist of his talent been given such free rein and unstinted support!

Adventures with Alumina

FRANCIS C. FRARY

WHEN I started out in research many years ago, I was an organic, not an inorganic, chemist. I was intrigued by the complexities of the compounds of carbon—untold thousands of them built up from simple fundamental types and related to one another through a vast network of reactions and properties. By comparison, inorganic chemistry sounded simple and tame. Metals and nonmetals, bases and acids, reacting with one another to form simple compounds which were strictly limited in number and related in simple fashion to one another. This apparent simplicity and lack of interesting possibilities in the field of general inorganic chemistry may account for its having been deserted by so many advanced academic workers for more enticing and apparently more remunerative fields. True, in recent years the physical chemists have developed many theories to unify and explain the vast accumulation of data in their branch of chemistry. My remarks here do not embrace that sort of complexity, but rather the factual complexity involved in what might be called the "descriptive chemistry" of some simple, common, and useful inorganic compounds.

Since my own connection with research has been for many years largely administrative, that small part of the work of our laboratories which I shall discuss represents the work of various members of our staff, not my own. In accepting this medal, I feel that I do it on behalf of my associates in Aluminum Research Laboratories and on the basis of their accomplishments. These, of course, cover a much wider field than the subject of my address, which is necessarily limited but which deals with a material of vital importance in the aluminum industry. As an example, therefore, of what I might call "complexity in simplicity", I would like to discuss briefly some of the work which our laboratories have done with the simple substance aluminum oxide and its simple derivatives.

PROPERTIES

Aluminum oxide and its hydrates present a variety of amazing contrasts. From the hardness of the sapphire to a softness similar to that of talc, from an apparent density of over 200 pounds to one of about 5 pounds per cubic foot, from high insolubility and inertness to ready solubility in acids or alkalies and marked activity, the properties can be varied over wide limits. Some forms flow and filter like sand; others are viscous, thick, unfilterable, or even thixotropic. Crystals may be of any size down to a fraction of a micron in diameter, with various allotropic forms, and there are also amorphous forms. Some varieties have a very high adsorptive power, others none at all. Some are catalytically active, others inactive. But they are all converted into α-alumina (corundum) if heated hot enough and long enough.

The formula, properties, amphoteric character, etc., of aluminum oxide are well known. The ordinary form, corundum, and another variety, γ-alumina, have been frequently described in the literature. The oxide formed at lower temperatures by the oxidation of the metal or the heating of the hydrate is believed to be amorphous. As the temperature of heating the hydrate is gradually increased, x-ray spectra seem to indicate the development of a number of different phases, in addition to γ-alumina and the final end product (which begins to appear at temperatures above about 800° C.), α-alumina itself. Figure 1 shows some of these spectra. Whether the differences actually represent different phases as indicated, or merely different crystal modifications or crystal sizes of the same phase, remains to be proved. The apparent simplicity of Al_2O_3 may be deceptive.

One of the most interesting properties of the varieties of alumina formed by heating the hydroxide at about 400–500° C. is their high adsorptive power for water vapor. They can dry gases as completely as does phosphorus pentoxide, yet the adsorbed water may be easily driven off again at moderate temperatures and the adsorbent used repeatedly. This commercially valuable property is due to the extremely large surface area exposed by this porous material and the affinity which this surface has for water. In our laboratories we have measured areas as high as 440 square meters per gram for samples of these so-called activated aluminas. Practically every variation in any step in the process of manufacturing activated alumina influences this area figure. Therefore the problem of producing a material with maximum adsorptive power combined with stability in use is very complex and must be solved by a large amount of ingenious experimental work.

The same type of alumina shows marked catalytic effects in the vapor-phase treatment of gases at elevated temperature (cracking, hydrogenation, etc.); these are enhanced or modified by the presence of impurities, either naturally present or purposely added. Extended heating naturally tends to recrystallize the alumina into the stable alpha variety and shrink the structure so as to bring about a more or less gradual deterioration in surface area and catalytic properties. The influence of manufacturing and use factors, purity, etc., upon this deterioration rate is a fertile field for study and investigation.

ALUMINUM HYDRATES

One of the most important derivatives of aluminum oxide is the hydroxide, which may be thought of as a compound of aluminum oxide and water. Actually, it is the ancestor of most commercial aluminum oxide because the pure oxide is made by calcination of the hydroxide.

All chemists are familiar with the gelatinous, slimy, amorphous aluminum hydroxide precipitated from aqueous solutions of aluminum salts, but few realize the complexities of this system. Like most gels, this material contains large amounts of loosely bound water, over and above the actual water of crystallization. The analyst is accustomed to see a funnel full of the gel dry down to a few small, solid fragments. Actually, under the most favorable conditions the maximum alumina content obtainable in this gelatinous material seems to be about 10%, and ordinarily less. When the gel is dried, x-ray patterns show that a crystalline hydrate has been produced, but slight differences in the conditions under which the gel was formed may entirely change the type of this hydrate. It may be either one of the two varieties of trihydrate (alpha or beta) or the alpha monohydrate, or a mixture of any of these but never, so far as we know, the beta monohydrate. Why not? I wish I knew! Such simple facts as temperature and rate of precipitation of the gel are among the most important variables affecting the type of hydrate eventually obtained. Speaking of gels, if a sample of a thixotropic modification of hydrated alumina is shaken vigorously, it becomes liquid and can be poured. After a moment it sets to an inorganic "blanc mange", another mystery of "simple" inorganic chemistry.

The crystalline hydrates differ among themselves, not only in x-ray spectra and crystal habits, but also in chemical properties. The two trihydrates are readily soluble both in acid and alkali; the alpha monohydrate is relatively insoluble in acid, and requires higher caustic concentrations at much higher temperatures and more time to dissolve; the beta monohydrate (diaspore) is hardly attacked at all by caustic soda solution under the same conditions. The alpha trihydrate is the mineral gibbsite, the principal constituent of the bauxites found in North and South America; the beta trihydrate is unstable and not found in nature; the alpha monohydrate is the principal constituent (boehmite) of the bauxites found in Europe. Each of these hydrates behaves differently on calcination. The beta monohydrate (diaspore) goes directly to a nonhygroscopic form of alumina at a relatively low temperature; the others at similar temperatures give amorphous or γ-alumina of varying degrees of hygroscopicity and reactivity. Presumably crystal lattice differences control this behavior, but what are they?

In general, the transformation of the gelatinous hydrates into the crystalline varieties on drying is irreversible, but the presence of a certain amount of chloride in the gel makes it readily susceptible to peptization in water. This is the basis of some of the dried forms of "aluminum hydrate" used medicinally for the treatment of stomach disorders. Recently we succeeded in producing a variety of dried reversible gel which does not contain chloride. Gardner (*1*) found this material to be quite efficient in insolubilizing finely divided silica in the lungs of animals and preventing the development of silicosis, an effect not produced by any of the crystalline hydrates. Why should these two forms act as reversible instead of irreversible colloids?

The possibility of obtaining a relatively stable supersaturated solution of alumina in caustic soda, containing about twice the equilibrium concentration, and of subsequently precipitating out the excess alumina as hydrate by seeding and gradual crystallization (extending over several days), is the basis of the Bayer process (*2*); but no one has yet determined why the decomposition of this supersaturated solution in the presence of a large amount of "seed" hydrate should be so gradual and relatively incomplete, in contrast with the usual behavior of supersaturated aqueous solutions. It appears possible that there is an equilibrium between the sodium aluminate and some colloidal, highly hydrated form of the hydroxide, and that the delay in precipitation is in some way connected with the slowness of removing this highly hydrated material from the reaction by its transformation to the crystalline trihydrate.

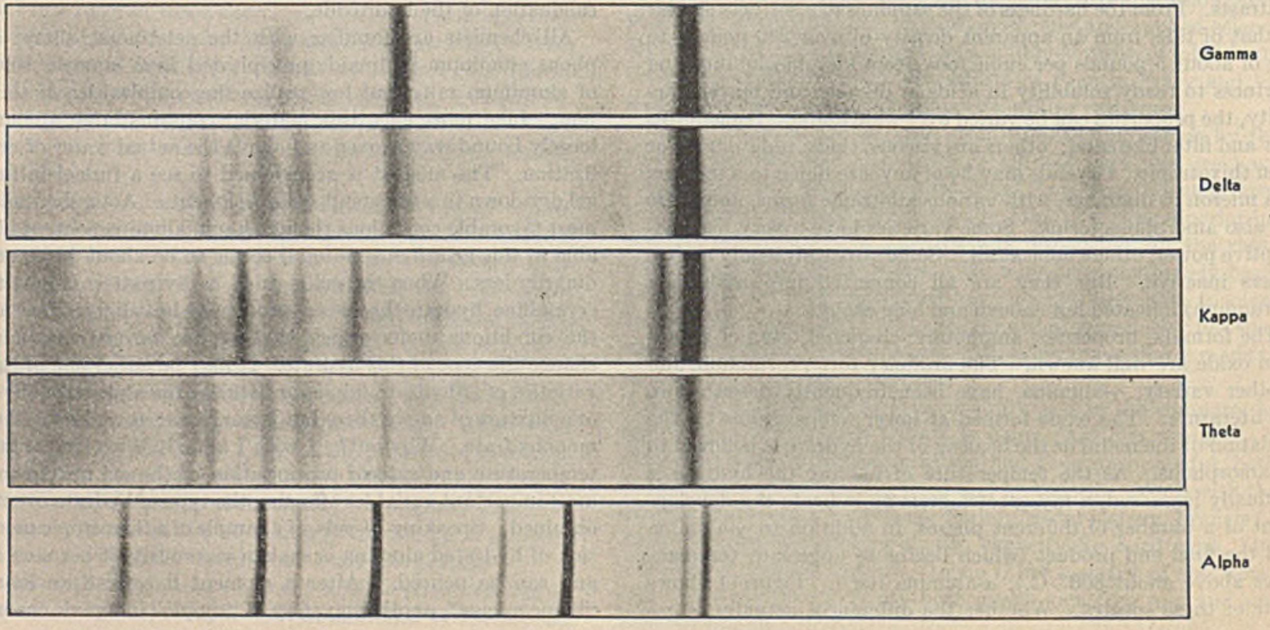
After many years of work to increase the size of the precipitated hydrate particles, so as to reduce the dust losses in the aluminum plant, it became necessary to go to the other extreme and find the conditions under which particles half a micron or less in diameter could be regularly produced for use as a rubber filler. Figure 2 is an electron microscope picture of such particles, and for comparison Figure 3 shows the alpha monohydrate as produced by treatment in hot dilute aqueous caustic (*4*). Monohydrate powder with an apparent density as low as 5 pounds per cubic foot has been produced by such a process. This is less than 10% of the apparent density of commercial trihydrate.

ALUMINUM HALIDES

The halides of aluminum are among its simplest compounds, generally resembling the well known chloride, $AlCl_3$. This, in the anhydrous form, is very hygroscopic and extremely active catalytically, and in the hydrated form is very soluble. However, the fluoride differs sharply from the other halides in that the anhydrous crystalline material is substantially insoluble and its series of crystalline hydrates run the whole gamut of solubility. Why there should be two distinct hydrates having the approximate formula $Al_2F_6.7H_2O$ (one practically insoluble and the other quite soluble) and a very soluble hydrate $Al_2F_6.18H_2O$ is still a mystery.

Some years ago spectrographers began to report data which indicated the possible existence of aluminum halides where aluminum had a valence of 1, such as AlCl. Nothing was known of their chemical behavior until we discovered their peculiarity of apparently being capable of existing in the vapor phase at temperatures above about 800° C. and decomposing spontaneously on condensation (at lower temperatures) into aluminum and the ordinary trivalent halide (*3*). The monofluoride, for example, may be easily formed by heating a mixture of aluminum and AlF_3 in vacuo at temperatures above about 800° C., and condenses on the cooler parts of the equipment as a mixture of metallic aluminum and the ordinary anhydrous AlF_3. In our experience the oxide does not undergo similar changes, although a recent German patent claims to the contrary.

Figure 1. X-Ray Diffraction Patterns of Alumina



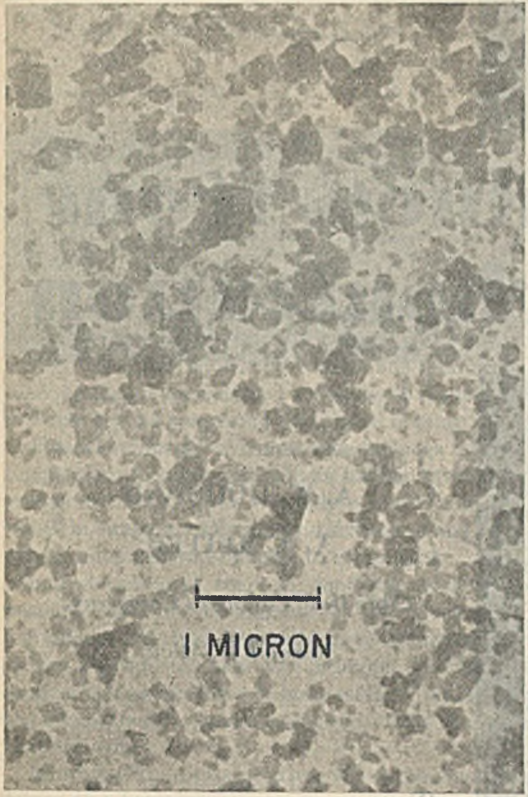


Figure 2. Electron Micrograph of Alumina Trihydrate

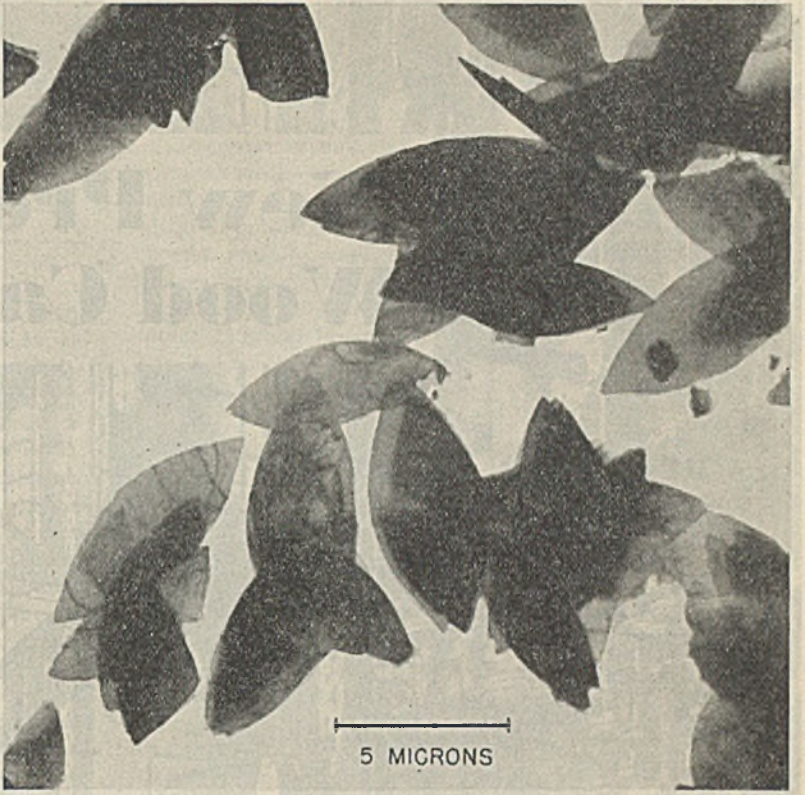


Figure 3. Electron Micrograph of α-Alumina Monohydrate

As far as I know, the sulfate and nitrate are more regular and normal in their behavior, perhaps because I know less about them. Both, however, form a series of soluble and insoluble basic salts, and the sulfate forms very insoluble double salts with sodium and potassium, which occur in nature as the mineral alunite.

COMPLEXITY OF INORGANIC CHEMISTRY

Considering all of this factual complexity in one small corner of the inorganic field, I am led to wonder whether potential investigators have not been unduly dazzled by visions of the millions of possible compounds of carbon and the intricacies of physical chemical theory, overlooking the extremely interesting and practically important field of what might be called "descriptive inorganic chemistry". If we look back to the great names of the early days—Berzelius, Moissan, Wöhler, Perkin, Faraday, and others—we find them to be masters of the facts of nature, absorbed in and fascinated by the intricacies of the behavior of elements and their compounds. Much of the highly interesting and important factual basis of inorganic chemistry has now been relegated to the archives or to ponderous handbooks. Our crop of investigations of purely theoretical interest appears to have flourished at the expense of much needed work on the chemistry of the common and commercially important elements and compounds. It should be possible for some investigators to find as much interest in practical things as others do in higher mathematical speculations which are so intriguing to the imagination. For the sake of the chemical industry which has to deal with the complexities of these so-called simple compounds, it is to be hoped that this field will not be indefinitely neglected.

We have been working on this problem of alumina for over twenty-five years, because cheap, pure alumina is a basic requirement of the industry, and we are continually finding new things. Economies in manufacturing do not depend entirely on elaborate mechanical devices, automatic controls, etc., in spite of the advertisements of their manufacturers. Better knowledge of the details of the simple chemistry involved in a process is often the key to a reduction in cost or improvement in quality, and better analyses of a product may prevent a great waste of money and time on developments that cannot possibly succeed because of inherent defects in the product.

By a careful study of the chemistry involved, the basis was laid for the commercial development of the so-called combination process, the only improved alumina process developed during the war that has thus far proved to be commercially practicable. Low-grade high-silica bauxite, when treated by the commercial Bayer process, produces a red-mud by-product containing 30–40% of the alumina in the charge and a corresponding amount of insolubilized soda. By a properly conducted calcination of this red mud with limestone and additional soda, 80% of the alumina and 60–70% of the soda can be rendered soluble. Upon leaching under carefully controlled conditions, the sodium aluminate may be extracted and returned to the Bayer process, where it is recovered as standard grade alumina. Simple enough, but made practical only by years of intensive study of the chemistry of aluminates and silicates.

Other available raw materials for the extraction of alumina are tempting because of their greater abundance and wider distribution. From years of work on them we have come to the conclusion that the solution of the problem of economically utilizing them requires a more painstaking and complete investigation of the simple chemistry of alumina compounds, rather than some brilliant revolutionary theory or reaction. Complexity in simplicity still balks us and beckons us on.

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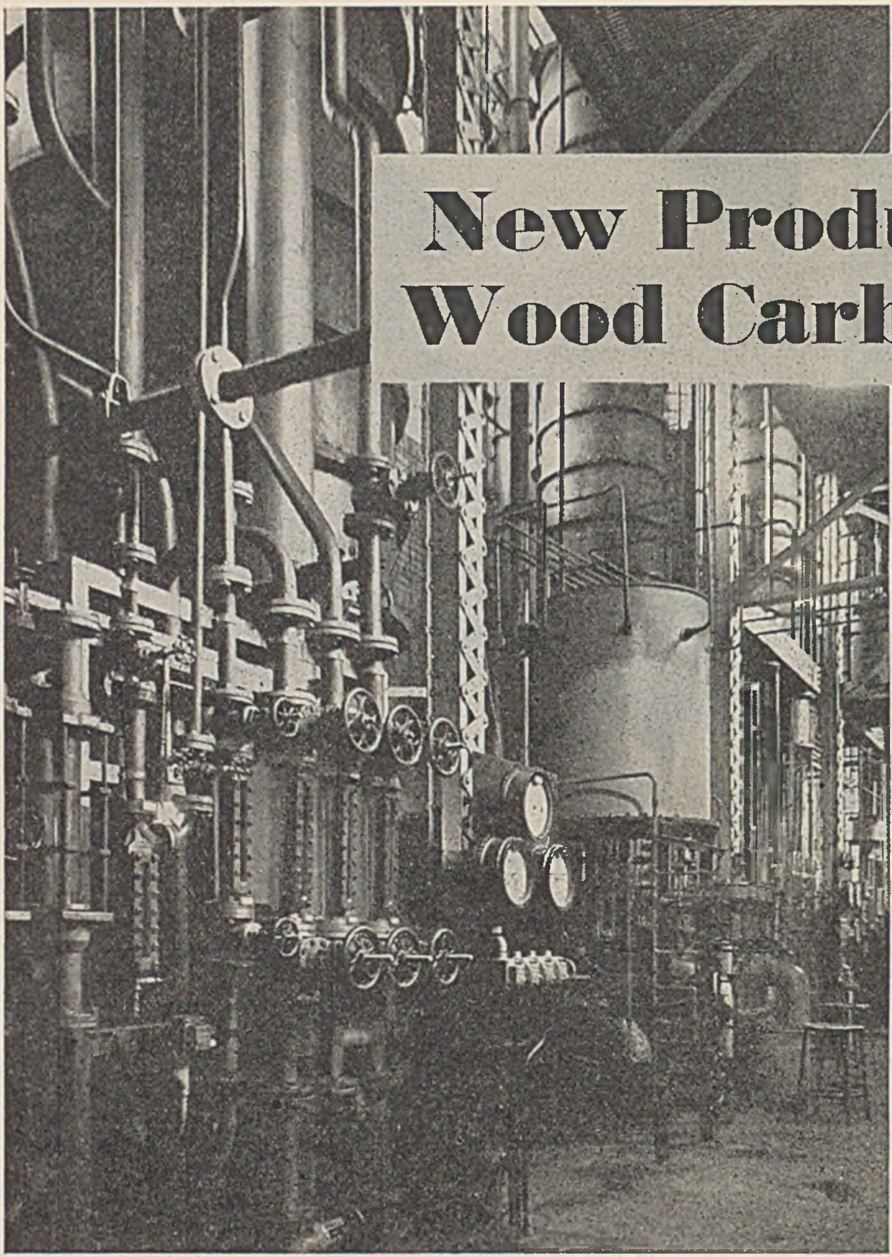
New Products from Wood Carbonization



A. W. GOOS AND

A. A. REITER

Cliffs Dow Chemical Company,

Marquette, Mich.

Tars and oils are obtained as by-products of hardwood carbonization to the extent of about 12.2% of the wood carbonized. These tars and oils are complex mixtures of a wide variety of compounds. A practical general procedure for separating such mixtures into their most important individual compounds is described, and specific examples are given. Lists of compounds that can be produced from by-product tars and oils are presented. The photograph at the left is a refinery view, showing a portion of the extraction equipment.

CHARCOAL is the primary product of the carbonization of hardwood, but some useful by-products are obtained and are a significant factor in this industry with a low profit margin. The standard by-products that are refined and marketed are practically limited to methanol, denaturing grade methanol, methylacetone, and acetic acid. Although these are the most important by-products in point of value, they are greatly exceeded in quantity by tars and oils which do not have any well established general uses. Some of these tars and oils have been separated into more or less crude fractions for specific uses, but there has been no general separation into wood tar chemicals analogous to coal tar practice. Probably most of the tars and oils obtained in the industry have been burned in plant boilers.

The problem has been recognized for many years, but the tars and oils are very complex and reactive mixtures so that commercially successful separation procedures have not been known. For a number of years this laboratory has carried out an intensive research program to develop such procedures. The work is by no means complete, but a few products are past the pilot plant stage and ready for plant practice.

The amount and character of tars and oils obtained vary with the kind and size of wood, with carbonization conditions, and with the refining processes used. Table I gives the main products from wood carbonization at Marquette. The yields are based on a cord of wood, defined as that amount of "chemical wood", including bark and rot, which if dried at 105° C. would weigh 3000 pounds.

The tars and oils amount to 12.2% of the wood carbonized or 66% of the total liquid organic product obtained. Although some of this material has been disposed of for various industrial purposes, the major part has been burned. Possibly a large part of that now used industrially might be utilized to better advantage if compounds present in the crude mixtures could be economically separated.

Many compounds found in pyroligneous liquors have been listed (*1–7*). These lists include products from the destructive distillation of hard- and softwoods, cellulose, and lignin. A few were found in acetone oils resulting from pyrolysis of calcium acetate to produce acetone, which is no longer practiced. It appears probable, however, that most of these may occur in hard-

Table I. Products from Hardwood Carbonization

	Yield/Cord	Pounds	Wt. %
Charcoal (17.5% volatile)	54.0 bu.	1080	36.0
Acetic acid (including formic and propionic)	14.3 gal.	125.8	4.2
Denaturing grade methanol + methanol + methylacetone	9.3 gal.	61.4	2.0
Tars and oils	38.4 gal.	366	12.2
Noncondensable gas	7260 cu. ft.	650	21.7
Water of pyrolysis and loss	......	....	23.9

wood distillates as well as many more that have not been identified. To show the variety of compounds, these lists are supplemented by a few additional compounds found and identified at Marquette and are classified according to the main chemical types in Table II; no compound was placed in more than one class.

This wide variety of compounds includes many types of functional groups, many individuals having several different active groups in the molecule. Usually a number of members of each series is present. Obviously mixtures containing all of these types and others are difficult to unscramble. Many of the individual constituents tend to condense with other compounds present, and therefore thermal and chemical treatment must be minimized. Mutual interferences of boiling points and of solubilities are the rule and even fractions having a narrow boiling range may contain three or more widely different compounds and show abnormal responses to chemical tests that make interpretation difficult.

All of the liquid product from the carbonization of wood is obtained as a heterogeneous, aqueous, tarry mixture at the retorts. An elaborate refining system is required to separate properly the two main pure compounds produced, acetic acid and methanol; and this system removes practically all the other organic matter from the water and partially separates it into several tar and oil fractions. Figure 1 is a flow diagram of the acetic acid and methanol refining systems, showing where the oils and tars are removed and the amounts obtained.

The investigations have been directed chiefly at the utilization of acetic oil and soluble tar. These have had least commercial utilization and are obtained in large quantities. Settled tar also occurs in large amounts, but it has had several fairly good outlets. From it is made a gasoline gum inhibitor, a creosote fraction, hardwood pitch, and flotation oil. However, it is expected that settled tar will also be processed for individual constituents at some future time.

Because the composition of the by-product oils and tars is dependent on the kind of wood, on the methods of carbonization, and on the methods of recovery of acetic acid and methanol, the detailed procedures for separating and purifying individual compounds must be worked out for each oil or tar. However, the general methods that have been successful in isolating compounds from complex and reactive wood oils may be used to separate other oil or tar products of wood carbonization or similar by-product mixtures.

GENERAL SEPARATION METHODS

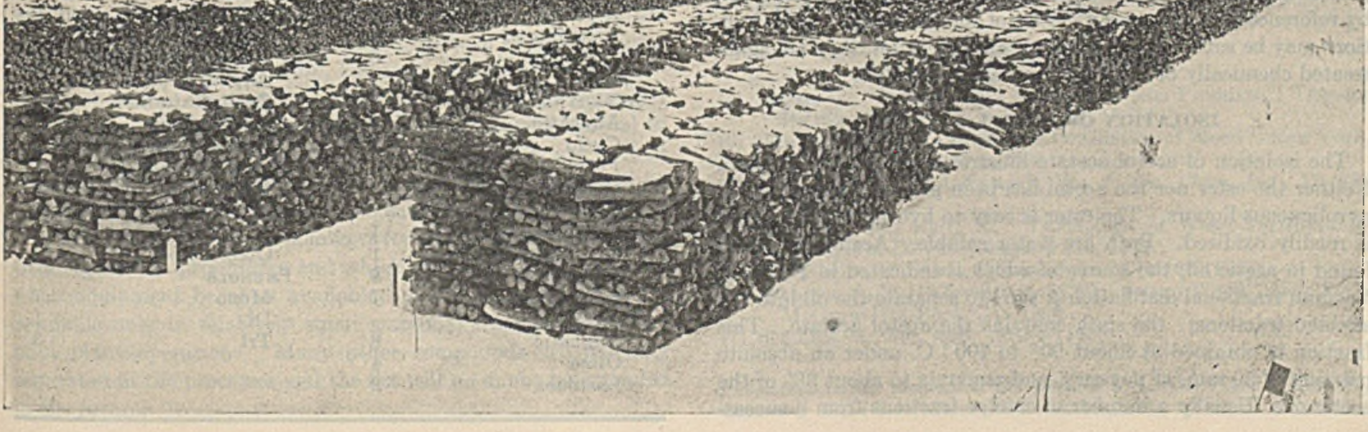
Complete isolation of every constituent of a tar or oil is impractical if not impossible. The best that may be expected is to obtain a large proportion of those present in greatest amounts, or those most readily separated, in fair states of purity. As a rule it would not be profitable to process a tar for only one or two compounds. Manipulations required to produce one item usually also perform a partial separation on one or more others, so that the cost of producing succeeding items is reduced.

Fractional distillation is the first step in working up an oil or tar. The purpose of this step is to divide the material into specially selected crude fractions suitable for further processing. These fractions withstand chemical and thermal treatments much better than the original tar or oil, probably because of the smaller number and variety of compounds present in each compared with the original material.

An effective fractionation is required. The tower has thirty bubble-cap trays or the equivalent, and the kettle capacity is proportioned to the tower so that about 100 hours are required to distill off a charge when refluxing about 10 volumes to 1 withdrawn. An absolute pressure of 50 mm. of mercury is maintained at the condenser.

The crude fractions are chosen by reference to the chemical and physical properties of the distillate. The chemical properties may include acidity, saponification, and bromine values, and car-

Plant and Portion of Reserve Wood Supply, Cliffs Dow Chemical Company



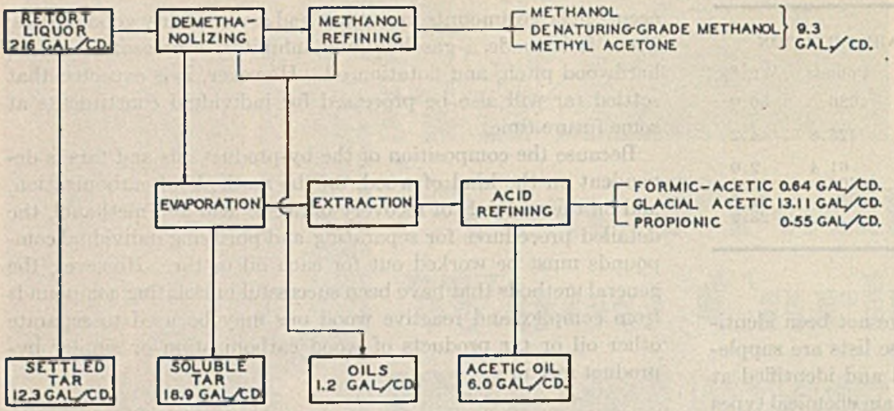


Figure 1. By-Products of Wood Carbonization (in Gallons per Cord)

bonyl, hydroxyl, and methoxyl determinations. Physical properties may include specific gravity and refractive index. Such properties, determined on, say, 5% increments of distillate, show variations which are useful in selecting fractions.

Cuts may be made at minimum values of a chemical property, or at inflection points of a physical property curve, or otherwise as may be determined by consideration of the major compounds present and of subsequent processing steps. A crude fraction usually contains one major compound along with a number of others less in quantity or importance. As a rule, fractions should be chosen to include the major compound so that preceding and following cuts do not contain it. To aid in subsequent purification of the major compound, it also may be important to exclude a compound of a different chemical type following or preceding it. The best cutting point may be determined from the chemical property curves.

After the desired cutting points have been established, the fractions can be conveniently duplicated by reference to specific gravity changes. The specific gravity of the distillate varies smoothly and continuously throughout a fractional distillation passing through a number of maxima and minima. This affords a useful operating guide for selection of fractions.

Subsequent operations on a crude fraction are aimed at isolation of the major compound, and may or may not result in parallel separation of minor constituents. Each crude fraction requires individual treatment, but as a general principle it may be stated that the mixture is partly broken up in some way, usually by chemical treatment. Treatment that alters or removes a class of compounds usually eliminates some azeotropic combinations so that further separations can be made by fractional distillation. Chemical treatment includes neutralization, saponification, esterification, and hydrogenation. Steam distillation, extraction, and crystallization methods are also used for the same purpose—that is, to break up partly or alter the mixture. The resultant portions are again fractionally distilled, and fractions are selected by reference to the property curves of the distillates. Such fractions may be sufficiently pure as obtained. If not, they are again treated chemically or otherwise and again distilled.

ISOLATION OF ACETOL ACETATE

The isolation of acetol acetate illustrates the general method. Neither the ester nor the acetol has been previously reported in pyroligneous liquors. The ester is easy to hydrolyze, and acetol is readily oxidized. Both are water soluble. Acetol acetate is found in acetic oil, the source of which is indicated in Figure 1. Vacuum fractional distillation is used to separate the oil into ten selected fractions; the sixth contains the acetol acetate. This fraction is obtained at about 90° to 100° C. under an absolute pressure of 50 mm. of mercury, and amounts to about 8% of the acetic oil. Usually a number of similar fractions from a succession of primary distillations are combined to make a charge for a still of the same size and type as used for the first distillation. This combined charge is fractionally distilled in the same manner as before.

Chemical and physical properties of the distillate are determined and plotted as in Figure 2. This chart shows the complexity of the material and makes evident the presence of other substances on both sides of the acetol acetate region. Preceding it and marked by the refractive index hump is methyl furyl ketone. Butyric acid is responsible for most of the acidity. Following the acetol acetate region and evidenced by the rise in refractive index and bromine values are methyl furoate and methylcyclopentenone. The portion of the distillate selected for further treatment includes the best portion of the ester value curve. It is important to cut before the bromine value and refractive index curves begins to rise because inclusion of the substances causing these rises with the acetol acetate fraction makes subsequent purification difficult.

Once the cutting points have been established they may be duplicated for plant control by specific gravity and refractive index tests. In this case the ester fraction was selected from 25.0 to 63.1% off. Saponification and acidity determinations indicate 84.9% ester calculated as acetol acetate and 7.5% acids calculated as butyric acid. Because the ester saponifies so readily, the acidity is best determined in methanol solution using alcoholic sodium hydroxide. Saponification is determined at room temperature for, if the alkaline solution is heated in the customary way, excessive alkali is consumed and deceptive values result.

To the ester fraction in a mixing tank is added $^1/_4$ volume of water. Sodium carbonate equivalent to the acid content is then added slowly. When neutralization is complete, the mixture is allowed to settle and the aqueous salt layer is withdrawn to be subsequently worked for butyric acid. The oil layer is vacuum distilled in a simple pot still to free it from any dissolved salt, and the distillate is then fractionally distilled and yields technical-grade acetol acetate.

Table II. Chemical Types of Compounds from Wood Distillation

Acids, aliphatic	
Saturated	19
Unsaturated	9
Other	6
Acetals	3
Amines	
Aliphatic	3
Pyridines	3
Alcohols	
Aliphatic	6
Unsaturated	3
Cyclo	6
Furyl	1
Aldehydes	
Aliphatic	7
Cyclo	2
Furyl	4
Unsaturated	3
Ethers	
Aliphatic	1
Aryl monohydroxy	1
Aryl dihydroxy	9
Aryl trihydroxy	7
Esters	
Aliphatic	8
Other	4
Lactones	2
Furanes	9
Hydrofuranes	2
Hydrocarbons	
Paraffins	8
Unsaturated	2
Aromatic	7
Condensed-ring	3
Terpenes	8
Ketones	
Aliphatic mono	9
Aliphatic di	4
Unsaturated mono	3
Aliphatic-furyl	1
Cyclic saturated	9
Cyclic dione	1
Cyclic unsaturated	6
Miscellaneous	
Oxypyrone	1
Glucosan	1
Cyclic ketol	1
Other ketol	1
Phenols	
Mono	7
Di	1
Tri	3

ISOLATION OF BUTYRIC ACID

The salt layer from the acetol acetate neutralization contains some ester in solution, amounting to about 10% of the total available. If desired this may be recovered by extraction with ethyl acetate. Much more butyric salt solution is obtained from the crude fraction preceding acetol acetate, and these solutions together constitute the sodium butyrate stock from which butyric acid is recovered.

Before acidifying the salt solution to liberate butyric acid, the solution is steam-distilled to remove any volatile impurities. Then sulfuric acid is added equivalent to the salt content, and steam distillation is continued to remove butyric acid. The distillate is extracted with ethyl acetate. The solvent is recovered by distillation, leaving the anhydrous crude acid which is fractionally distilled to yield good quality butyric acid.

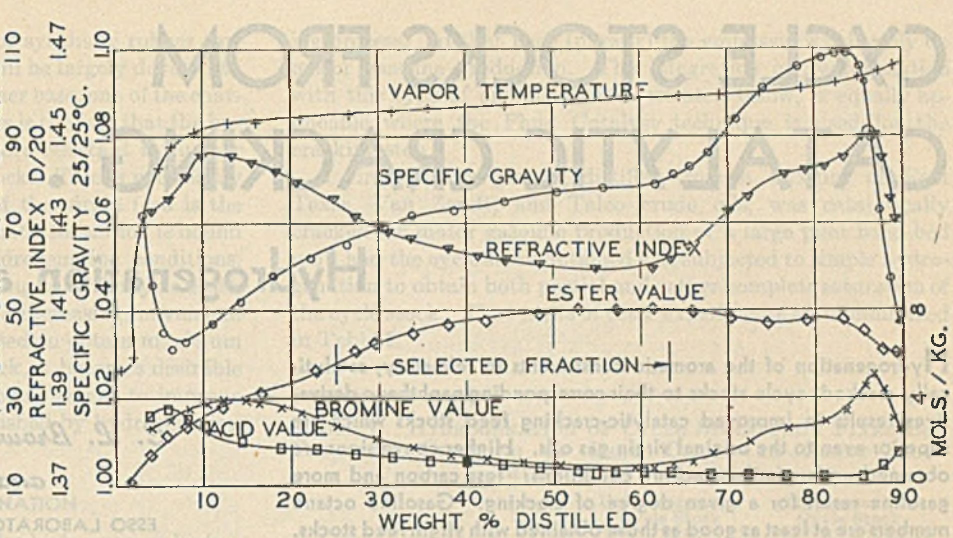


Figure 2. Property Curves for Selecting the Crude Acetol Acetate Fraction

ISOLATION OF MALTOL

Usually compounds present in large proportions are most readily isolated and purified. However, some compounds present in small amounts can easily be recovered in a high state of purity; maltol is an example for, although its concentration in the retort liquor probably does not exceed 0.03%, the pure substance can be isolated by relatively simple procedures. Maltol is soluble in hot solvents such as water, methanol, ethyl acetate, and many others, and it crystallizes readily when the solutions are cooled. It crystallizes out of soluble tar fractions obtained by the fractional distillation of soluble tar in the temperature range 130° to 150° C. and an absolute pressure of 25 mm. of mercury. The crude crystals from these fractions are recrystallized from methanol solution to yield pure, white crystals melting at 160° C.

The utility or value of a product has a bearing on the amount of steam, chemicals, equipment, and work that it pays to expend in its production. Cheap compounds now on the market may not be worth separating. For example, both ethanol and toluene occur in hardwood oils, and it is possible to isolate and to purify them. However, in view of their low market value it would probably be uneconomical to separate them as pure compounds. On the contrary, compounds that are not now available commercially and are difficult and expensive to synthesize may warrant considerable work and expense in isolation and purification if suitable uses for the material exist or can develop. Many of the compounds in wood tars and oils appear to be of the latter type.

It may be well to emphasize, however, that many of the individual chemicals that can be isolated by the methods described do not occur in large amounts, and it would be uneconomical to produce them singly. However, if the tars and oils are worked up systematically, the average unit cost of all the items will be low and the total production will be substantial.

A list of wood tar products follows for which we now have practical separation procedures and which can be made in quantity when equipment becomes available. Until such time they are available only in relatively small amounts, from laboratory or pilot plant operations. Many other compounds are partially separated in the processes and the list will no doubt be extended in the future.

Guaiacol
Creosol
Butyrolactone
Acetol acetate
Butyric acid
Crotonic acid
Maltol [3-oxy-2-methyl-(4)-pyrone]
2-Hydroxy-3-methyl-Δ2-cyclopentenone
2,6-Dimethoxyphenol
Tiglaldehyde
Methyl isopropyl ketone
Methyl ethyl ketone
Methyl furyl ketone
4-Ethylguaiacol

Commercial uses for some of these substances are not known but will probably develop after they are made available. One disadvantage in the use of chemicals that have been obtained as hardwood carbonization products is the definite limit to their production, depending both on the amount of wood carbonized by the industry and on the number of producers that will be able to process the tars and oils. Because the equipment requires rather large expenditures and the processes require an unusually high degree of chemical supervision and control, probably only a few of the larger charcoal producers will enter into by-product recovery. It would be possible, however, to utilize all the tars and oils produced by shipping them or crude fractions from them to the plants that are suitably equipped.

The total capacity of United States hardwood distillation plants is now estimated to be 1377 cords per day, of which about 29% is in the southern, 35% in the eastern, and 36% in the north central region. The economic position of the industry in general has been somewhat precarious, and the low prices that may be expected for acetic acid and methanol when more normal conditions return makes additional revenue appear particularly desirable. We believe that this additional revenue may be obtained from chemicals from the oils and tars, and that these by-products will become an important part of the wood carbonization industry.

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CYCLE STOCKS FROM CATALYTIC CRACKING . . .

Hydrogenation and Desulfurization

Hydrogenation of the aromatic constituents in refractory, catalytically cracked, cycle stocks to their corresponding naphthene derivatives results in improved catalytic-cracking feed stocks which are superior even to the original virgin gas oils. Higher conversions are obtained under similar cracking conditions; less carbon and more gasoline result for a given degree of cracking. Gasoline octane numbers are at least as good as those obtained with virgin feed stocks. Hydrogenation conditions used are generally the same as for the conventional high-pressure destructive hydrogenation of gas oils directly to gasoline except for the catalyst which, similarly, is sulfur resistant. Yields of hydrogenated cycle stock are 100% or more in all cases, with little change in boiling range and virtually complete sulfur removal. A combination of catalytic cracking with hydrogenation of all cycle stock and recracking to ultimate gasoline yield combined with fullest utilization of light hydrocarbons (C_3, C_4, C_5) by isomerization, alkylation, etc., is shown by calculation to result in an over-all volumetric yield of over 90% of 100-octane gasoline. Lower pressures (750 compared to 3000 lb. sq. in. gage) result in partial saturation of aromatics with rather complete desulfurization.

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THE high pressure hydrogenation of petroleum with sulfur-resistant catalysts has had many and varied applications, which have been described in the literature over the past several years. The production of aviation fuels by high pressure hydrogenation was discussed by Murphree, Gohr, and Brown (*3*), and more recently the same authors summarized the hydrogenation of petroleum with particular reference to the production of aviation gasoline, motor fuel, aviation blending agents, and Diesel fuel (*2*).

During the war the high pressure hydrogenation process made a valuable contribution to the 100-octane aviation gasoline program in the following three types of operation: (*a*) production of commercial iso-octane from polymers of isobutylene and normal butylenes; (*b*) saturation of catalytically cracked aviation base stock to improve stability and leaded octane number; and (*c*) direct manufacture of high quality aviation base from virgin and cracked kerosene fractions of predominantly cyclic character. Operations (*a*) and (*b*) involve merely the addition of hydrogen to convert olefins to paraffins. This is called "simple" or "saturation" hydrogenation. In the case of the catalytically cracked, aviation base stock it is important to restrict the hydrogen addition to the olefins without permitting saturation of the aromatics to naphthenes. Fortunately this is readily accomplished by choice of catalyst and control of operating conditions. These two olefin hydrogenation processes, (*a*) and (*b*), are also amenable to the low pressure techniques; and commercial low pressure hydrogenation plants likewise contributed valuable production to the 100-octane program. The direct manufacture of aviation base from kerosene fractions, process (*c*), is an example of destructive hydrogenation since it involves a combination of simple hydrogenation and other catalytic reactions, such as cracking and isomerization.

The purpose of the present paper is to discuss briefly another adaptation of the hydrogenation process, which has not yet been commercially applied but whose potentialities for the future will be apparent, particularly in conjunction with catalytic cracking. The process is also a case of simple hydrogenation, although not restricted to olefins, but rather directed principally to the saturation of aromatics, especially the refractory condensed-ring molecules prevalent in catalytically cracked cycle stocks. The destructive hydrogenation of virgin or cracked kerosenes and gas oils gives directly aviation or motor gasoline. In contradistinction, the simple hydrogenation of these same feed stocks results in negligible production of gasoline; the principal effect is the saturation of aromatics and incidental olefins, together with the elimination of sulfur, without significant change in the boiling range of the feed. Here again is another instance of the versatility of the hydrogenation process; the same feed stock and the same range of operating conditions are employed as for destructive hydrogenation, and only the catalyst is changed to accomplish the desired selective simple hydrogenation. However, even the catalysts for the two processes have considerable similarity in that they are both sulfur resistant and rugged as to physical and chemical life.

In the case of the simple hydrogenation of aromatics, as in destructive hydrogenation, high pressures are preferable from thermodynamic considerations (*4*). However, with sufficiently active catalysts, it is possible to get appreciable hydrogenation and extensive desulfurization at moderate pressures. The data discussed in this paper are principally those obtained at the conventional high pressure of about 3000 pounds per square inch gage at reaction temperatures of 550° to 750° F. However, a limited amount of data is also given for hydrogenation at 750 pounds in approximately the same temperature range. To avoid needless repetition, the ensuing discussion in referring to hydrogenation will mean simple or saturation hydrogenation unless stated otherwise.

Virgin gas oils can obviously be improved as Diesel fuels by saturation of aromatics to improve cetane number and by elimination of sulfur. In the case of cracked gas oils, the margin of improvement by hydrogenation is much greater, and excellent Diesel fuels can be prepared from very poor material. However, the broadest field in the future for the saturation hydrogenation of gas oils may be in the upgrading of catalytically cracked cycle stocks for further catalytic cracking; hence the data to be discussed refer principally to this application.

The catalytic cracking process is an efficient and satisfactory means of producing high quality aviation and motor gasolines from virgin gas oils. Throughout the war period the commercial catalytic cracking units were devoted to the production of aviation base stock together with large quantities of butanes and butylenes that are alternatively used (*a*) to make alkylate as a high-octane aviation blending agent, or (*b*) for synthetic rubber raw materials. Postwar, these same plants will be largely devoted to the production of motor gasoline. In either case, one of the characteristics of the catalytic cracking process is the fact that the by-product cycle stocks are considerably more resistant to further cracking than the original virgin feed stock. This is necessarily so, since the more easily cracked part of the virgin feed is the first to be converted, and since some aromatic formation is bound to occur in the absence of favorable hydrogenation conditions. In fact, it is axiomatic in catalytic cracking that the cycle stock becomes progressively more refractory with increasing conversion.

If recycle catalytic cracking is to be used to obtain maximum yield of gasoline from a given charge stock, it becomes desirable to consider methods for upgrading the cycle stocks to improve their quality. How this can be accomplished by hydrogenation is discussed below.

HIGH PRESSURE HYDROGENATION

The standard type of small pilot unit for high pressure hydrogenation used in these studies is shown in simple diagrammatic form in Figure 1. The feed stock to be hydrogenated is introduced into the system by a high pressure feed pump. After mixing under pressure with excess hydrogen, it is preheated to the reaction temperature in a coil and then passed through the catalyst bed in the reactor. The products are cooled, the liquid and excess gas are separated, and the excess gas is recycled to the high pressure system by means of a compressor. Fresh hydrogen is continuously added to replace that consumed by chemical reaction and that lost from the system by solubility in the liquid product. The product from the high pressure separator, after reduction in pressure to atmospheric conditions, is separated from dissolved gases in a low pressure separator.

As already stated, the principal object in high pressure hydrogenation of catalytically cracked cycle stocks has been to improve these materials for subsequent catalytic cracking. A considerable amount of data has been obtained both with respect to the hydrogenation operation and to the catalytic cracking of the hydrogenated cycle stock. Catalytically cracked cycle stocks from a variety of virgin feeds have been studied, and the hydrogenated products have been tested as catalytic cracking stocks for the production both of motor gasoline and aviation gasoline. These cracking experiments have been obtained on pilot plants both of the fixed bed and Fluid Catalyst type. Carlsmith and Johnson (*1*) recently described the Fluid Catalyst pilot plants.

EAST TEXAS–VAN ZANDT–TALCO GAS OIL

Before the development of Fluid Catalyst cracking, considerable work was done at these laboratories on the fixed-bed cracking process. At that time (prewar) the emphasis was largely on motor gasoline production. The integration of hydrogenation with this type of operation, as illustrated below, is equally applicable where the Fluid Catalyst technique is used for the cracking step.

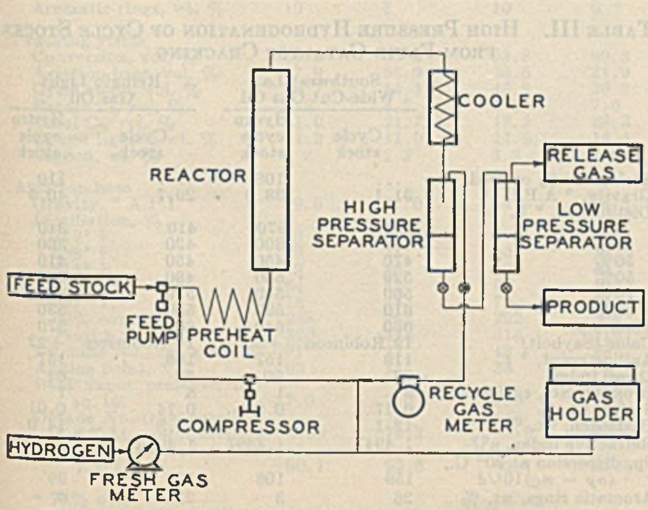

Figure 1. Laboratory High Pressure Hydrogenation Unit

A virgin heavy gas oil, distilled from a mixture of East Texas, Van Zandt, and Talco crude oils, was catalytically cracked for motor gasoline production in a large pilot fixed-bed unit, and the cycle stock obtained was subjected to simple hydrogenation to obtain both partial and rather complete saturation of the cycle stock. The results of these experiments are summarized in Table I.

Table I. Hydrogenation of Cycle Stock from Fixed-Bed Catalytic Cracking of East Texas–Van Zandt–Talco Mixed Heavy Gas Oil

	Unhydrogenated Cycle Stock	Hydrogenated Cycle Stock	
Degree of hydrogenation	...	Partial	Almost complete
Pressure, lb./sq. in. gage	...	3000	3000
Feed rate, vol./vol./hr.	...	2	2
Yield, vol. % on feed	...	104	110
Gravity, ° A.P.I.	27.2	31.0	35.0
Distillation, ° F.			
5% over	500	470	430
10%	520	500	470
30%	590	570	550
50%	640	620	600
70%	690	670	650
% over at 700° F.	77	83	85
Color (Saybolt)	5 Robinson	+4	+18
Aniline point, ° F.	156	165	181
Diesel index	42	51	63
Bromine No., cg./gram	8	2	2
Sulfur, wt. %	0.78	0.21	0.06
Hydrogen, wt. %	12.2	13.0	13.7
Refractive index, n_D^{30}	1.5051	1.4845	1.4692
Sp. dispersion at 30° C., $(n_F - n_C)10^4/d$	170	125	112
Aromatic rings, wt. %	22	14	6

The yields of hydrogenated product were over 100 volume % and there was comparatively little formation of light ends even at the more complete saturation level. The sulfur content of the feed stock was reduced from 0.78% to as low as 0.06% for the more highly saturated product. The extent of saturation of the hydrogenated products from the two runs is shown particularly by their low aromatic contents, high Diesel indices, high hydrogen percentages, and low specific dispersions as compared with the corresponding properties of the unhydrogenated cycle stock. The percentage of aromatics represents the proportion of carbon that occurs in aromatic rings and was determined by the method of Vlugter, Waterman, and van Westen (*5*). The relatively high space velocity employed in these runs (namely, 2 volumes of liquid feed per volume of catalyst per hour) is indicative of high catalyst activity. From general experience in high pressure hydrogenation in other applications on the large scale units, it is expected that the life of the catalyst would be from six months to more than a year, before it would have to be discharged from the reactors for reworking.

Catalytic cracking results were obtained in small fixed-bed pilot units on the unhydrogenated cycle stock as well as on the hydrogenated cycle stocks produced at the two levels of saturation. These cracking runs were made at the same conditions as employed on the virgin gas oil in order to give a direct comparison among the various feed stocks. Synthetic silica-alumina catalyst was employed at a cracking temperature of 850° F., a feed rate of 1.8 volumes of feed per volume of catalyst per hour, and cracking periods lasting 20 minutes between regenerations. Atmospheric pressure was used. The cracking data are summarized in Table II. Conversion is expressed as 100% minus the volume percentage of liquid distilling above the motor gasoline range, and excess C_4 represents that portion of the total butane produced which is beyond that required to make a gasoline of 10-pound Reid vapor pressure.

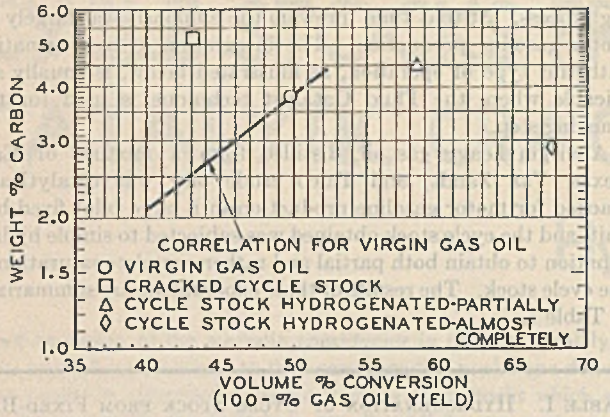

Figure 2. Carbon Yield vs. Feed Conversion for Fixed-Bed Catalytic Cracking of East Texas–Van Zandt–Talco Mixed Heavy Gas Oil with Synthetic Catalyst

The conversions obtained at equivalent conditions indicate that both of the hydrogenated cycle stocks are much less refractory than the unhydrogenated cycle stock, and are even less refractory than the virgin gas oil. This is particularly true of the more completely hydrogenated cycle stock, which is shown to be a remarkable feed stock for catalytic cracking. Yield of 10-pound Reid vapor pressure motor gasoline is also highest for the more completely hydrogenated cycle stock and lowest for the unhydrogenated cycle stock. Both the conversion and the gasoline yield from these various feed stocks increase with decreasing aromaticity, as indicated by lower specific dispersion.

It is well known in catalytic cracking that the yield of various products from a given feed stock is a function of the conversion obtained at a specified cracking temperature on any particular catalyst. Thus, as conversion is raised, the yields of gas and carbon increase. With increasing conversion the gasoline yield at first grows larger, reaches a maximum, and finally begins to decrease at excessively high conversions due to recracking. Table II shows merely the results obtained at a given feed rate and cycle length. The conversions are directly indicative of the relative ease of cracking of the feed stocks; but the comparison of the product distribution from the various feeds could be more accurately shown by obtaining results at the same conversion level. It is obvious that the more completely hydrogenated cycle stock gives much lower carbon than the virgin gas oil, because the carbon yield is lower (2.9 compared to 3.8%) even though the conversion is higher (67.7 compared to 49.8%). In the case of the less completely hydrogenated cycle stock, it is difficult to tell from Table II whether the carbon-forming tendency of this material is less than that of the virgin gas oil because, although the carbon yield is higher (4.5 compared to 3.8%), so is the conversion (58.5 compared to 49.8%). In order to bring out more clearly the relative carbon-producing tendencies of the various feed stocks, the data on carbon formation in Table II are plotted against the conversions for comparison with a correlation available for the virgin gas oil; Figure 2 indicates that the less completely hydrogenated cycle stock has a lower carbon-forming tendency than the virgin feed.

TABLE II. FIXED-BED CATALYTIC CRACKING WITH SYNTHETIC CATALYST OF FEED STOCKS DERIVED FROM EAST TEXAS–VAN ZANDT–TALCO MIXTURE

	Virgin Gas Oil	Cracked Cycle Stock	Hydrogenated Cycle Stock	
Feed				
Degree of hydrogenation	..	..	Partial	Almost complete
Vol. % on virgin gas oil	100	64	66	70
Gravity, ° A.P.I.	26.9	27.2	31.0	35.0
Distillation, %				
400° F.	0	1	2	4
700° F.	30	77	83	85
Mid-boiling point, ° F.	780	640	620	600
Aniline point, ° F.	188	156	165	181
Diesel index	51	42	51	63
Sulfur, wt. %	1.10	0.78	0.21	0.06
Hydrogen, wt. %	12.9	12.2	13.0	13.7
Sp. dispersion at 30° C., $(n_F - n_C)10^4/d$	133	170	125	112
Yields				
Conversion, vol. %	49.8	43.2	58.5	67.7
Gasoline, vol. %	42.5	33.7	46.6	55.4
Gas oil, vol. %	50.2	56.8	41.5	32.3
Excess C_4, vol. %	8.8	6.9	10.5	13.6
C_3 and lighter, wt. %	4.5	4.1	5.7	6.4
Carbon, wt. %	3.8	5.2	4.5	2.9
Gasoline				
Gravity, ° A.P.I.	61.3	59.9	59.0	60.8
Distillation, %				
158° F.	31	28	24	28
212° F.	52	48	47	52
257° F.	65	59	58	62
90% over, ° F.	371	379	372	359
Final b.p., ° F.	406	407	403	391
Bromine No., cg./gram	53	40	28	30
Aniline point, ° F.	92	90	87	90
Reid vapor pressure, lb./sq. in.	10	10	10	10
Octane No.				
A.S.T.M. Motor method	80.2	80.0	80.6	80.4
A.S.T.M. Motor method + 3 cc. T.E.L./gal.	86.5	87.9–88.6	90.1	90.1

It is interesting to observe in Table II the quality of gasolines produced by catalytic cracking of the various feed stocks. Despite the differences in the aromaticity of the four charging stocks, there is no discernible difference in the octane numbers of the catalytically cracked gasolines. As indicated by aniline points, the gasolines from the hydrogenated cycle stocks, even from the more completely saturated product, appear to be just as aromatic as that from the unhydrogenated cycle stock.

LOUISIANA AND REFUGIO GAS OILS

Virgin gas oils from Southwest Louisiana crude and from Refugio (Texas Coastal) crude are among the many feed stocks that have been catalytically cracked in the 100-barrel-per-day fluid catalyst pilot unit at 975° F. and 60% conversion to produce aviation gasoline and C_4 hydrocarbons for alkylation and for synthetic rubber raw materials. The hydrogenation results on the cycle stocks from these two feeds are discussed below as illustrative of the possibilities of the hydrogenation technique. The hydrogenated products are compared in Table III with the unhydrogenated cracked material.

The hydrogenation operations were carried out at 3000 pounds pressure with sulfur-resistant catalysts in the standard hydrogenation pilot unit. Again, the liquid yields were in excess of 100%, and there was comparatively little formation of light ends. These hydrogenation runs were made to give complete saturation of the aromatics as indicated by specific dispersions on the hydrogenated product of 106 and 99, and aromatic ring contents of 3 and 0% by weight. The high degree of refinement of the hydro-

TABLE III. HIGH PRESSURE HYDROGENATION OF CYCLE STOCKS FROM FLUID CATALYST CRACKING

	Southwest La. Wide-Cut Gas Oil		Refugio Light Gas Oil	
	Cycle stock	Hydro cycle stock	Cycle stock	Hydro cycle stock
Yield, vol. % on feed	...	108	...	110
Gravity, ° A.P.I.	31.1	38.0	29.7	40.9
Distillation, ° F.				
5% over	390	370	410	340
10%	410	390	420	360
30%	470	450	450	410
50%	520	500	480	440
70%	560	540	510	470
90%	610	590	550	530
Final b.p.	660	640	600	570
Color (Saybolt)	19 Robinson	+30	14 Robinson	+22
Aniline point, ° F.	119	157	106	157
Diesel index	37	60	32	64
Bromine No., cg./gram	9	1	8	1
Sulfur, wt. %	0.17	0.02	0.14	0.01
Hydrogen, wt. %	12.1	13.8	11.8	14.0
Refractive index, n_D^{20}	1.4947	1.4597	1.4985	1.4496
Sp. dispersion at 20° C., $(n_F - n_C)10^4/d$	159	106	161	99
Aromatic rings, wt. %	26	3	27	0

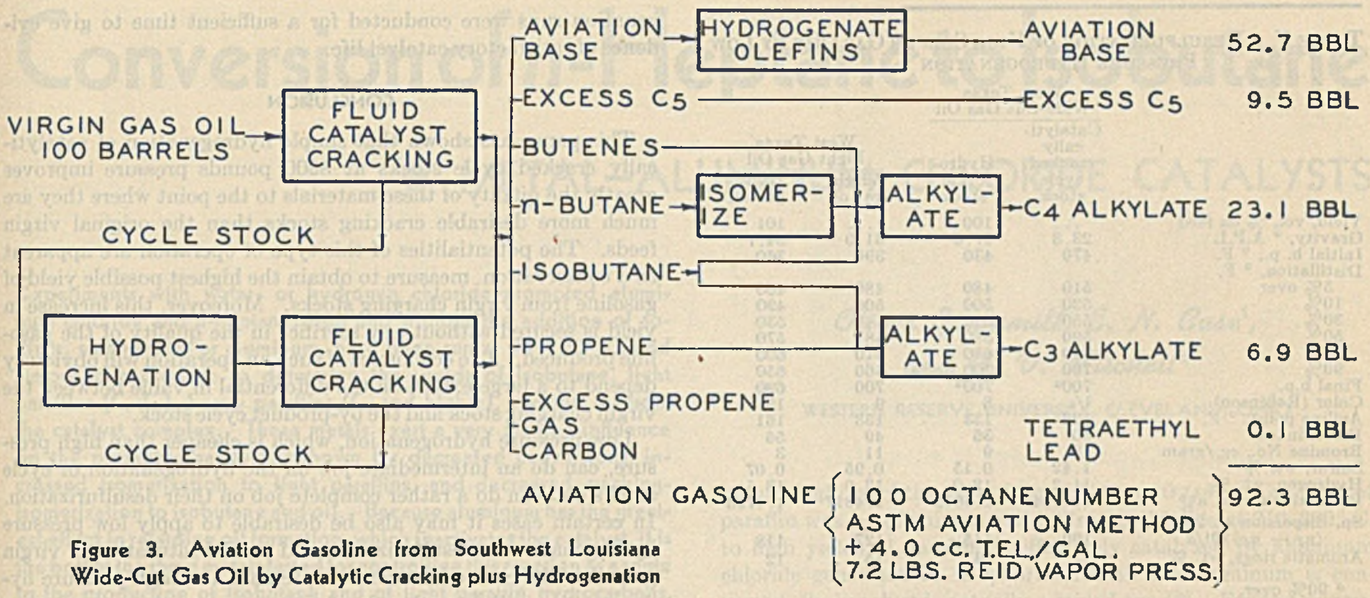

Figure 3. Aviation Gasoline from Southwest Louisiana Wide-Cut Gas Oil by Catalytic Cracking plus Hydrogenation

genated products is further indicated by their excellent colors (+30 and +22 Saybolt). In these operations the cycle stock being hydrogenated represented the total cracked product boiling above the aviation gasoline, because it was of interest to find the maximum yield of aviation gasoline and C_4 hydrocarbons that could be obtained by combining catalytic cracking of the virgin feed stock with catalytic cracking of the hydrogenated cycle stock. To accomplish this, the hydrogenated products indicated in Table III were catalytically cracked in a small Fluid Catalyst pilot unit; previous operation had shown that this unit produces cracking results similar to those of the 100-barrel-per-day Fluid Catalyst plant when run at comparable conditions. The same type of synthetic silica-alumina catalyst and the same cracking temperature (975° F.) used with the original virgin feeds were employed at a cracking severity level sufficient to produce a cycle stock of essentially the same hydrogen content as that of the original unhydrogenated cycle stock. Table IV summarizes the comparative cracking data on virgin feeds and hydrogenated cycle stocks.

TABLE IV. FLUID CATALYST CRACKING WITH SYNTHETIC CATALYST

	Southwest La. Wide-Cut Gas Oil		Refugio Light Gas Oil	
	Virgin gas oil	Hydro-cycle stock	Virgin gas oil	Hydro-cycle stock
Feed				
Vol. % on virgin gas oil	100	44	100	51
Gravity, ° A.P.I.	32.2	38.0	31.4	40.9
% distd. at 325° F.	0	2	0	4
Mid-boiling point, ° F.	620	500	520	440
Final b.p., ° F.	700[a]	640	630	570
Aniline point, ° F.	176	157	142	157
Diesel index	57	60	45	64
Sulfur, wt. %	0.27	0.02	0.11	0.01
Hydrogen, wt. %	13.4	13.8	12.7	14.0
Sp. dispersion at 20° C., $(n_F - n_C)10^4/d$	122	106	120	99
Aromatic rings, wt. %	10	3	10	0
Cracking yields				
Conversion, vol. %	59.3	65.6	53.8	69.8
Aviation base, vol. %	27.9	35.9	26.5	31.9
Cycle stock, vol. %	40.7	34.4	46.2	30.2
Excess C_5, vol. %	6.3	4.7	3.6	7.5
Total C_4, vol. %	21.0	21.7	17.2	23.3
C_3 and lighter, wt. %	11.3	11.0	11.9	14.4
Carbon, wt. %	4.2	2.2	3.3	2.9
Aviation base				
Gravity, ° A.P.I.	59.0	57.0	54.5	54.2
Distillation, %				
140° F.	13	8	8	8
158° F.	29	21	22	19
212° F.	59	46	50	45
221° F.	64	52	55	49
257° F.	76	68	70	66
90% over, ° F.	288	292	292	294
Final b.p., ° F.	320	318	316	316
Bromine No., cg./gram	71	27	43	28
Aniline point, ° F.	62	71	38	60
Reid vapor pressure, lb./sq. in.	7.0	7.0	7.0	7.0
Octane No. (raw gasoline)				
A.S.T.M. motor method	83.0	79.3	83.9	82.5
Aviation method + 4 cc. T.E.L./gal.	90.1	92.6	92.1	92.5

[a] 79% over.

The hydrogenated cycle stocks in both cases, being virtually free of aromatics, are considerably better feed materials than the virgin gas oils. This is shown by the cracking yields. (In this case, since aviation gasoline is produced rather than motor fuel, the conversions represent 100% minus the volume percentage of liquid distilling above the aviation gasoline range. Excess C_5 represents that portion of the total pentane produced which cannot be included in the gasoline because of vapor pressure specifications—7-pound Reid vapor pressure.) For example, the hydrogenated cycle stocks give higher aviation gasoline yields and the same or higher total C_4 despite lower carbon formation. Also, the leaded octane numbers of the raw aviation gasoline (92.6, 92.5) are as good as or better than those obtained from the virgin feeds (90.1, 92.1).

Table IV indicates that a very efficient combination process for obtaining high yields of high-octane aviation gasoline could be established by combining catalytic cracking with simple hydrogenation of the cracked cycle stock. In this process the first-pass cycle stock from high temperature, high conversion Fluid Catalyst cracking would undergo simple hydrogenation for saturation of aromatics and olefins and would then be catalytically cracked with return of cycle stock for further hydrogenation and catalytic cracking in a recycle type of operation to ultimate yield of aviation gasoline. Experimentally the recycle process has been demonstrated in stages and not as an integrated operation. However, the estimates for ultimate yield should be reasonably firm, as they are based on second-pass cracking results where the cycle oils from the cracking of the hydrogenated cracked cycle stocks had nearly the same characteristics (same hydrogen content) as the original first-pass cracked cycle stocks before hydrogenation.

Accordingly, calculations have been made to show the yield and quality of aviation gasoline obtainable by this integrated recycle catalytic cracking process, involving hydrogenation of the catalytically cracked cycle stock. These estimates for total aviation base yield and quality include fullest utilization of the light

Table V. Desulfurization of High Sulfur Gas Oils by Low Pressure Hydrogenation

	West Texas Wide-Cut Gas Oil		West Texas Light Gas Oil	
	Catalytically cracked cycle stock	Hydro-cycle stock	Virgin gas oil	Hydro gas oil
Yield, vol. % on feed	...	100	...	101
Gravity, ° A.P.I.	23.3	27.3	31.9	34.7
Initial b. p., ° F.	470	430	390	360
Distillation, ° F.				
5% over	510	480	480	460
10%	520	500	500	490
30%	550	540	540	530
50%	590	580	580	570
70%	640	630	610	600
90%	700	700	660	650
Final b.p.	700[a]	700[a]	700	690
Color (Robinson)	1/3	8	9	19
Aniline point, ° F.	128	133	153	161
Diesel index	30	36	49	56
Bromine No., cg./gram	18	9	11	3
Sulfur, wt. %	1.42	0.15	0.95	0.07
Hydrogen, wt. %	11.2	12.0	13.0	13.5
Refractive index, n_D^{20}	1.5174	1.5012	1.4817	1.4723
Sp. dispersion at 20° C., $(n_F - n_C)10^4/d$	180	145	127	118
Aromatic rings, wt. %	27	24	15	12

[a] 90% over.

hydrocarbons (C_3, C_4, and C_5). The small quantity of *n*-butane (about 20% of the saturated butanes) is isomerized, and the total isobutane is alkylated with butylenes, any excess isobutane being employed to alkylate propylene. The C_5 cut from catalytic cracking is utilized as a vapor pressure blending agent. For further improvement in octane number, the catalytically cracked aviation base stock is subjected to simple hydrogenation to saturate olefins. These calculations indicate that such a process would give from the virgin gas oils (Southwest Louisiana or Refugio) an over-all volumetric yield of over 90% of 100-octane gasoline. The case for the Southwest Louisiana feed stock is shown diagrammatically in Figure 3.

LOW PRESSURE HYDROGENATION

As mentioned earlier, it is possible to hydrogenate catalytically cracked cycle stocks at lower pressures with the same type of sulfur-resistant catalyst employed for simple hydrogenation at 3000 pounds pressure. Obviously conditions are less favorable for complete saturation at lower pressures; but an appreciable degree of hydrogenation is obtainable at conditions consistent with adequate catalyst life. The process is especially effective where the principal object is desulfurization. Naturally, low pressure hydrogenation may also be applied to desulfuring and saturating virgin feed stocks; and in this case desulfurization is easier because of the less refractory character of the sulfur-containing molecule. By way of illustration, hydrogenation data at 750 pounds per square inch gage on a high-sulfur virgin gas oil and a high-sulfur catalytically cracked cycle stock, both derived from West Texas crude, are presented in Table V. These results were obtained in a pilot unit similar to that shown in Figure 1 except for a smaller catalyst capacity and once-through gas operation.

The yields are high, and there is comparatively little change in boiling range on hydrogenation. The various indices of aromaticity (specific dispersion, aniline point, hydrogen content, Diesel index, weight per cent aromatic rings) indicate appreciable hydrogenation of aromatic rings. But the most conspicuous improvement is shown in the sulfur content of the hydrogenated products. Thus the catalytically cracked cycle stock is reduced in sulfur from 1.42 to 0.15% and the virgin gas oil from 0.95 to 0.07%. This degree of desulfurization is especially notable in the case of the cracked cycle stock because the sulfur-containing molecules in such materials are very refractory. These low pressure hydrogenation runs were conducted for a sufficient time to give evidence of satisfactory catalyst life.

CONCLUSION

This paper has shown that simple hydrogenation of catalytically cracked cycle stocks at 3000 pounds pressure improves greatly the quality of these materials to the point where they are much more desirable cracking stocks than the original virgin feeds. The potentialities of this type of operation are apparent as a conservation measure to obtain the highest possible yield of gasoline from virgin charging stocks. Moreover, this increase in yield is secured without any sacrifice in the quality of the gasoline produced. The economics of such an operation will obviously depend to a large extent on the differential in value between the virgin charging stock and the by-product cycle stock.

Low pressure hydrogenation, which is cheaper than high pressure, can do an intermediate job on the hydrogenation of cycle stocks and can do a rather complete job on their desulfurization. In certain cases it may also be desirable to apply low pressure hydrogenation to desulfurization and partial saturation of virgin gas oil. The choice between low pressure and high pressure hydrogenation will depend on local situations and the general price structure for petroleum and its products, which hinges on the cost and scarcity of crude oil and the relation of coal and fuel oil prices.

As a means of conserving petroleum supplies from a standpoint of national policy, the hydrogenation of catalytically cracked cycle stocks should command thoughtful attention.

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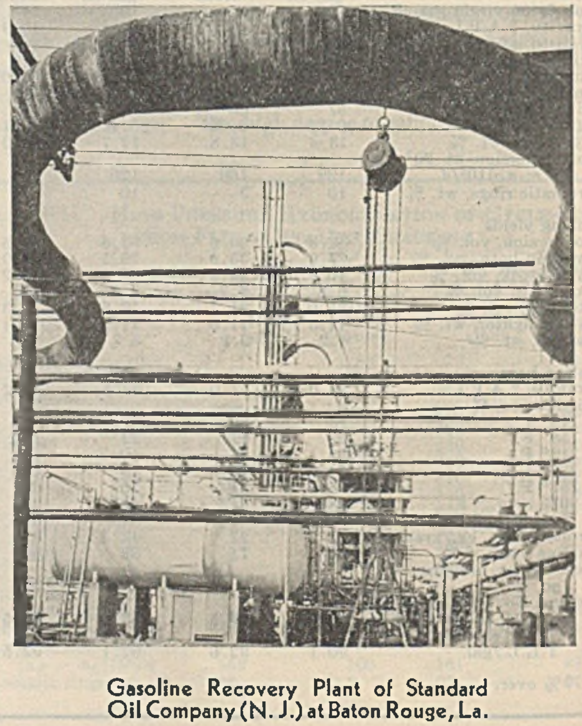

Gasoline Recovery Plant of Standard Oil Company (N. J.) at Baton Rouge, La.

Conversion of *n*-Heptane to Isobutane

• METAL–ALUMINUM CHLORIDE CATALYSTS

Experiments with water- or hydrogen chloride–promoted aluminum chloride and *n*-heptane, with and without the addition of sodium, magnesium, or aluminum, have been run at 95–100° C. and atmospheric pressure to determine the yields of isobutane, light paraffins (C_5–C_7), heavy paraffins (C_8 and higher), and the oil from the catalyst complex. These metals exert a very marked influence on the promoted catalyst as shown by decreased conversions, increased isomerization to light paraffins, and decreased cracking-isomerization to isobutane and oil. Because aluminum has the greatest effect in retarding oil formation, which inactivates the catalyst, it is the best of the three metals tested for controlling this reaction as a route to the production of isobutane and of light paraffin hydrocarbons.

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NUMEROUS studies of the action of aluminum halides on paraffin hydrocarbons have shown that isomerization and cracking may occur; the relative extent of these reactions depends on the nature of the hydrocarbon, activity of the catalyst, and other experimental conditions. Isomerization, for example, predominates in the *n*-butane–aluminum chloride reaction, if hydrogen chloride or other promoter is present, and this process is now commercially important as a source of isobutane for aviation gasoline manufacture. Higher paraffin hydrocarbons may undergo both isomerization and cracking, and isobutane has frequently been a prominent product from these reactions (*1, 2, 3, 11, 19*).

Recently, conditions were studied that will convert a single normal paraffin, *n*-heptane, to isobutane in the presence of aluminum chloride (*6*). With water or hydrogen chloride as catalyst promoters, a maximum yield of 76% isobutane was obtained by the action of aluminum chloride on *n*-heptane at 95–100° C. and at atmospheric pressure in an apparatus which permitted the isobutane to distill as rapidly as formed; the reaction mixture was thus kept concentrated with respect to catalyst, intermediate products, and *n*-heptane. Complete conversion of the heptane and the maximum yield of isobutane were obtained with a heptane/aluminum chloride mole ratio of 3/1, plus the addition of about 7.5% water with respect to the aluminum chloride. The remainder of the heptane is converted to a highly unsaturated mixture of hydrocarbons which forms a catalytically inactive complex with aluminum chloride. Less vigorous conditions and, therefore, less severe cracking-isomerization result from higher reactant ratios and less intensive promotion of the catalyst. Such conditions produce smaller conversions, lower yields of isobutane, but higher yields of C_5–C_7 paraffins.

The purpose of the present investigation was to determine the effect of certain added metals on the heptane–aluminum chloride reaction when carried out under conditions which give relatively high isobutane yields. Combination metal–aluminum chloride catalysts have already been studied in several hydrocarbon reactions and Friedel-Crafts syntheses. In the catalytic cracking of gas oil with aluminum chloride, the addition of 20% aluminum with respect to the catalyst is claimed to increase by 50% the yield of hydrocarbons boiling to 200° C. and to decrease coke formation (*14*). In the cracking of heavy naphtha to isobutane and a light isoparaffinic naphtha by aluminum chloride, the addition of 20% aluminum to the catalyst decreases the isobutane/light naphtha ratio from 0.5–1.0 to 0 (*15*). Cracking of paraffin wax by aluminum and hydrogen chloride at 210–260° C. to high yields of gasoline is effectively catalyzed by aluminum chloride generated in situ, but until all the aluminum is converted, the catalyst is actually a mixed one (*8*). For the conversion of propane to isobutane a mixture of aluminum, iron, or other metal with aluminum chloride is said to be a particularly effective catalyst combination (*18*).

In the polymerization of ethylene by aluminum chloride, Hall and Nash (*7*) observed that added aluminum inhibited cracking and the formation of a catalyst-hydrocarbon complex without hindering polymerization. An improved process for the polymerization of tertiary olefins to lubricating oils by Friedel-Crafts catalysts plus 25–100% of an alkali metal is claimed (*13*).

Metal–aluminum chloride catalysts have been most frequently proposed for paraffin hydrocarbon isomerization processes. Undesirable side reactions are suppressed by the presence of aluminum in the hydrogen chloride–promoted isomerization of *n*-butane (*16*) and *n*-pentane (*17*). Isomerizations, in which the aluminum halide is generated in situ by the action of a hydrogen halide, alkyl halide, or halogen on aluminum, gave better yields of isoparaffins than comparable reactions with the aluminum halide (*9, 12*).

The catalyst for Friedel-Crafts reactions may advantageously be made in the reaction mixture from aluminum metal and hydrogen chloride (*10*), or the mixed catalyst itself may be used, as in the preparation of dibenzyl from benzene and ethylene chloride (*20*). The presence of aluminum in the Friedel-Crafts synthesis of benzophenone from benzene and benzoyl chloride caused consecutive reactions of reduction. Hydrogen, formed by the action of hydrogen chloride on aluminum, the hydrogen chloride being a product of the acylation, was the reducing agent (*5*).

From these examples of cracking, polymerization, and isomerization, it appears that the effect of added aluminum or other metal is to diminish the severity of cracking and thereby to increase the yields of light naphtha, polymer, or isoparaffin, and extend the life of the catalyst through diminished rate of complex formation.

EXPERIMENTAL PROCEDURE

n-Heptane was the California Chemical Company's knock-rating grade: boiling point (760 mm.) 98.42° C., freezing point −90.64° C., n_D^{20} 1.38776, d_4^{20} 0.68367. Reagent-grade aluminum chloride was weighed into glass ampoules holding enough for one run (33.3 grams, 0.25 mole) in a dry box so that the purity and, therefore, activity of the catalyst would be constant in the various experiments. The aluminum and magnesium metals were 100-mesh powders thoroughly washed and dried before using. Sodium metal was converted into sodium shot in the usual way.

The apparatus consisted of a 500-ml. three-neck flask fitted with a water-addition pipet or gas inlet tube, stirrer, and Friedrich's reflux condenser, at the top of which was a low-temperature, glass-helix-packed, jacketed, fractionating column. By means of circulating pumps and cooling baths the column was automati-

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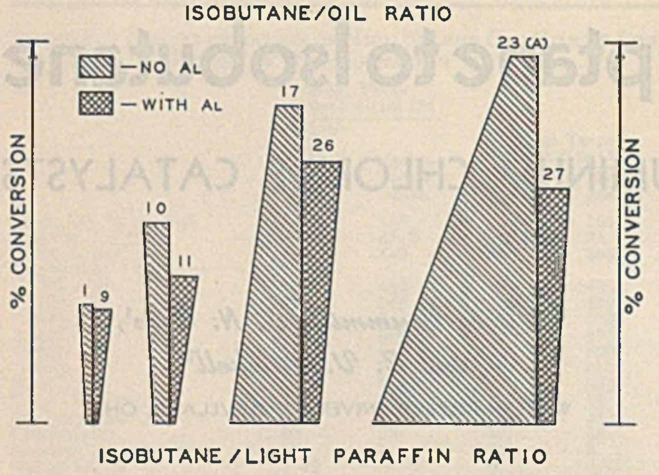

Figure 1. Conversion and Relative Yields from Aluminum–Aluminum Chloride Experiments

cally maintained at a temperature so that isobutane was slowly and continuously distilled during the reaction, higher-boiling hydrocarbons being returned to the flask. Isobutane vaporized at the head of the column, passed through soda lime and calcium chloride, and was collected in carbon dioxide–cooled ampoules. Water for catalyst promotion was uniformly added directly to the flask from a specially designed pipet at the rate of 0.05 ml. per 3 minutes. When hydrogen chloride was used, it was passed from a Harshaw Chemical cylinder directly into the reaction mixture.

An experiment was carried out by first carefully displacing all air and moisture from the whole apparatus by purified nitrogen. The aluminum chloride, heptane, and metal were then added to the flask, and the reaction was carried out under the conditions indicated in Table I. Refractionation of the isobutane in a low-temperature Podbielniak column showed it to be at least 98% pure. Small amounts of propane were found in a few experiments; any material boiling above isobutane was added to the liquid-layer products. The residual reaction mixture was vacuum-distilled at 95–100° C. and 10–15 mm. to collect higher hydrocarbons, which were then fractionated into a light paraffin cut (C_5–C_7), *n*-heptane, and a heavy paraffin cut (C_8 and above). The dark red catalyst lower layer was decomposed by the addition of ether. Filtration of the ether solution to remove unreacted metal, hydrolysis of the filtrate, and distillation of the ether gave the unsaturated oil. The ether probably reacts with the complex to form an ether–aluminum chloride addition compound which is then hydrolyzed:

$$\text{catalyst complex} + (C_2H_5)_2O \longrightarrow AlCl_3\cdot(C_2H_5)_2O + \text{oil}$$

Addition compounds with ether are known (*4*). The weight of oil obtained by direct hydrolysis of the complex or by reaction with ether first was the same, but direct hydrolysis had the serious disadvantage of allowing the metal to displace hydrogen from the aqueous acid layer, which made it difficult to separate the oil.

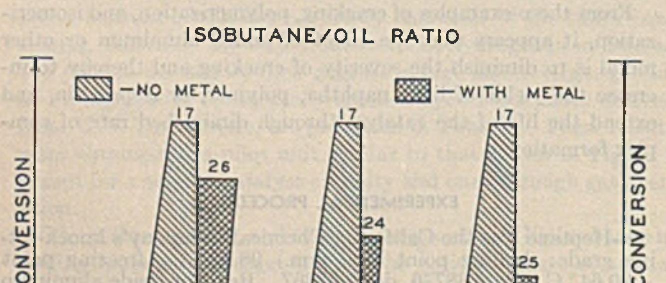

Figure 2. Conversion and Relative Yields from Metal–Aluminum Chloride Experiments

All of the experiments were run with 125 grams (1.25 moles) of *n*-heptane and 33.3 grams (0.25 mole) of aluminum chloride. When the reaction time was 4 hours, the promoter was uniformly added during the first 2¹/₂ hours. Otherwise, the promoter was added during the whole time of reaction.

The whole procedure was standardized so that fairly satisfactory checks, considering the nature of the reaction and analysis, could be obtained from duplicate experiments; e.g., two experiments similar to 17 (Table I) gave 84.0 and 83.5% conversions, compared to 84.7%; 69.0 and 66.7% isobutane, compared to 67.8%.

The results of several experiments with water or hydrogen chloride–promoted aluminum chloride, with and without aluminum, magnesium, or sodium, are summarized in Table I and Figures 1 and 2. All reactions were run at 95–100° C. and at atmospheric pressure with a mole ratio of heptane/aluminum chloride of 5 and a reaction time of 4 hours, unless otherwise indicated. The amount of metal present was 50% with respect to the weight of aluminum chloride.

The products from these experiments were placed in four groups: isobutane, light paraffins (C_5–C_7), heavy paraffins (C_8 and higher), and the unsaturated oil obtained by hydrolysis of the catalyst complex. In Table I the percentage yields of these products are calculated, on the basis both of heptane taken and of total products. From these data the relative yields of isobutane, oil, and light paraffins are shown by means of the ratios: isobutane/oil and isobutane/light paraffins. The conversions and relative yields are given in Figures 1 and 2 by blocks whose heights are proportional to per cent conversion, top widths to isobutane/oil ratio, and bottom widths to isobutane/light paraffin ratio.

ALUMINUM CHLORIDE ACTIVITY

Experiment 1 was a blank to determine the activity of aluminum chloride without the addition of water or hydrogen chloride. Since the same catalyst was used throughout and since relatively large amounts of promoters were to be added, the fact that the aluminum chloride was not absolutely pure and therefore inactive was considered unimportant. The low ratio of isobutane/light paraffins shows that the extent of cracking-isomerization (or "destructive isomerization") to form isobutane is somewhat less than the isomerization reaction, the latter term being used broadly to cover the formation of light paraffins. In experiment 9 the same catalyst was modified by the addition of metallic aluminum. It was surprising to learn that there was no great change in the conversion and in the over-all distribution of products. The greatest effect was the diminished oil yield which thereby increased the isobutane/oil ratio (Figure 1).

In experiments 10 and 11 the catalyst was moderately promoted by the addition of 1.5% water. In the absence of aluminum this brought the conversion to 53.5% and increased both the isobutane/light paraffin ratio and the isobutane/oil ratio; that is, the over-all reaction was increased, especially cracking-isomerization to form isobutane, but the isomerization to light paraffins was decreased. The addition of aluminum to this promoted catalyst in experiment 11 had a marked effect: conversion was decreased, the formation of both isobutane and oil was decreased, with the reduction in oil yield being slightly greater, and the yield of light paraffins was greatly increased (Figure 1). Comparison of experiments 1 and 9 with 10 and 11 indicates that aluminum exerts a much greater influence on a promoted reaction, such as 10, where the cracking-isomerization reaction is relatively more important than the isomerization to light paraffins. The smaller yield of oil in 11 probably permits the catalyst lower layer to retain greater catalytic activity than that from the other experiments. In view of this, the high yield of light paraffins, and the very substantial yield of isobutane, experiment 11 is probably the most efficient of this group of four experiments.

Table I. Summary of Heptane–Metal–Aluminum Chloride Experiments

Experiment No.	1		9		10		11		17		26		24	
Added to $AlCl_3$, %[a]	0		50 Al		1.5 H_2O		1.5 H_2O 50 Al		7.5 H_2O		7.5 H_2O 50 Al		7.5 H_2O 50 Mg	
Heptane converted, %[b]	31.6		30.5		53.5		38.9		84.7		69.7		54.4	
Products[c], %														
Isobutane	6.7	29.3	8.0	33.1	22.2	48.0	12.0	33.6	55.0	67.8	35.3	54.6	19.1	37.4
Oil	4.3	18.9	3.4	13.9	6.9	14.8	3.6	10.1	17.8	21.9	7.6	11.8	8.0	15.6
Light paraffins	10.2	44.4	11.0	45.4	13.0	27.9	16.2	45.1	6.5	7.9	17.3	26.8	19.5	38.2
Heavy paraffins	1.7	7.3	1.8	7.6	4.3	9.3	4.0	11.2	1.9	2.4	4.4	6.8	4.5	8.9
Loss	8.7	..	6.4	..	7.1	..	3.1	..	3.6	..	5.1	..	3.3	..
Isobutane/oil	1.6		2.4		3.2		3.3		3.1		4.6		2.4	
Isobutane/light paraffins	0.7		0.7		1.7		0.7		8.5		2.0		1.0	

Experiment No.	25		23(a)[d]		27[d]		28[d]	
Added to $AlCl_3$, %[a]	7.5 H_2O 50 Na		33.0 HCl		42 HCl 50 Al		18 g. HCl[e] 7 g. Al	
Heptane converted, %[b]	44.5		98.0		62.8		41.3	
Products[c], %								
Isobutane	18.8	45.1	71.0	73.1	32.0	53.5	14.7	39.4
Oil	7.2	17.2	22.3	23.0	8.6	14.4	3.4	9.2
Light paraffins	12.4	29.7	3.6	3.7	15.5	26.0	15.0	40.1
Heavy paraffins	3.4	8.0	0.2	0.2	3.7	6.1	4.2	11.3
Loss	2.7	..	0.9	..	3.1	..	4.0	..
Isobutane/oil	2.6		3.2		3.7		4.3	
Isobutane/light paraffins	1.5		19.7		2.1		1.0	

[a] Per cent with respect to $AlCl_3$ taken.

[b] Heptane converted equals (heptane taken minus heptane recovered) divided by heptane taken.

[c] The left-hand column for each experiment gives percentage yield based on heptane taken. The right-hand column gives percentage yield based on total weight of product. The total weight of products equals the weight of heptane consumed, exclusive of loss. This is equivalent to prorating the material loss over the products in proportion to the amounts in which they formed.

[d] Reaction time for expt. 23(a), 7.5 hours; for 27, 8 hours; for 28, 9 hours.

[e] No $AlCl_3$ was used here other than that formed from Al + HCl. If all of the metal reacted, 33.3 grams of aluminum chloride (the same quantity used in the other experiments) would be formed.

Previous work showed that the maximum conversion to isobutane by a water-promoted reaction in which the mole ratio of heptane/aluminum chloride was 5 was obtained by the addition of 7.5% water, as in experiment 17 (*6*). The high ratio of isobutane/light paraffins indicates that cracking-isomerization is the dominant reaction. The effect of added aluminum metal under these conditions is noted in experiment 26. Again, there is a diminution in total conversion, and both isobutane and oil yields are reduced, the effect on oil yield being greater; but most noteworthy is the large increase in light paraffin formation (Figure 1).

EFFECT OF ADDED METALS

Experiments 23(a) and 27 were run to determine the effect of added aluminum on a heptane–aluminum chloride reaction promoted with hydrogen chloride. The almost complete conversion of heptane obtained in 23(a) compared to the 85% conversion in water-promoted experiment 17 is undoubtedly due to destruction of part of the catalyst through hydrolysis in 17, and possibly to the formation of additional catalyst in 26 from the aluminum plus hydrogen chloride reaction. Other than the difference in conversion, water and hydrogen chloride appear to promote essentially the same reactions (*6*). The effect of added aluminum was typical. Despite approximately one third reduction in conversion, there was a great increase in light paraffin formation and the usual decrease in both isobutane and oil yields (Figure 1). Experiments 26 and 27 gave about the same result, but the latter is probably more economical since no aluminum chloride was lost by hydrolysis.

The results of experiment 28, in which all of the aluminum chloride was generated in situ from aluminum metal and hydrogen chloride, indicate, as might be anticipated, that the catalyst was a hydrogen chloride-promoted, aluminum–aluminum chloride type, rather than hydrogen chloride-promoted aluminum chloride. Formation of aluminum chloride under these conditions was slow, no isobutane being collected until 2-hour reaction time had elapsed, and even in 9 hours the conversion was only 41%. The amount and distribution of products are somewhat the same as in experiment 11, where both water and aluminum were added. The high isobutane/oil ratio of 4.3 and low isobutane/light paraffin ratio of 1.0 observed in 28 are typical of the aluminum-modified experiments.

Experiments 24 and 25 employed magnesium and sodium metals, instead of aluminum, in a water-promoted reaction similar to 17 (Figure 2). All three metals effected a decrease in conversion, the order of activity in this respect being Na > Mg > Al. The fact that this is the decreasing order of activity as metals is probably significant, although a generalization based on only three metals may not be justified. The isobutane/light paraffin ratio was greatly decreased by all the metals; magnesium exerted the greatest effect, sodium next, and aluminum least. The outstanding difference between the three metals was in their effect on the isobutane/oil ratio. Both sodium and magnesium decreased this ratio because of a greater reduction in isobutane yield relative to oil, but aluminum increased this ratio by about 50% because of its ability to retard oil formation to a greater extent than isobutane formation. This property of aluminum makes it the best of the three metals for the purpose of moderating and controlling these promoted heptane–aluminum chloride reactions, because decreased oil formation should prolong the life of the catalyst.

All of the metals become more or less coated with chlorides and catalyst complex during the reaction and probably lose some activity. In the case of aluminum and magnesium the amount of metal consumed was found to be very small, since 95% of the metal taken in experiments 24 and 26 was recovered This shows that the amount of additional catalyst formed from aluminum in experiment 26 was small. When the sodium was removed from the catalyst complex of 25, it had the dark blue color characteristic of the sodium–sodium halide mixture from a Wurtz-Fittig reaction.

The important effects of aluminum on the promoted heptane–aluminum chloride reaction which is carried out under conditions leading to substantial yields of isobutane may be summarized as follows: (1) The amount of heptane converted is decreased by as much as 30% [23(a) and 27], an indication that the over-all activity of the aluminum chloride catalyst has been reduced; (2) both the formation of isobutane and the highly unsaturated oil associated with the catalyst are retarded, but the effect is somewhat greater on the oil; (3) the formation of light paraffins (C_5–C_7) is favored (effects 2 and 3 show that aluminum has moderated the severity of the cracking reactions and enhanced the isomerization reaction); (4) by decreased oil formation the efficiency of the aluminum chloride for converting additional heptane is presumably increased.

These properties of aluminum lend considerable flexibility to this process in terms of light paraffin and isobutane production. If the demand for isobutane were great, no aluminum should be used and the vigorous cracking conditions of experiments 17 and 23(a) would be employed. If light paraffins were needed as well as isobutane, aluminum should be present as in 11 or 17 (water-promoted) or in 27 (hydrogen chloride-promoted). By a proper choice of conditions, an isobutane/light paraffin ratio anywhere in the range noted here (0.7 to 19.7) could be obtained. The conditions selected should employ aluminum, if at all possible, because of its ability to retard the formation of oil. For example, both experiments 10 and 26 give isobutane/light paraffin ratios of about 2, but 26 is preferable because its conversion and isobutane yield are greater, its light paraffin yield is almost as great, but the formation of oil and subsequent inactivation of the catalyst are less.

MECHANISM OF REACTION

The mechanism of the reactions by which *n*-heptane is converted to isobutane is not well understood (*3*), and therefore the mechanism of the action of a metal cannot be thoroughly explained. However, the hydrogen formed by combination of the metal and hydrogen chloride has frequently been mentioned as a key factor in aluminum-aluminum chloride reactions. This hydrogen may reduce olefinic products or olefinic or free-radical intermediate products. Such reactions would favor the formation of saturated products at the expense of the highly unsaturated ones which combine with the aluminum chloride. This hypothesis suggests that the addition of hydrogen during the course of the reaction should alter the product distribution. Although the experimental evidence is not complete, it now appears that hydrogen added at atmospheric pressure to a water-promoted reaction similar to 17 has little or no effect (*6*). Further discussion of this aspect of the reaction will be made in a later paper.

Another result of the interaction of metal and hydrogen chloride may be to reduce the catalyst activity by shifting the equilibrium, $AlCl_3 + HCl \rightleftharpoons HAlCl_4$, in the direction of the reactants and thus decreasing the concentration of what is often considered to be the real catalyst, $HAlCl_4$.

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Dehydroisomerization of *n*-Butane

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ISOBUTYLENE is in considerable demand for the production of hydrocodimer and alkylate as well as for the production of synthetic elastomers. It may be produced from *n*-butane by two paths: (*a*) isomerization of *n*-butane to isobutane, followed by dehydrogenation of the latter; or (*b*) dehydrogenation of *n*-butane with subsequent isomerization of the olefin. Since the steps of the second method have been shown (*2, 4*) to proceed in the presence of solid catalysts of the oxide type at temperature ranges which overlap, the present work was undertaken to determine whether the conversion of *n*-butane into isobutylene might be carried out as a one-stage process (*1*).

Two catalyst systems were investigated. In the first, equal volumes of granular olefin-isomerization catalyst, $20SiO_2:1Al_2O_3:0.1ThO_2$ (*5*), and granular dehydrogenation catalyst, 10% Cr_2O_3 on Al_2O_3 (*3, 4*), were mixed. In the second, the two catalysts were ground together in approximately the same proportions, and the powdered mixture was then formed into pellets. The first catalyst system (which will be called a "mixed catalyst") was investigated at various space velocities at temperatures of 500° to 600° C. The second (which will be called a "composited catalyst") was tested only at 500° and 550°, over a range of space velocities.

EXPERIMENTAL PROCEDURE

CATALYSTS. A chromia-alumina dehydrogenation catalyst was prepared by mixing 90 grams of 6-10 mesh activated alumina particles with 50 grams of a 20% solution of chromium trioxide in water at 20° C. After the chromium trioxide solution was absorbed by the alumina, the material was dried first at 100° and then at 200° to 230° C.

A catalyst having the approximate molecular composition of $20SiO_2:1Al_2O_3:0.1ThO_2$ was prepared by suspending a highly purified, substantially alkali-free silica gel in a solution of aluminum and thorium salts, and precipitating aluminum and thorium hydroxides in the presence of the silica gel by the addition of ammonia. The resulting mixture was filtered to remove the aqueous solution, washed with distilled water, and filtered to

The conversion of *n*-butane into a mixture of *n*-butylenes and isobutylene has been carried out at atmospheric pressure with a catalyst comprising a dehydrogenating component (chromia-alumina) and an olefin-isomerizing component (silica-alumina-thoria). A catalyst bed composed of a mixture of granules of the two components was much more effective than a bed of granules made of the mixed powders. Under the most favorable conditions (525–575° C., gaseous hourly space velocities of 500–1200), butylene yields of 25–30% were obtained with a dehydrogenating efficiency of approximately 85%. About one fourth of the yields of butylene was isobutylene.

separate the precipitated material as a filter cake. The filter cake was dried at about 150° C. The dried material was formed into 6–10 mesh particles by pressing, crushing, and screening, and finally was calcined at 500° C. for 2 hours.

A composite catalyst was prepared by grinding together two parts by weight of the chromia-alumina dehydrogenation catalyst and one part by weight of the silica-alumina-thoria olefin-isomerizing catalyst. The mixed powder was then pressed hydraulically to form a compact cake which was broken into pieces of 6–10 mesh particle size.

Procedure. *n*-Butane (Phillips Petroleum Company) was measured by a wet test meter, dried by calcium chloride, and then passed through a Pyrex or quartz tube containing the dehydrogenation and isomerization catalysts heated to the desired temperature by an aluminum bronze block furnace. The treated gases were collected and analyzed by low-temperature fractional distillation and absorption methods.

Results. Conditions employed and results obtained are set forth in Tables I and II, and the several variables studied with the mixed catalyst are correlated with the results in Figures 1 and 2. The curves of Figure 2 are derived from those of Figure 1. Although in some cases the activity comparisons were made with catalysts which had different past histories (that is, different times of use and different numbers of regeneration), experience with catalysts of this nature indicates that the catalysts were in substantially the same state of activity.

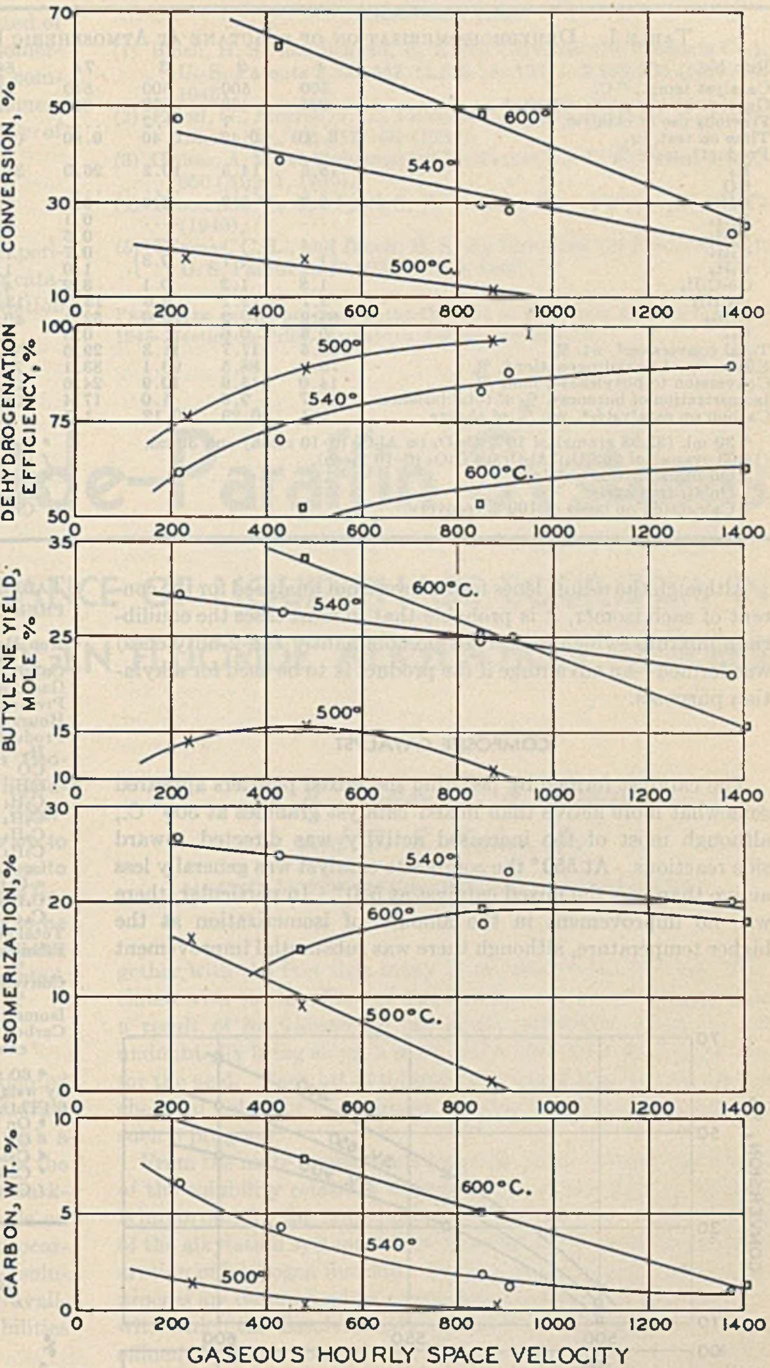


Figure 1. Effect of Space Velocity and Temperature on Results with Mixed Catalyst

MIXED CATALYST

At 500° C. the conversion was small and the dehydrogenation efficiency was high; at 600° the conversion was 45 to 65% per pass and the efficiency of dehydrogenation became low. The conversion is the percentage of *n*-butane decomposed, and the dehydrogenation efficiency (expressed as per cent) is 100 times the ratio of the total amount of butylenes formed to the total amount of *n*-butane decomposed. The optimum results appeared to be those obtained in the temperature range 525° to 575° C. at gaseous hourly space velocities of 500 to about 1200. As Figure 2 indicates, at about 565° C. the same degree of isomerization of *n*-butylenes to isobutylene was obtained over a wide range of space velocities. This result points to a balance in the rates of the isobutylene-making and the isobutylene-consuming reactions at this temperature.

Experiments 4 and 5 (Table I) show the effect on catalyst activity of the deposition of carbonaceous matter on the catalyst. Experiment 4 was conducted in the presence of a freshly reactivated catalyst, and experiment 5 in the presence of a catalyst which had been used for 3 hours at the same conditions of operation as for the freshly reactivated catalyst. With continued use the catalyst activity dropped considerably, but the side reactions declined more rapidly than the desired reactions. The efficiency therefore increased and the rate of formation of catalyst deposit declined considerably, while the rate of dehydrogenation decreased relatively slightly and that of isomerization decreased an intermediate amount.

Table I. Dehydroisomerization of n-Butane at Atmospheric Pressure in the Presence of Mixed Catalyst[a]

Run No.	1	2	3	7[f]	6[g]	8	9	4[h]	5	10[i]	11	12
Catalyst temp., ° C.	500	500	500	540	540	539	541	541	546	600	601	601
Gaseous hourly space velocity[b]	238	479	878	850	428	910	1375	215	215	478	853	1405
Previous use of catalyst, run No.	....	1	1, 2	....	....	6	6, 8	....	4	....	10	10, 11
Time on test, hr.	0.50	0.40	0.40	0.60	0.50	0.40	0.25	0.75	3.6	0.60	0.30	0.35
Product[c], mole %												
H_2	18.5	14.5	10.2	26.0	33.9	23.1	20.4	39.2	23.2	39.1	30.2	16.4
CO	....	....	....	....	0.5	....	....	0.7	0.1	0.4	0.2	0.2
CH_4	0.7	0.7	0.2	0.2	2.3	1.2	0.9	3.8	2.3	7.5	7.4	4.4
C_2H_4	....	....	....	0.1	0.2	....	0.3	0.2	0.3	1.3	2.0	2.0
C_2H_6	....	....	....	0.5	1.4	0.4		2.3	1.4	6.3	5.7	2.6
C_3H_6	1.8	0.7	0.3	0.7	1.3	....	1.0	1.7	....	3.9	3.9	2.8
C_3H_8				1.0	1.5	1.1		2.1	1.1	2.5	1.4	1.0
iso-C_4H_8	1.8	1.2	0.1	3.2	4.5	4.4	3.3	4.7	3.2	2.7	3.0	2.2
n-C_4H_8	9.7	12.1	9.6	15.2	13.6	14.7	13.4	13.0	14.3	15.5	12.8	10.1
C_4H_{10}	66.9	70.2	79.6	52.6	40.2	54.8	60.7	31.3	54.1	20.1	32.8	58.2
C_{5+}	0.6	0.6	....	0.5	0.6	0.3	.....	0.9	....	0.7	0.6	.....
Total conversion[d], wt. %	18.5	17.7	11.3	29.6	39.2	28.5	23.5	47.8	28.4	63.5	47.9	25.3
Efficiency of dehydrogenation[d], %	75.8	88.5	96.1	83.1	70.0	87.5	89.5	61.6	81.8	52.2	52.6	62.5
Conversion to butylenes[d], mole %	14.0	15.6	10.9	24.6	27.4	24.9	21.0	29.4	23.2	33.1	25.2	15.8
Isomerization of butenes[d], % of total butenes	15.7	9.0	1.0	17.4	24.8	23.0	19.8	26.6	18.3	14.8	19.0	17.9
Carbon on catalyst[d,e], wt. % of charge	1.4	0.29	0.12	1.7	4.2	1.1	0.89	6.5	1.8	7.8	5.0	1.2

[a] 30 ml. (33.98 grams) of 10% Cr_2O_3 on Al_2O_3 (6–10 mesh) and 30 ml. (14.03 grams) of $20SiO_2:1Al_2O_3:0.1ThO_2$ (6–10 mesh).

[b] On basis of total catalyst.

[c] On air-free basis.

[d] Calculated on basis of 100% recovery.

[e] Calculated from carbon-hydrogen balance.

[f] Fresh catalyst.

[g] Conducted with catalyst reactivated in air at 480–550° C.

[h] Conducted with catalyst reactivated in air at 480–540° C.

[i] Conducted with catalyst reactivated in dry air at 480–540° C.

Although the n-butylenes formed were not analyzed for the content of each isomer, it is probable that in most cases the equilibrium mixture (which comprises predominantly the 2-butylenes) was formed—an advantage if the product is to be used for alkylation purposes.

COMPOSITE CATALYST

The catalyst formed by pelleting the mixed powders appeared somewhat more active than mixed catalyst granules at 500° C., although most of the increased activity was directed toward side reactions. At 550° the composite catalyst was generally less active than was the mixed catalyst at 540°. In particular, there was no improvement in the amount of isomerization at the higher temperature, although there was substantial improvement

Table II. Dehydroisomerization of n-Butane at Atmospheric Pressure in the Presence of Composited Catalyst[a]

Run No.	13[f]	14	15	16[f]	17	18
Catalyst temp., ° C.	500	500	500	550	550	550
Gaseous hourly space velocity[b]	237	500	860	212	415	808
Previous use of catalyst, run No.	..	13	13, 14	..	16	16, 17
Hours on test	0.40	0.20	0.13	0.30	0.17	0.12
Product[c], mole %						
H_2	22.0	20.4	13.5	34.8	23.9	14.6
CO	0.3	0.3	0.1	0.4	0.2	0.2
CH_4	2.4	1.8	0.6	5.8	3.6	2.0
C_2H_4	..	0.3	...	0.4	0.5	0.8
C_2H_6	..	0.9	...	2.7	2.7	1.5
C_3H_6	0.4	1.6	Trace	1.6	1.2	0.7
C_3H_8	1.6	5.2	Trace	1.7	0.8	1.3
iso-C_4H_8	1.8	1.5	1.2	1.5	1.2	0.5
n-C_4H_8	10.7	10.7	11.7	16.1	14.8	12.4
C_4H_{10}	59.8	57.3	72.9	34.9	50.8	65.3
C_{6+}	1.0	..	...	..	0.3	0.5
Total conversion[d], wt. %	23.2	26.2	15.4	44.0	30.8	21.0
Efficiency of dehydrogenation[d], %	69.2	60.0	97.5	64.1	71.0	74.6
Conversion into butylenes[d], mole %	16.1	15.7	15.0	28.2	21.8	15.6
Isomerization of butenes[d], %	14.4	12.3	9.3	8.5	7.5	3.9
Carbon on catalyst[d,e], wt. % of charge	2.3	2.1	0.17	5.7	2.4	0.60

[a] 60 ml. (50 grams) of 6–10 mesh catalyst formed by compositing 2 parts by weight of 10% Cr_2O_3 on Al_2O_3 with 1 part by weight of $20SiO_2:1Al_2O_3:0.1ThO_2$.

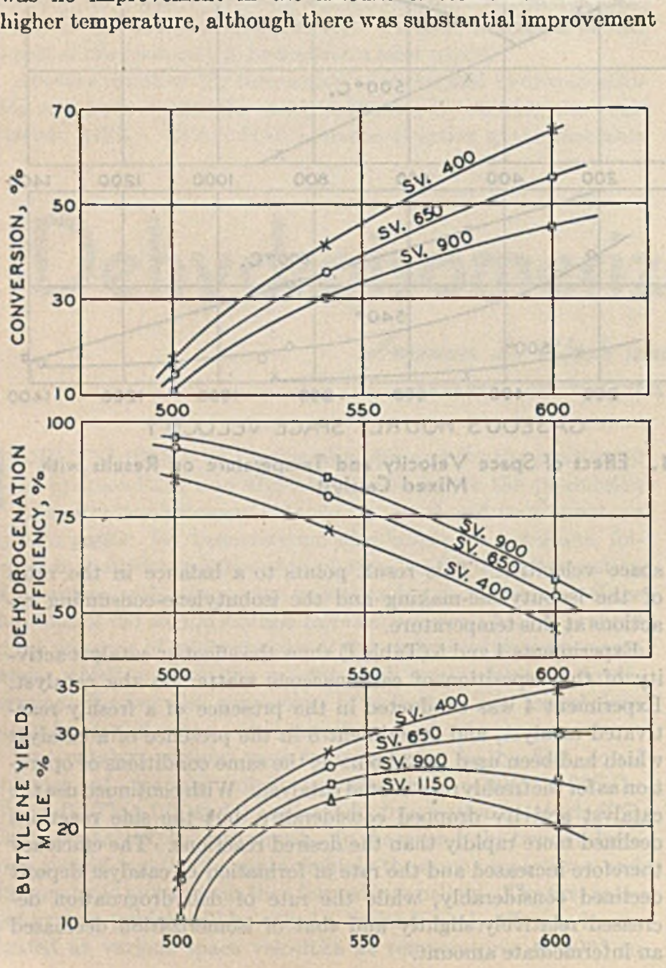
[b] On basis of total catalyst.

[c] On air-free basis.

[d] Calculated on basis of 100% recovery.

[e] Calculated from carbon-hydrogen balance.

[f] Conducted in presence of catalyst after reactivation in air at 480–550° C.



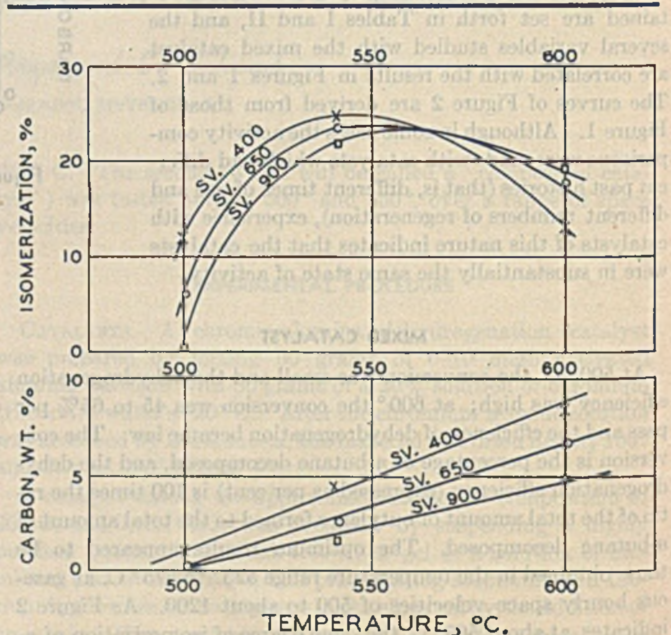


Figure 2 (Left and Above). Curves Derived from Figure 1

with the mixed-bed catalyst. The mixed bed, which consisted of a mixture of the separate granules of dehydrogenation and isomerization catalyst, was definitely superior to the one made of composited granules, probably because in the latter case the isomerizing component was inactivated by too great an intimacy of contact with the dehydrogenating component.

ACKNOWLEDGMENT

The authors are indebted to J. D. Danforth for the experiments carried out in the presence of the composite granular catalyst made from the powdered mixture of the dehydrogenation and isomerization catalysts.

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Hydrogen Fluoride–Paraffin Systems

• SIGNIFICANCE OF LIQUID-PHASE EQUILIBRIA IN THE HYDROGEN FLUORIDE ALKYLATION PROCESS

Mutual solubilities of low-molecular-weight hydrocarbons (isobutane, *n*-butane, propane) and of hydrogen fluoride in two liquid-phase systems, with and without water and alkylate, were determined for the range 0–50° C., with alkylate concentrations up to 30 weight % in the hydrocarbon phase, and water contents up to about 10 weight % in the acid phase. Anomalous solubilities of isobutane in the presence of alkylate and water are considered to be related to the greater alkylating activities of isoparaffins. Tentative correlations of the data with analyses of plant streams are presented.

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UNDER the stimulus of wartime demands for unprecedented volumes of aviation grade gasoline, the hydrogen fluoride alkylation process was developed in this country with a speed and efficiency which mark it as a major achievement of the petroleum industry (*1*). The development is even more remarkable in view of the limited information which was available on the physical properties of hydrogen fluoride–paraffin hydrocarbon systems. Aside from the work of Simons (*2*) on the solubility of gaseous hydrogen fluoride in *n*-octane, no data were available which could be used as a basis for approximating solubilities in HF–paraffin systems.

At the time of our entry into the war the process had been under consideration for some time by several independent industrial organizations and was being actively developed. However, the sudden expansion of activity in the field had the result, not uncommon during World War II, that much laboratory data was sought in pilot plants and much of the actual development work had to be done in full-scale commercial plants. With the emphasis upon accomplishment rather than upon the "why" of alkylation reactions, it is understandable that little has been published of the fundamental data relating to physical equilibria in the hydrogen fluoride reactor systems.

In this laboratory some effort was directed toward establishing liquid-liquid solubility relations both for the purpose of expediting process operation and control and in the hope that some additional clues could be obtained concerning the chemical behavior of hydrogen fluoride, particularly as regards its activity in catalyzing alkylation reactions.

An excess of productive capacity for anhydrous hydrogen fluoride in the postwar era appears likely. Such a circumstance, together with the fact that many of the misgivings formerly associated with the handling of this substance are now dissipated as a result of its widespread use in the petroleum industry, will undoubtedly bring about a more active search for additional uses for the acid. Each bit of information concerning the physical or chemical behavior of hydrogen fluoride is of potential value in such a program.

From the more immediately practical point of view, knowledge of the solubility relations in hydrogen fluoride–paraffin systems is important for the proper design and operation of those portions of the alkylation systems whose function is the recovery and separation of hydrogen fluoride. For example, the economics of the process are determined to a considerable extent by the efficiency with which the dissolved hydrogen fluoride is recovered from the effluent hydrocarbon streams. Despite the rather small solubility of hydrogen fluoride in these streams, the value of this dissolved acid may amount to a large fraction of the value of the alkylate produced.

In the hydrogen-fluoride-catalyzed alkylation of olefins with isobutane, the olefin is consumed rapidly and completely. Thus, the emulsion leaving the alkylator consists largely of hydrogen fluoride and saturated hydrocarbons. The acid contains small quantities of dissolved water and may have traces of sulfur dioxide, sulfuric acid, fluosilicic acid, and iron, the impurities normally encountered in commercial anhydrous hydrogen fluoride. In addition, the acid phase may contain variable quantities of high-molecular-weight polymeric substances, the amounts depending upon reactor temperature and other factors. The fact that these "polymers" are encountered largely in the acid phase suggests that they exist in solution as highly hydrofluorinated olefinic bodies. However, the "polymers" are actually isolated as dark colored, viscous hydrocarbon residues containing little or no fluorine in the still bottoms from the recovery of hydrogen fluoride by distillation. The molecular weight of the "polymer" is variable; indeed, appreciable quantities of a light oil distillate boiling just above the gasoline range can be recovered from the acid.

Of the lighter hydrocarbons present in the reactor emulsion, only the C_4 paraffins appear in the acid phase in appreciable quantities. Propane is usually not present in important amounts in the butane-butene fraction (B-B) fed to the reactor. Debutanized alkylate, of which as much as 99+% may boil in the aviation gasoline range, dissolves in the acid phase to a very small extent. Small amounts of alkyl fluorides—e.g., *sec*-butyl fluoride—are also formed and appear largely in the hydrocarbon phase.

The present solubility data refer to systems considerably less complicated than those encountered in plant practice, but tentative correlations with pilot plant analyses are presented. The experimental method used in this work is described in some detail in the hope that it will be of value to others contemplating investigations with similar systems.

MATERIALS AND APPARATUS

Anhydrous hydrogen fluoride was obtained from the Harshaw Chemical Company and contained, according to their analysis, less than 0.5% of total impurities (SO_2, H_2SO_4, H_2SiF_6, H_2O, Fe, and nonvolatiles). The acid was transferred to the equilibrium apparatus by distillation from the stock cylinder.

Isobutane containing less than 0.5% impurities, largely *n*-butane, was obtained from the Phillips Petroleum Company and was used without further purification. The *n*-butane was a product of Magnolia Petroleum Company. Low temperature fractionation analysis showed it to have the following composition: *n*-butane, 99.1%; isobutane, trace; and isopentane and higher, 0.9%. This material was used without further purification.

The alkylate was a deisobutanized product of the reaction of isobutane with butenes and was obtained from Magnolia's HF-alkylation pilot plant. The samples used were of nearly constant composition, as indicated by the following approximate ranges, in weight per cent: isobutane, absent or trace; *n*-butane, 3–5; pentanes, 2–3; hexanes, 2–3; heptanes and higher (largely octanes), 88–92. In one sample 3.1 weight % of isobutane was found, necessitating a correction in calculating the composition of the charge to the equilibrium apparatus.

The propane, with a specified purity of 99.94%, was also obtained from Phillips Petroleum Company.

The standard potassium hydroxide solutions were prepared from analytical-grade KOH and were standardized periodically against reagent-grade potassium acid phthalate. The stock solutions were protected from carbon dioxide absorption by soda-lime tubes, and the solutions were drawn off through siphons.

The liquid-phase equilibrium apparatus is shown in Figure 1. It was designed and constructed to allow equilibrium to be attained with two liquid phases at temperatures above their boiling points and, consequently, at superatmospheric pressures, and to allow sampling of each phase at the equilibrium temperature and pressure. Therefore, it was essentially a closed system in which pressure and temperature could be maintained the same throughout; the possibility was thus eliminated of obtaining a nonrepresentative sample as a result of fractional distillation during sampling. It was constructed of steel throughout, with the exception of the sample bombs and the connecting lines and fittings which were of copper. The special valves (*C* and *D*) were welded directly to the main cylinder, which had a volume of 900 cc. The sample bombs for the hydrocarbon phase and for the hydrogen fluoride phase had volumes of approximately 30 and 6 cc., respectively. During solubility experiments, the apparatus was immersed in a water or ethylene glycol–water bath thermostatically controlled within ±0.025° C. Adequate agitation was effected by mechanically rotating the immersed unit end over end.

The sampling bombs were made from 3-inch lengths of copper tubing with Hoke $^1/_8$-inch brass needle valves soldered on each end. The standard pipe threads on these valves were sawed off and replaced with $^1/_8$-inch inner brass flare fittings, silver-soldered in place. The valve handles were removed, and a hole was drilled through each valve stem to permit insertion of a steel pin which served as a valve key. A special clamp (Figure 2) for holding these sample bombs in place while withdrawing the contents for analysis was found necessary to avoid the erratic changes in the tare weight of the bombs which result when metal fittings are employed. Gaskets made of Saran tubing were found to be very satisfactory for use with this clamp.

The diagram of the apparatus used for titrimetric analysis of acid in samples of the hydrocarbon phase (Figure 2) is self-explanatory. Dissolved light hydrocarbons in the hydrogen fluoride phase were determined in the apparatus illustrated in Figure 3. It consisted essentially of two gas absorption pipets, a gas buret, and the necessary leveling bulbs.

CHARGING THE EQUILIBRIUM APPARATUS

The apparatus (Figure 1) was first washed with acetone and dried with a stream of dry nitrogen. The main cylinder was evacuated, flushed with the appropriate light hydrocarbon (propane, isobutane, or *n*-butane), and again evacuated. The whole apparatus was then weighed and allowed to cool slightly in a dry-ice box. When it had become sufficiently cold to allow rapid condensation

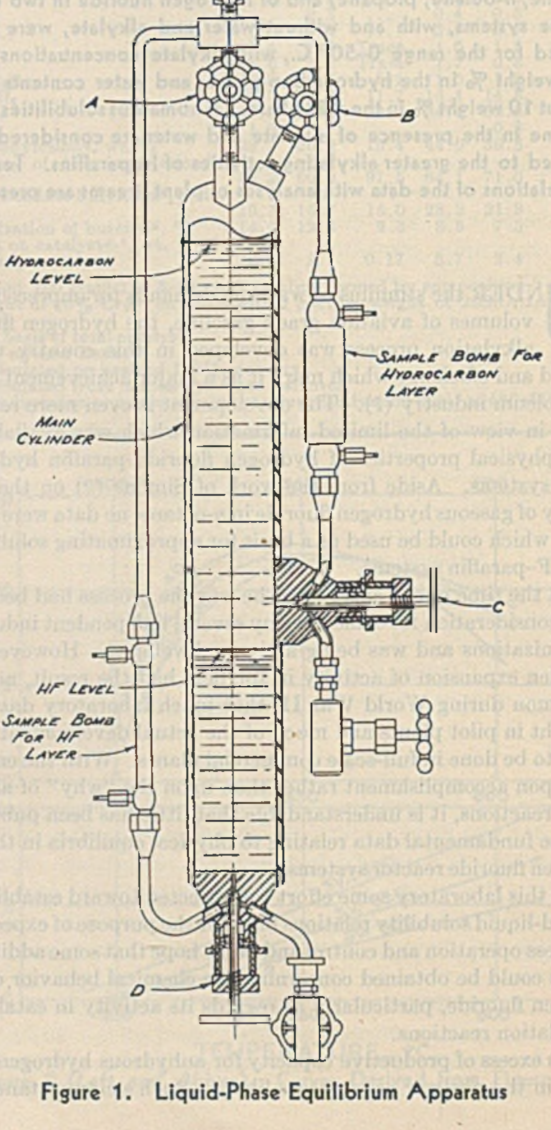


Figure 1. Liquid-Phase Equilibrium Apparatus

of hydrogen fluoride (after about 15 minutes), it was removed and valve *B* was connected to the source of the acid by a short copper tube and appropriate brass fittings. The fitting closest to valve *B* was made up loosely, and the copper tube flushed with a small amount of hydrogen fluoride to remove air from the line. This valve was then opened, and about 140 grams of hydrogen fluoride entered the apparatus. This amount was sufficient to fill the apparatus to a level just below valve *C*. Valve *B* was then closed, and the apparatus disconnected from the hydrogen fluoride source and weighed. If more than 140 grams of the liquid had been added, the apparatus was warmed to room temperature and inverted, and some liquid allowed to escape through *B*. If too little had entered, more was added by the procedure just described. The apparatus was again cooled in the dry-ice box, and sufficient hydrocarbon (usually about 300 grams) added to bring the liquid level to within about 2 inches of the top of the main cylinder. The weight of hydrocarbon added was adjusted in the same manner as the weight of hydrogen fluoride. In this case, however, excess hydrocarbon was allowed to escape as vapor through *B* while the apparatus was in an upright position.

A somewhat different procedure was employed when the hydrocarbon phase was a mixture of alkylate and either iso- or *n*-butane. In such cases the apparatus was first charged with hydrogen fluoride as described previously, and the desired amount of alkylate weighed in from a glass bulb of known volume as follows: After the apparatus was cooled, the tube at one end of the calibrated bulb was connected to valve *B* which was then opened. First, the lower stopcock on the bulb was opened and then the upper stopcock. As soon as the liquid in the bulb had passed the lower stopcock, this stopcock was closed, and *B* was closed. The butane was added last from a calibrated steel buret equipped with a sight glass.

Charging with Aqueous HF of Known Composition. The water was first weighed in a small glass bulb having stopcocks at either end. The bulb was then connected at *B* (Figure 1) by a short piece of heavy rubber tubing. Valve *B* was opened and then the lower stopcock on the bulb, causing the water to flow into the previously evacuated apparatus. After several minutes *B* and the stopcock were closed, in that order. The emptied bulb was reweighed, and the amount of water added was obtained by difference. The apparatus, containing the water, was then chilled in a dry-ice box for about 20 minutes, in preparation for charging with hydrogen fluoride.

A small steel bomb of about 130-cc. capacity measured the hydrogen fluoride added. The bomb was fitted with a $^{1}/_{8}$-brass Hoke needle valve at one end and was connected to a small steel expansion chamber by a second $^{1}/_{8}$-needle valve at the other end. The standard pipe thread on the first valve was replaced by a male brass pressure fitting.

The hydrogen fluoride bomb was evacuated, and both valves were then closed. After chilling in contact with dry ice for 20 minutes, the bomb was connected to the hydrogen fluoride source and the connecting line was flushed with a small amount of hydrogen fluoride. The entry valve was opened and, when the bomb had filled, was closed again. The second needle valve was then opened to the expansion chamber. After warming up, the bomb was weighed. The bomb was next connected to the chilled equilibrium apparatus and was allowed to drain for 20–30 minutes with continued dry-ice cooling of the latter. The bomb was then removed and reweighed to obtain by difference the amount of hydrogen fluoride added.

Butane was added to the apparatus as previously outlined.

Charging Alkylate plus Iso- or *n*-Butane. The alkylate was weighed in a glass bulb having stopcocks at either end. A steel bomb, with $^{1}/_{8}$-Hoke stainless steel bar-stock needle valves at either end and about 1000-cc. capacity, was pumped down and chilled in the dry-ice box. The bulb containing the alkylate was connected to one end of the steel bomb by a short piece of heavy rubber tubing. The valve on the top of the steel bomb and the lower stopcock on the bulb were opened, and the alkylate was allowed to flow into the steel bomb. The stopcock and valve were then closed, the glass bulb was reweighed, and the weight of alkylate added was obtained by difference.

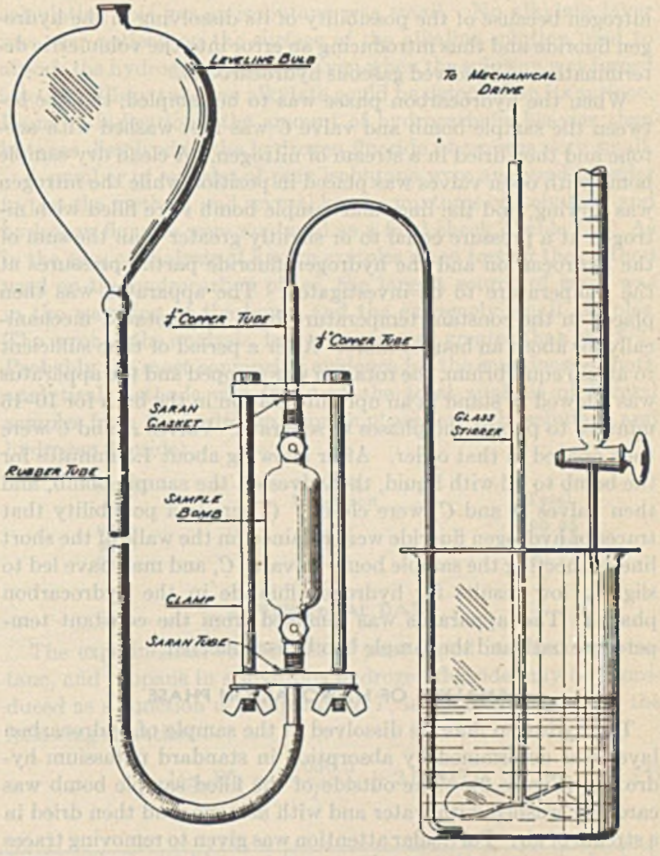


Figure 2. Apparatus for Analysis of Hydrogen Fluoride in Hydrocarbon Phase

About 350 grams of isobutane entered into the steel bomb containing the alkylate. The bomb was then allowed to warm and, after weighing, was connected by a copper tube and flare fittings to valve *B* of the equilibrium apparatus, which had been previously charged with water and hydrogen fluoride and chilled in the dry-ice box. *B* and the lower valve on the steel bomb were opened, and the isobutane-alkylate solution was allowed to enter the equilibrium apparatus. The bomb was reweighed and the amount of alkylate and isobutane determined by difference.

SAMPLING THE TWO LIQUID PHASES

The original plan for sampling the two liquid phases while in equilibrium with the vapor phase at constant temperature and constant pressure involved the first step of flushing the sample lines and sample bomb with vapor from the top of the main cylinder of the equilibrium apparatus. It was soon discovered, however, that appreciable quantities of hydrogen fluoride from the vapor were adsorbed on the walls of the sample bomb; in the case of the hydrocarbon phase this procedure led to high and erratic results for dissolved hydrogen fluoride. When the hydrogen fluoride phase was sampled, the amount of adsorbed hydrogen fluoride was negligible compared to the total hydrogen fluoride present in the sample, and in this case no error was introduced by the use of this procedure.

The alternative procedure adopted in the case of the hydrocarbon phase was to bring the pressure in the sample lines and sample bomb up to the pressure in the main cylinder (Figure 1) by means of nitrogen. The hydrogen fluoride phase, on the other hand, could not be sampled in the presence of nitrogen because of the possibility of its dissolving in the hydrogen fluoride and thus introducing an error into the volumetric determination of dissolved gaseous hydrocarbons.

When the hydrocarbon phase was to be sampled, the line between the sample bomb and valve *C* was first washed with acetone and then dried in a stream of nitrogen. A clean dry sample bomb with open valves was placed in position while the nitrogen was flowing, and the lines and sample bomb were filled with nitrogen at a pressure equal to or slightly greater than the sum of the hydrocarbon and the hydrogen fluoride partial pressures at the temperature to be investigated. The apparatus was then placed in the constant temperature bath and rotated mechanically for about an hour or more. After a period of time sufficient to attain equilibrium, the rotation was stopped and the apparatus was allowed to stand in an upright position in the bath for 10–15 minutes to permit the phases to separate. Valves *A* and *C* were then opened in that order. After allowing about 1.5 minutes for the bomb to fill with liquid, the valves on the sample bomb, and then valves *A* and *C*, were closed. (There is a possibility that traces of hydrogen fluoride were retained on the walls of the short line connecting the sample bomb to valve *C*, and may have led to slightly low results for hydrogen fluoride in the hydrocarbon phase.) The apparatus was removed from the constant temperature bath and the sample bomb disconnected.

ANALYSIS OF HYDROCARBON PHASE

The hydrogen fluoride dissolved in the sample of hydrocarbon layer was determined by absorption in standard potassium hydroxide (Figure 2). The outside of the filled sample bomb was carefully washed with water and with acetone, and then dried in a stream of air. Particular attention was given to removing traces of hydrogen fluoride adhering to the tips of the valves. The bomb was weighed and then placed in the special clamp, which served to make a gastight connection between the top valve and the copper delivery tube which extended below the surface of the dilute aqueous alkaline solution contained in a 1000-ml. beaker coated with paraffin wax. (Approximately 200 cc. of distilled water, a few cubic centimeters of the standard base from the buret, and a few drops of phenolphthalein indicator were added to the beaker before the contents of the sample bomb were admitted.) The mechanically driven stirrer (also coated with paraffin) was started and adjusted to a speed which gave good agitation without splashing. The top valve on the bomb was barely opened to permit slow escape of vapor into the aqueous alkaline solution. As the phenolphthalein color faded, more standard base was added from the buret.

TABLE I. ANALYSIS OF KNOWN SAMPLES OF HYDROGEN FLUORIDE IN ISOBUTANE

Total Wt. of Samples, Grams	Wt. % of HF Present	Wt. % HF Found by Analysis	% Deviation
5.928	0.789	0.783	−0.7
4.898	0.544	0.554	+1.8
4.325	0.635	0.640	−0.7
0.493	0.493	0.502	+1.9

Care was taken never to allow the color to fade completely during this period. After all the gas had escaped from the bomb, the lower valve was opened and water filled the bomb from a leveling bulb attached through rubber tubing to the lower tube on the clamp. After allowing a few minutes after each filling, during which time both valves were closed and opened, the water was displaced into the beaker. This operation was repeated until only a drop or two of base was needed to restore the color of the indicator; about 50 cc. of water were usually required in this step. The bomb was then removed from the clamp, and the bomb, the Saran gasket, and the copper tube were carefully washed with a stream of water directed into the beaker from a wash bottle. The solution in the beaker was titrated to the pink phenolphthalein end point. The bomb was washed with acetone, evacuated, and weighed.

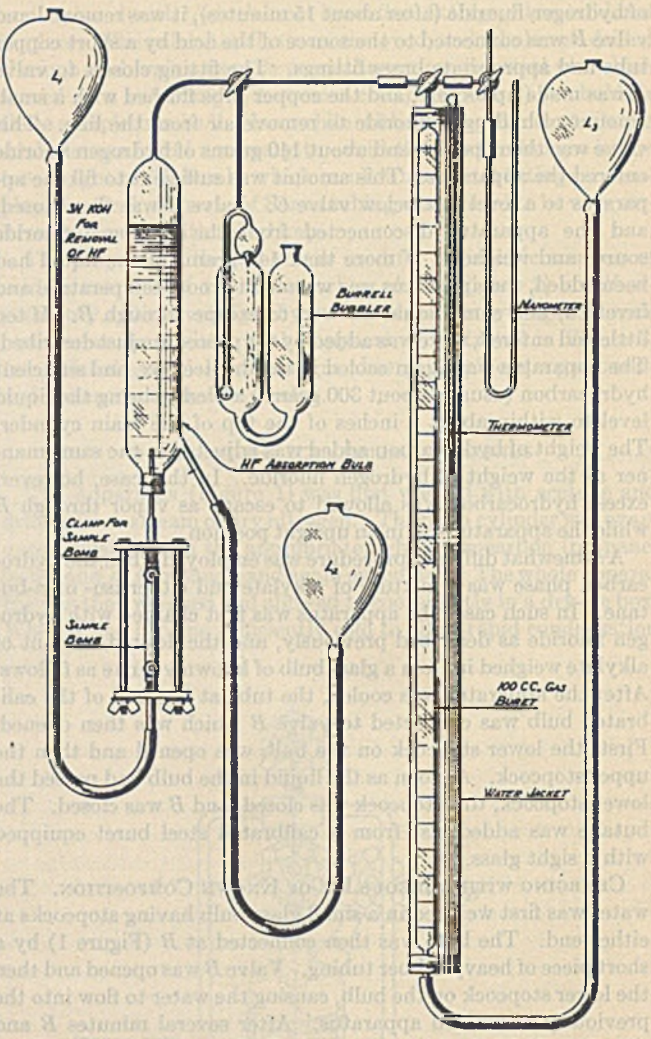


Figure 3. Apparatus for Determination of Light Hydrocarbons in Hydrogen Fluoride Phase

This method was used without modification for all of the hydrocarbon phases studied, and was shown to give reliable results on known mixtures of hydrogen fluoride and isobutane (Table I) in spite of rather large uncertainties in the weights of the known samples. When applied to samples taken from the equilibrium apparatus, only two weights were involved, whereas four weights were required in making up known samples. In the case of mixtures of single hydrocarbons with hydrogen fluoride, the method probably had an accuracy of about ±0.5%—e.g., 1.000 ± 0.005% hydrogen fluoride in hydrocarbon. With increasing complexity of the systems studied, the method gave increasingly poorer results, as shown by the greater scattering of data.

ANALYSIS OF HYDROGEN FLUORIDE PHASE

The hydrogen fluoride phase was analyzed volumetrically for dissolved gaseous hydrocarbons with the apparatus shown in Figure 3. The sample bomb was weighed and then placed in a clamp in the same manner as described for analysis of the hydrocarbon phase. The upper valve on the bomb was barely opened, and the contents allowed to bubble slowly into 3 *N* potassium hydroxide solution (previously saturated with isobutane) contained in the first absorption pipet. Leveling bulb L_2 was held approximately level with the bottom of this pipet, and the insoluble isobutane gas was allowed to collect at the top of the pipet. After cessation of gas flow from the bomb, the lower valve was opened and the bomb was flushed with water from leveling bulb L_1. The bomb valves were then closed, and the isobutane gas was forced into the Burrell bubbler pipet (containing very dilute potassium hydroxide solution and a few drops of phenolphthalein) to remove the last traces of hydrogen fluoride and to saturate the gas with water vapor. Leveling bulb L_3 was lowered and the gas transferred to the gas buret. The gas was passed back and forth several times between the gas buret and the bubbler to ensure saturation with water vapor and was finally measured in the gas buret after pressure adjustment was made through leveling bulb L_3. The bomb was removed, washed with water and then acetone, evacuated, and weighed. The weight per cent hydrocarbon in the sample was calculated from the corrected gas volume and the weight of the total sample.

This same procedure was used for analysis of all hydrogen fluoride samples obtained in this work. Some error was probably involved when analyzing samples of the hydrogen fluoride phase from the HF–isobutane–alkylate system for isobutane, since traces of hydrocarbons other than isobutane were undoubtedly associated with the gas collected in the buret. The error involved in calculating this gas as isobutane was small. No alkylate layer was ever noticed on the surface of the alkaline solution used to absorb the hydrogen fluoride. Even when the solution was forced into a capillary tube, no alkylate could be detected on its surface. From all indications, the amount of hydrocarbons heavier than butanes dissolved in the hydrogen fluoride phase was very small.

Table II. Analysis of Known Samples of Isobutane in Hydrogen Fluoride

Total Wt. of Sample, Grams	Weight % Isobutane		% Deviation
	Present	Found	
0.4143	0.4143	0.415	+0.3
0.2130	0.2130	0.211	−0.9
0.2060	0.2060	0.208	+1.0
4.6215	0.770	0.772	+0.3

A number of samples of pure isobutane were analyzed in order to test the method, and several known mixtures of isobutane and hydrogen fluoride were analyzed as a final check (Table II). As in the case of analysis of known samples when testing the method used on the hydrocarbon phase, the largest source of error was in the weighing of the bomb and the extremely small samples. The error in the analysis, however, was not greater than ±0.5%. Probably the most convincing evidence for the soundness of both analytical methods was found in the total analysis of several samples from the hydrogen fluoride phase for both isobutane and hydrogen fluoride:

Wt. % HF	Wt. % Isobutane	Total
98.0	1.95	99.95
98.0	2.50	100.50
98.1	2.03	100.13

EXPERIMENTAL DATA

The experimental solubilities of pure liquid isobutane, *n*-butane, and propane in anhydrous hydrogen fluoride may be reproduced as a function of temperature T, in degrees Kelvin, by the following equations:

$$\log_{10} W_i = \frac{-630.3}{T} + 2.69027 \quad (1)$$

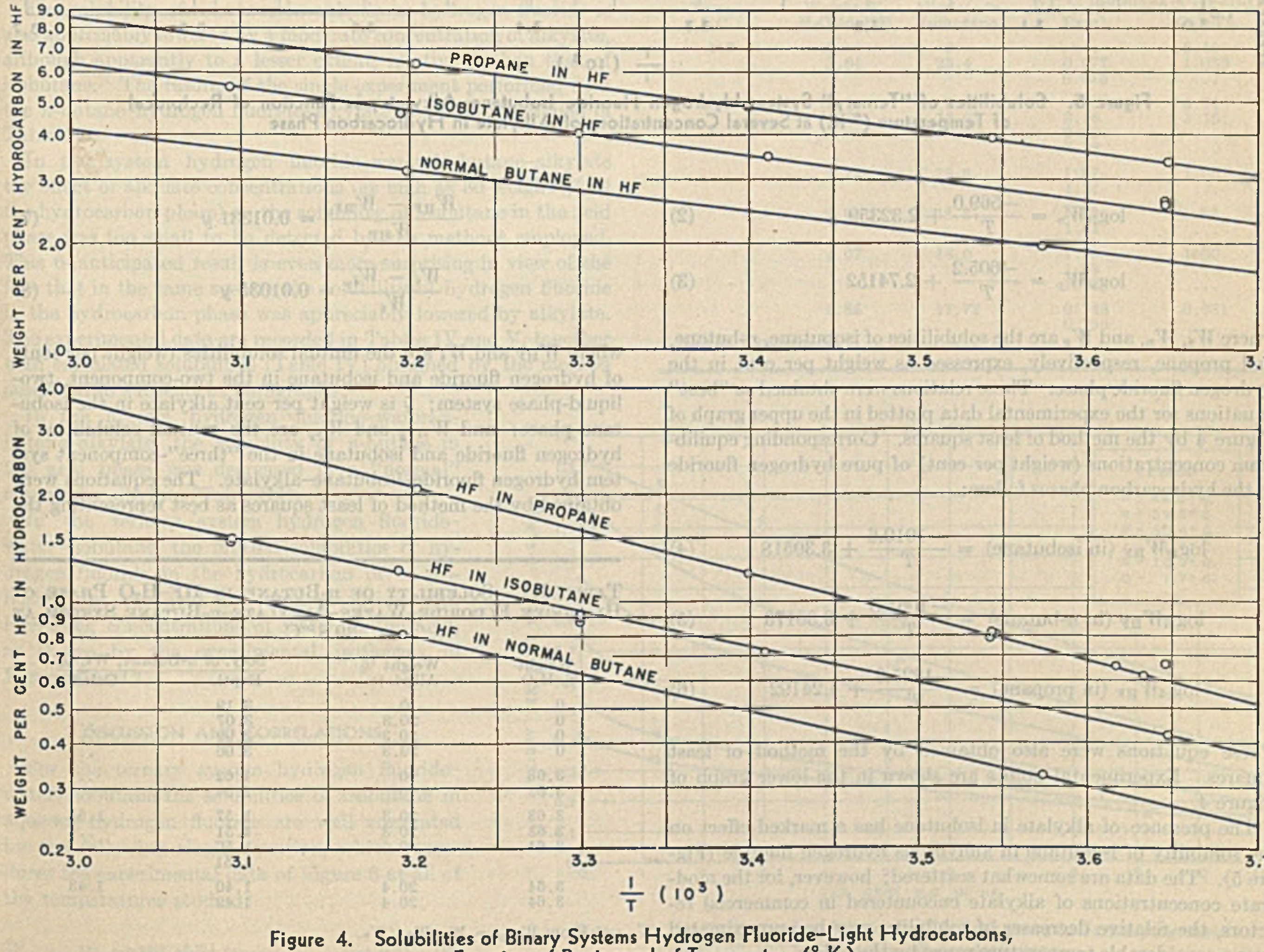


Figure 4. Solubilities of Binary Systems Hydrogen Fluoride–Light Hydrocarbons, as Function of Reciprocal of Temperature (° K.)

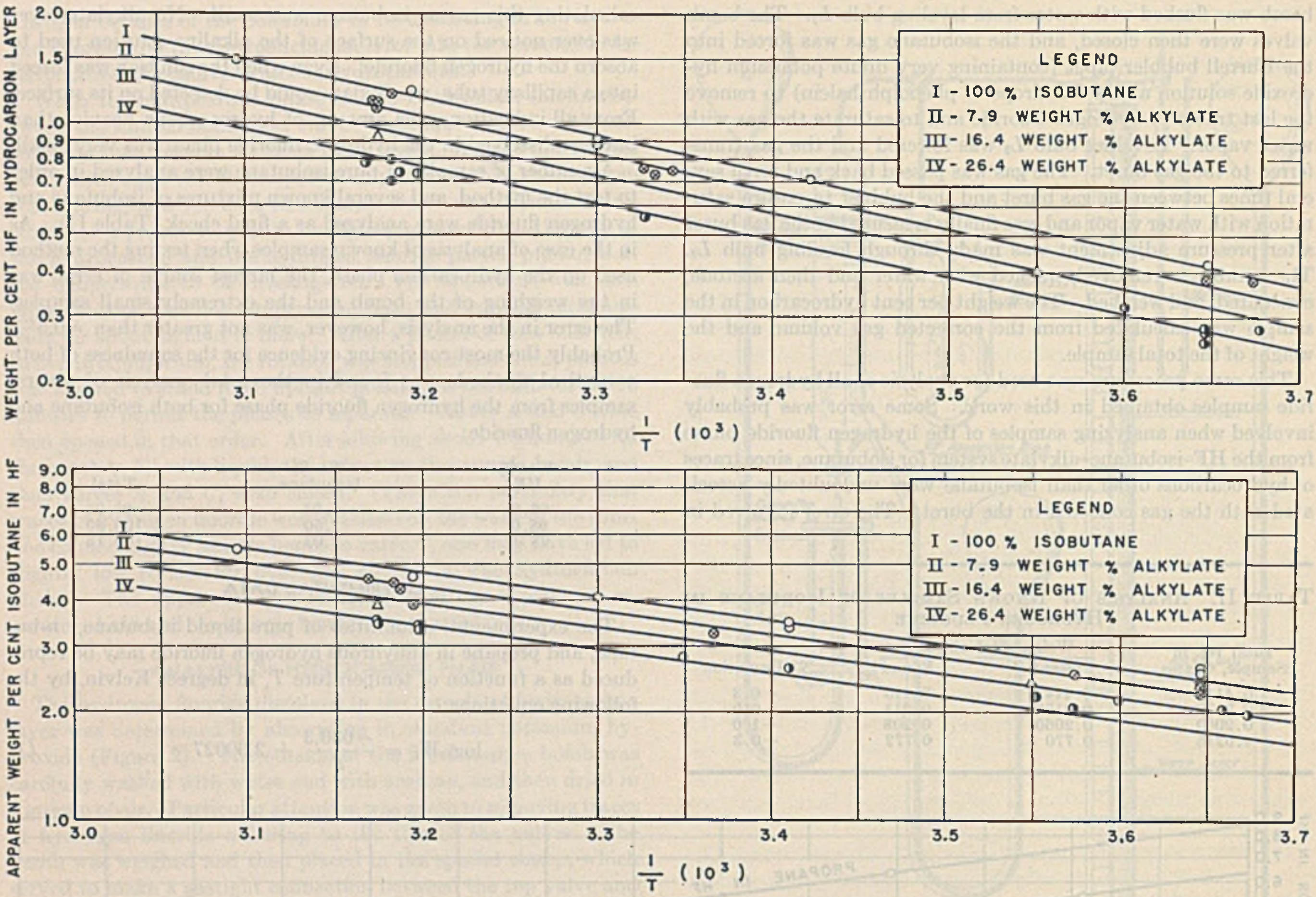


Figure 5. Solubilities of "Ternary" System Hydrogen Fluoride–Isobutane–Alkylate, as Function of Reciprocal of Temperature (° K.) at Several Concentrations of Alkylate in Hydrocarbon Phase

$$\log_{10} W_n = \frac{-569.0}{T} + 2.32359 \quad (2)$$

$$\log_{10} W_p = \frac{-605.2}{T} + 2.74152 \quad (3)$$

where W_i, W_n, and W_p are the solubilities of isobutane, *n*-butane, and propane, respectively, expressed as weight per cent in the hydrogen fluoride phase. These relations were obtained as "best" equations for the experimental data plotted in the upper graph of Figure 4 by the method of least squares. Corresponding equilibrium concentrations (weight per cent) of pure hydrogen fluoride in the hydrocarbon phases follow:

$$\log_{10} W_{HF} \text{ (in isobutane)} = \frac{-1010.6}{T} + 3.30518 \quad (4)$$

$$\log_{10} W_{HF} \text{ (in } n\text{-butane)} = \frac{-1061.8}{T} + 3.30173 \quad (5)$$

$$\log_{10} W_{HF} \text{ (in propane)} = \frac{-1225.3}{T} + 4.24192 \quad (6)$$

These equations were also obtained by the method of least squares. Experimental points are shown in the lower graph of Figure 4.

The presence of alkylate in isobutane has a marked effect on the solubility of isobutane in anhydrous hydrogen fluoride (Figure 5). The data are somewhat scattered; however, for the moderate concentrations of alkylate encountered in commercial reactors, the relative decreases of solubility may be approximated over a considerable temperature range by the following equations:

$$\frac{W_{HF} - W_{HF_y}}{W_{HF}} = 0.01331\, y \quad (7)$$

$$\frac{W_i - W_{i_y}}{W_i} = 0.01035\, y \quad (8)$$

where W_{HF} and W_i are the mutual solubilities (weight per cent) of hydrogen fluoride and isobutane in the two-component, two-liquid-phase system; y is weight per cent alkylate in the isobutane phase; and W_{HF_y} and W_{i_y} are the mutual solubilities of hydrogen fluoride and isobutane in the "three"-component system hydrogen fluoride–isobutane–alkylate. The equations were obtained by the method of least squares as best representing the

Table III. Solubility of *n*-Butane in HF–H_2O Phase of Hydrogen Fluoride–Water–Alkylate–*n*-Butane System at 39.8° C.

Weight % H_2O	Weight % Alkylate	Soly. of *n*-Butane, Wt. % Exptl.	Soly. of *n*-Butane, Wt. % Calcd.[a]
0	0	3.19	...
0	20.3	3.07	..
0	20.3	2.99	..
0	20.3	3.06	..
3.63	0	1.62	..
3.63	0	1.64	..
3.63	20.3	1.57	1.55
3.63	20.3	1.51	..
3.64	0	1.50	..
		1.51	..
3.64	20.4	1.40	1.43
3.64	20.4	1.42	..

[a] From $W_{nxy} = W_{nx} W_{ny} / W_n$.

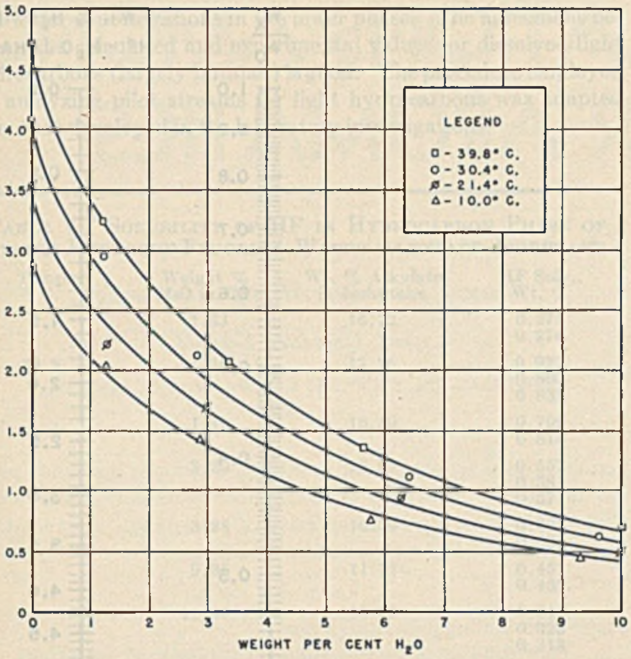


Figure 6. Isotherms for Solubility of Isobutane in Aqueous HF in Ternary System Hydrogen Fluoride–Water–Isobutane

experimental data plotted in Figure 5. The relations obviously do not apply at concentrations of alkylate considerably above the range studied.

The solubility of n-butane in anhydrous hydrogen fluoride is also appreciably lowered by a moderate concentration of alkylate, although apparently to a lesser extent, relatively, than that of isobutane. The results of the single experiment performed with the n-butane–hydrogen fluoride–alkylate system are included in Table III.

In the system hydrogen fluoride–water–isobutane–alkylate the effect of alkylate concentrations (as high as 30 weight % of the hydrocarbon phase) on the solubility of isobutane in the acid phase was too small to be detected by the methods employed. This unanticipated result is even more surprising in view of the fact that in the same system the solubility of hydrogen fluoride in the hydrocarbon phase was appreciably lowered by alkylate. The experimental data are recorded in Tables IV and V, together with calculated solubilities (Table IV) obtained by the method described in subsequent paragraphs.

In the system hydrogen fluoride–water–n-butane–alkylate, the solubility of n-butane in the acid phase was decreased in a "normal" manner by alkylate (Table III).

In the ternary system hydrogen fluoride–water–isobutane, the mutual solubilities of hydrogen fluoride in the hydrocarbon or of isobutane in the acid decreased smoothly with increasing concentrations of water in the acid, as shown by the experimental isotherms in Figures 6 and 7.

DISCUSSION AND CORRELATIONS

For the ternary system hydrogen fluoride–water–isobutane the solubilities of isobutane in aqueous hydrogen fluoride are well correlated by the following single equation, which reproduces the experimental data of Figure 6 at all of the temperatures studied:

$$W_{i_x} = W_i e^{-0.3227\, x^{0.784}} \quad \text{(temp. = constant)} \qquad (9)$$

where W_i = solubility of isobutane in anhydrous HF, wt. %
x = grams water per $(100 - x)$ grams hydrogen fluoride
W_{i_x} = wt. % isobutane in aqueous HF at x % water
e = base of natural logarithms

Equation 9 is probably not valid at water concentrations much above 10 weight %. Equations 1 and 9 may be combined to yield Equation 10, which specifies the equilibrium concentration (weight per cent) of isobutane in aqueous hydrogen fluoride over a wide range of temperature and water concentration. This relation is given in nomographic form in Figure 8.

$$\log_{10} W_{i_{x,T}} = \frac{-630.3}{T} - 0.1401\, x^{0.784} + 2.69027 \qquad (10)$$

A corresponding mathematical or graphical correlation of the solubilities of hydrogen fluoride in the isobutane phase was not obtained for this ternary system.

In the "quaternary" system hydrogen fluoride–water–isobutane–alkylate, the remarkable absence of effect of moderate concentrations of alkylate upon isobutane solubility in the acid phase is not easily explained. As Table IV shows, the experimental solubilities can be reproduced closely by Equation 10. In the corresponding system in which isobutane is replaced by n-butane, the solubility of n-butane in the acid phase can be approximated by calculations (Table III) according to Equation (11):

$$W_{n_{x,y}} = W_{n_x} W_{n_y}/W_n \qquad (11)$$

Table IV. Solubility of Isobutane in Acid Phase of System Hydrogen Fluoride–Water–Alkylate–Isobutane

Temp., ° C.	Weight % H_2O in HF	Wt. % Alkylate in Isobutane	Wt. % Isobutane in HF–H_2O	
			Exptl.	Calcd.[a]
1.7	0	0	...	2.49
	3.61	23.4	0.977	1.030
			0.975	...
39.8	0	0	...	4.74
	1.33	13.96	3.16	3.16
			3.08	...
			3.18	...
	3.74	28.2	1.87	1.90
			1.81	...
	3.99	18.8	1.82	1.82
			1.81	...
	4.07	18.0	1.76	1.80
			1.69	...
			1.73	...
	9.85	11.72	0.748	0.681
			0.756	...

[a] From Equation 10.

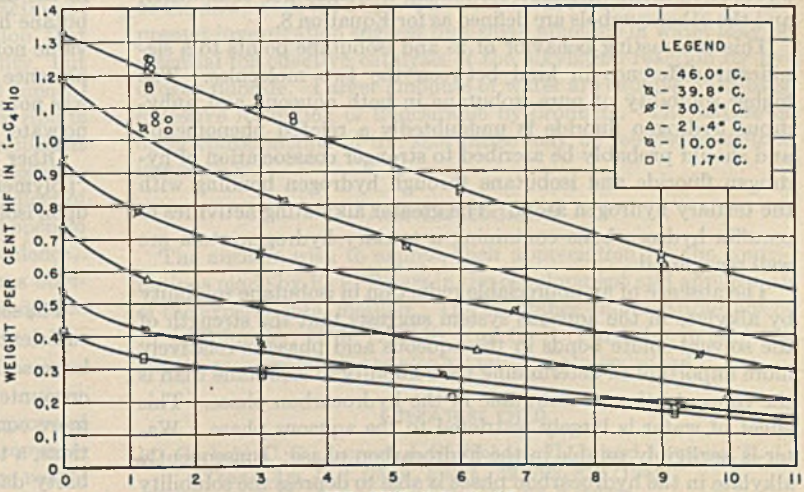
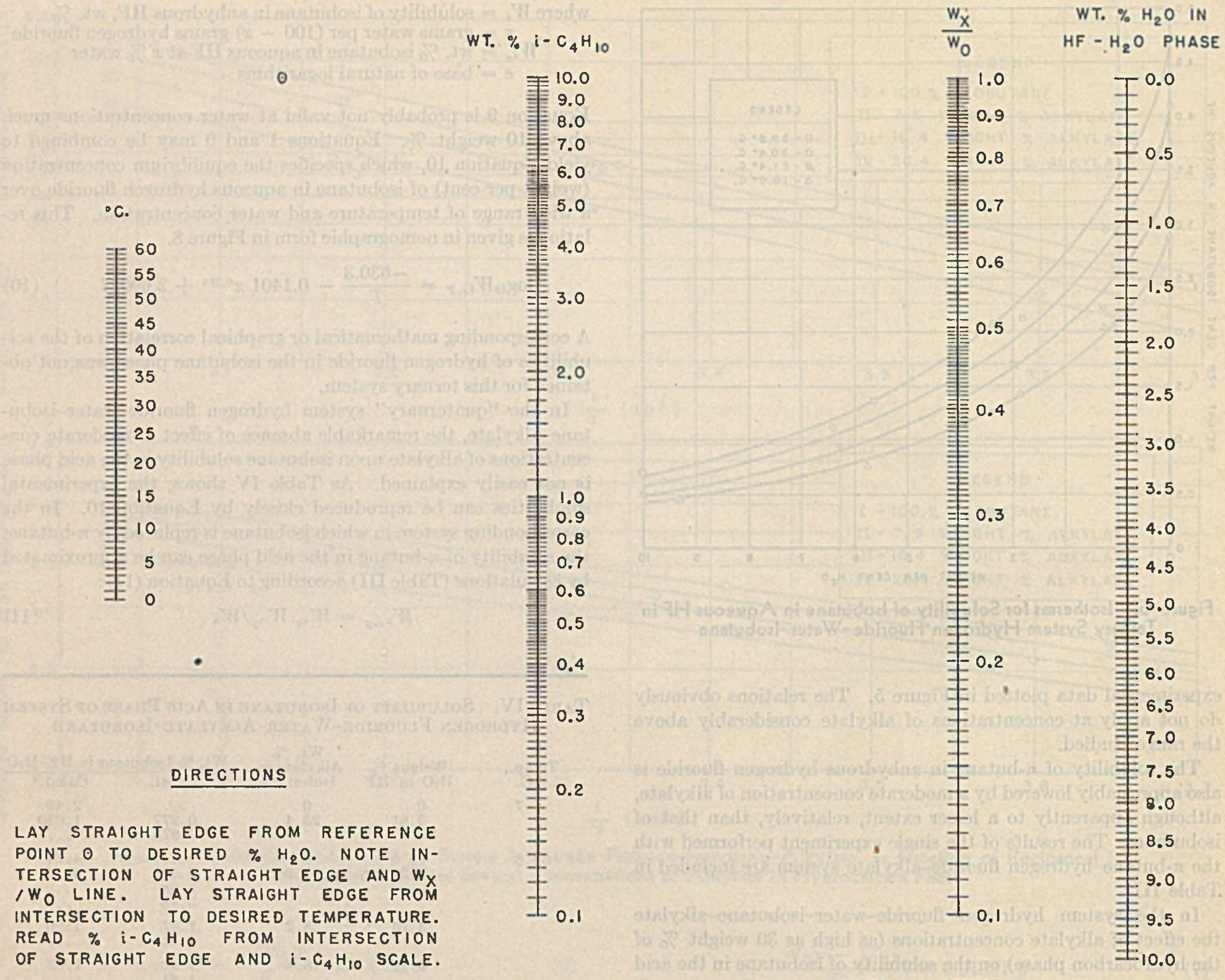


Figure 7. Isotherms for Solubility of HF in Isobutane in Ternary System Hydrogen Fluoride–Water–Isobutane



DIRECTIONS

LAY STRAIGHT EDGE FROM REFERENCE POINT 0 TO DESIRED % H_2O. NOTE INTERSECTION OF STRAIGHT EDGE AND W_X/W_O LINE. LAY STRAIGHT EDGE FROM INTERSECTION TO DESIRED TEMPERATURE. READ % $i\text{-}C_4H_{10}$ FROM INTERSECTION OF STRAIGHT EDGE AND $i\text{-}C_4H_{10}$ SCALE.

Figure 8. Nomograph Relating Isobutane Solubility to Temperature and Per Cent Water in the HF Phase of Ternary System Hydrogen Fluoride–Water–Isobutane

where $W_{n_{x,y}}$ is the solubility (weight per cent) of *n*-butane, from the hydrocarbon phase containing *y* weight per cent alkylate, in aqueous hydrogen fluoride containing *x* weight per cent water, and the other symbols are defined as for Equation 8.

This contrasting behavior of *n*- and isobutane points to a significant difference in kind between the two molecules. The higher solubility of pure isobutane in both aqueous and anhydrous hydrogen fluoride is undoubtedly a related phenomenon and should probably be ascribed to stronger coassociation of hydrogen fluoride and isobutane through hydrogen bonding with the tertiary hydrogen atom. The greater alkylating activities of paraffin hydrocarbons containing a tertiary hydrogen atom are well recognized.

The absence of an appreciable reduction in isobutane solubility by alkylate in the aqueous system suggests that the strength of the solvent-solute bonds in the aqueous acid phase is relatively more important in determining the solubility of isobutane than is the concentration of isobutane in the hydrocarbon phase. This effect of water is largely restricted to the aqueous phase. Water is negligibly soluble in the hydrocarbon phase; consequently alkylate in the hydrocarbon phase is able to depress the solubility of hydrogen fluoride in approximately the expected manner.

The apparently small effect of alkylate activity upon isobutane solubility in the "quaternary" system received partial confirmation by the results of some roughly quantitative experiment (unreported). In these experiments the concentration of isobutane in the acid phase was studied in systems from which liquid isobutane had been removed. When the pressure was reduced to a value not less than about 90% of the equilibrium pressure in the presence of liquid isobutane, no reduction in the concentration was noted in aqueous (2–3% H_2O) hydrogen fluoride; but when no water was present, a considerable decrease occurred.

Other qualitative experiments indicated a very small effect of "polymer", at concentrations up to 5–10% in the acid phase, upon isobutane solubility in the acid phase.

CORRELATION WITH PILOT PLANT DATA

The solubility data obtained in the present investigation are not sufficient to permit unequivocal correlations with analyses in large-scale alkylator systems. The two-phase liquid systems encountered in pilot or commercial operations are considerably more complex than the systems studied. Despite such limitations, a tentative correlation was made between the present solubility data and pilot plant analyses for light hydrocarbons dissolved in the acid phase of the alkylator. The results are presented in Table VI. The ten pilot plant runs for which data are recorded were selected to give a wide range of polymer, light oil, and water concentrations in the lower phase. The agreement between the calculated and experimental values for dissolved light hydrocarbons (largely butanes) is good. The procedure employed for analyzing pilot streams for light hydrocarbons was adapted from that developed in the laboratory investigations.

TABLE V. SOLUBILITY OF HF IN HYDROCARBON PHASE OF SYSTEM HYDROGEN FLUORIDE–WATER–ALKYLATE–ISOBUTANE

Temp., ° C.	Weight % H_2O in HF	Wt. % Alkylate in Isobutane	HF Soly., Wt. %
1.7	1.63	16.72	0.275 0.276
39.8	1.34	13.96	0.937 0.890 0.833
	1.49	16.50	0.799 0.815
	3.20	28.93	0.557 0.581 0.571
	3.28	16.59	0.683 0.680
	9.85	11.72	0.457 0.452
	11.49	16.83	0.340 0.323 0.313

TABLE VI. CORRELATION OF SOLUBILITY DATA WITH RESULTS OBTAINED IN PILOT PLANT ALKYLATION (AT 32.2° C.) OF BUTENES WITH ISOBUTANE

Pilot Plant Run No.[a]	129	130	128	131	132	139	140	141	142	143
Acid phase, wt. %[b]										
Experimental										
Titratable acidity	83.5	86.9	89.3	92.7	94.1	90.8	89.6	89.8	89.3	87.7
Polymer	5.3	3.9	2.6	1.2	0.5	2.7	2.6	1.8	1.4	1.2
Water	1.1	1.1	1.2	1.1	1.2	0.9	2.3	3.2	5.0	7.2
Light hydrocarbons	2.6	2.8	2.6	2.7	2.5	2.7	2.1	1.7	1.2	0.6
Calculated										
Iso-C_4 in HF[c]	2.154	2.175	2.153	2.258	2.197	2.345	1.703	1.386	0.983	0.674
n-C_4 in HF[d]	0.478	0.484	0.462	0.466	0.462	0.504	0.367	0.295	0.206	0.137
Light hydrocarbons, wt. %[e]	2.63	2.66	2.61	2.72	2.66	2.85	2.07	1.68	1.19	0.81
Hydrocarbon phase, mole %[f]										
Isobutane	65.87	65.43	66.04	66.64	65.87	66.27	66.57	66.80	66.40	67.95
n-Butane	21.04	21.07	20.50	19.91	20.14	20.47	20.57	20.42	20.10	19.72

[a] Olefin feed = mixed butane-butene fraction (B-B) in all runs.

[b] From alkylator; remainder consists of light oil boiling between alkylate and polymer.

[c] Calculated by equation: $W_i = N_i W_o e^{-0.3277} x^{0.784}$, where N_i = mole fraction iso-C_4 in C_4 fraction of hydrocarbon phase (i.e., effect of alkylate and polymer assumed to be negligible); x taken as weight % H_2O in H_2O-HF fraction of acid phase.

[d] Calculated by equation: $W_n = 1.17 N_n W_o e^{-0.3227} x^{0.784}$, where N_n = mole fraction n-C_4 in total hydrocarbon phase. The correction factor 1.17 arises from an attempt to fit the isobutane equation to the results with the n-C_4–HF–H_2O system (Table V). The equation is obviously not valid at zero % H_2O ($H_2O = x$).

[e] Sum of iso-C_4 and n-C_4.

[f] Calculated from weight %, assuming average mol. weight of $C_7{}^+ = 114$; debutanized upper phase boils substantially 100% in gasoline range.

It should be noted (Table VI) that the application of the correction factor N_i (mole fraction of isobutane in the C_4 fraction of the hydrocarbon phase) is equivalent to the assumption that alkylate has a negligible effect upon isobutane solubility, but that n-butane reduces the solubility in proportion to its concentration. This apparent confirmation of the anomalous results obtained in the present work is interesting. Similarly, an apparent confirmation of the absence of an effect of moderate concentrations of polymer and light oil is indicated. The assumed effect of water upon n-butane solubility in hydrogen fluoride is open to some question, since it is based on meager experimental evidence.

This method of calculating solubilities in plant streams obviously requires further confirmation before its usefulness can be fully assessed.

SIGNIFICANCE OF METHOD AND DATA

The analytical methods and data reported here should prove of considerable importance in expediting process control in commercial alkylation plants, and in providing means for a more nearly complete characterization of the concentration variables of importance to the process. It has been customary in the analysis of the acid phase in the alkylator to determine directly only the titratable acidity, water, and polymer. The total light hydrocarbons are determined by difference, and thus it has not been possible to distinguish between dissolved light paraffins and the light oils boiling between these light paraffins and the heavier polymer residue. Separate determination of the dissolved light paraffins by the method developed in this work makes possible the estimation of the light oils by difference and, thus, leads to more adequate pilot plant correlations. Further elucidations of the nature of the light oil should constitute another step forward in the characterization of the catalyst phase.

It is also of interest that there are considerable data from alkylation units to show (*a*) that titratable acidity is an important variable in the process and (*b*) that various acid-phase diluents which determine the value of the titratable acidity are not necessarily equivalent in their effect on the process. For example, at higher temperatures (e.g., near 90° F.) extensive correlations of titratable acidity with product yield and quality have been made, with strong evidence for optimum acidities near 90 weight %, essentially independent of water contents as high as 7 weight %. At considerably lower temperatures, however, polymer and alkyl fluorides are formed more readily, and the yield of these substances is greatly enhanced by high concentrations of water in the reactor emulsion; i.e., at identical values for titratable acidity, the yields of by-products may be variable according to the nature of the diluents in the acid. The anomalous results obtained in the present investigation suggest that small amounts of water may be essential for effective catalysis of the alkylation reaction by hydrogen fluoride. Larger amounts of water are capable of causing excessive formation of undesirable by-products. The nature of other contaminants in the acid phase may be relatively of little importance.

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BOILING POINT RELATIONS AMONG MONONUCLEAR AROMATICS

The variation of boiling point with the number of carbon atoms has been determined for ten homologous series of mononuclear aromatic hydrocarbons. The equation for this relation is in the form: $t = a \log (n_c + 4.4) + k$. The variation of the difference in boiling point between an aliphatic compound and its phenyl derivatives with the number of carbon atoms has been determined for nine homologous series. The equation is in the form: $\delta = p + q \log n_s$. Comparisons have been made among phenylalkanes, phenylalkenes, and phenylalkynes; phenylalkanes and phenylcyclanes; 1-phenyl and 2-phenyl compounds, and monophenyl and polyphenyl compounds.

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THE boiling points of mononuclear aromatic hydrocarbons were recently collated and critically evaluated (*3*). The relation between boiling point and structure will be treated here. Boiling points of a wide variety of hydrocarbons may be calculated by the use of equations and "boiling point numbers" developed by Kinney (*5, 6, 7*) or by similar relationships set forth by Klages (*8*). A different approach was used by Egloff, Sherman, and Dull (*4*) who determined the relation between boiling point and number of carbon atoms for thirty-one homologous series of aliphatic hydrocarbons. Kinney's and Klages' methods are capable of application to a greater number of compounds; Egloff's method generally yields more accurate results for those compounds which can be included in a homologous series. The latter method was used in this study.

The data for boiling points of aliphatic hydrocarbons are well represented by an empirical equation (*4*) of the form:

$$t = a \log (n_c + b) + k$$

where t = temperature
n_c = number of carbon atoms

For thirty-one homologous series, including both saturated and unsaturated aliphatics, the constants a and b did not vary, while constant k differed from series to series. The values for a and b were: $a = 745.42$, $b = 4.4$.

A similar study of boiling points of mononuclear aromatic hydrocarbons showed that an empirical equation of the same form could be used. The value of 4.4 for constant b fits the available aromatic data for all series except one. The value of constant a differs widely from one series to another, depending on the position of the phenyl group or groups, and on the position of the unsaturation in phenyl-substituted alkenes and alkynes.

Constants a and k were evaluated for ten homologous series by the method of least squares. The value of 4.4 was used for constant b in all series except one. Later work may indicate that some other value should be assigned to this constant, but the paucity of data available at present makes it impossible to determine whether any other value would fit the data better.

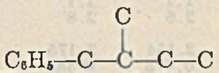
Phenyl-substituted straight-chain alkanes, alkenes, alkynes, and phenyl-substituted cyclanes were the only types of compounds for which sufficient data were available to calculate an equation for a homologous series. In an effort to include some branched-chain aromatics in the study, the differences between the boiling points of aliphatic compounds and the same compounds with phenyl substitutions were investigated. The boiling points of the aliphatic and alicyclic compounds used in this study were taken from Egloff (*2*). The boldface or "best" values were used whenever they were given. The differences in boiling points for nine series gave substantially a straight line when plotted against the logarithm of the number of carbon atoms in the aliphatic hydrocarbons, irrespective of branching. This relation may be expressed by an equation of the form:

$$\delta = p + q \log n_s$$

where δ = boiling point difference
n_s = number of carbon atoms in aliphatic hydrocarbon

The only marked deviation from this relation occurs when a tertiary carbon atom is present.

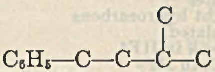
An objection to this method is that unsymmetrical branched-chain hydrocarbons with the phenyl group at one end would have the same calculated boiling point as the compound with the phenyl group at the other end. For example,



$C_6H_5-C-\overset{\displaystyle C}{\overset{|}{C}}-C-C$

1-Phenyl-2-methylbutane

and



$C_6H_5-C-C-\overset{\displaystyle C}{\overset{|}{C}}-C$

1-Phenyl-3-methylbutane

are derived from the same aliphatic and would have the same calculated boiling point. Logically their boiling points would be expected to differ. Few boiling points have been reported for compounds of this type, but available data indicate that the boiling points are not widely separated. The difference would probably increase with the length of the chain, but the only data available are on short-chain compounds. For these short branched-chain compounds the difference between the boiling point of the aromatic and that of the aliphatic is nearly the same as in the case of the straight-chain compounds, and is usually within the limits of experimental error. Until more data are available, the inclusion of branched-chain phenyl-substituted hydrocarbons with the straight-chain compounds seem justified.

EQUATIONS AND GRAPHS

Table I lists the constants of equations for boiling point difference of a number of series. Figures 1, 2, and 3 show observed and calculated boiling points plotted against log (n_c + 4.4); the boiling point differences are plotted against log n_s where n_s represents the number of carbon atoms in the side chain.

The graph of boiling points of toluene, diphenylmethane, triphenylmethane, and tetraphenylmethane plotted against the logarithm of n_c + 4.4 showed a definite curvature. However, when the boiling points were plotted against the logarithm of n_c, substantially a straight line resulted.

The agreement of the observed and calculated values is good in some series and poor in others. The deviation is usually greater in the higher members of a series, probably because of the inaccuracy of the data for these compounds. The inaccuracy and scarcity of data for all except the first few members of a series are accounted for by the increased molecular weight and consequent high boiling points. This problem is not encountered with the aliphatic hydrocarbons. In many cases only one or two boiling

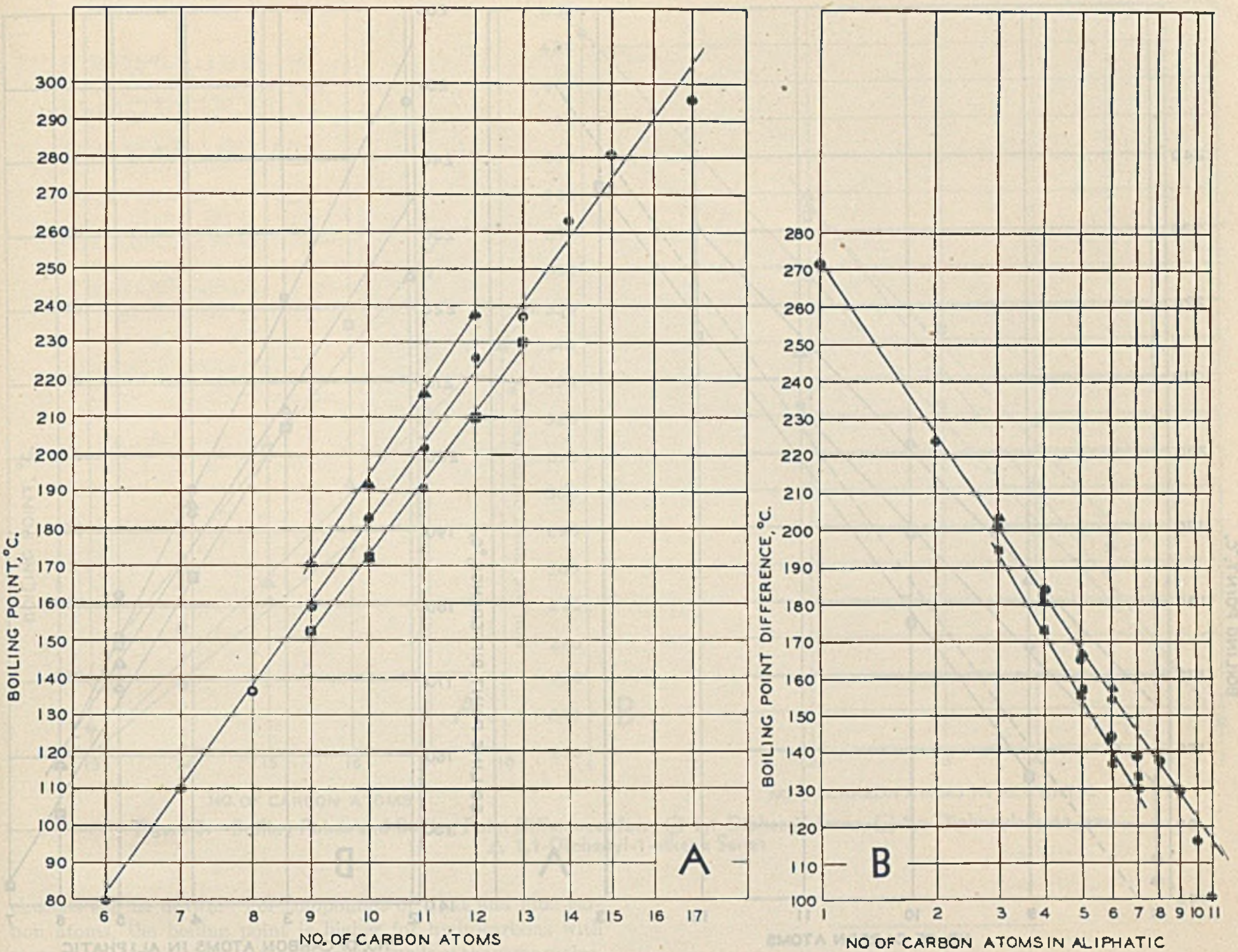


Figure 1. Boiling Points and Boiling Point Differences for: ○ 1-Phenylalkane, □ 2-Phenylalkane, and △ 1-Phenylcyclane Series

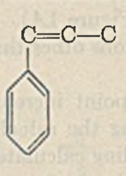
points for a compound are available, and critical evaluation cannot be carried out. Boiling points of many of the higher members of a series are reported at reduced pressures, but these data are not consistent enough to permit their use in calculating an equation for relating boiling point to structure.

The poor agreement and brevity of most of the series make it impossible to extrapolate the equations with any degree of confidence or to make comparisons between series on the basis of experimental values. However, comparison of the calculated values for the different series shows some trends.

TRENDS IN CALCULATED VALUES

Change from a single to a double bond in the 1-position of both 1-phenyl and 1,1-diphenyl compounds causes a rise in boiling point (Figures 1*A*, 2*A*, and 3*A*). The increment decreases with increasing carbon content in the 1,1-diphenyl series. A 1-phenyl compound with a triple bond in the 1-position has a higher boiling point than the corresponding phenylalkene (Figure 2*A*). The increment decreases with increasing carbon content. Replacement of a single bond by a double bond in the position farthest from the phenyl group in 1-phenyl compounds, on the other hand, lowers the boiling point; the increment increases with increasing carbon content (Figures 1*A* and 2*A*).

The difference in effect on the boiling point of position of double bond may be explained by comparison with the effect of unsaturation in the aliphatic hydrocarbons. Here the effect of a single unsaturation is to lower the boiling point, as is the case in the aromatics when the double bond is not beta to the benzene ring. Alkadienes with conjugated double bonds, on the other hand, have higher boiling points than the corresponding alkanes (*1*). This is comparable to the aromatic compounds with a double bond in the position beta to the benzene ring:



Here the double bond in the side chain is conjugated with the double bonds in the benzene ring, and the boiling point is raised.

TABLE I. CONSTANTS OF EQUATIONS

Series	Boiling Point		B.P. Difference	
	a	*k*	*q*	*p*
1-Phenylalkane	712.38	−642.67	−150.209	272.57
2-Phenylalkane	679.54	−614.40	−178.136	279.63
1-Phenyl-1-alkene	537.36	−432.61	−204.460	318.22
1-Phenyl-($n-1$)-alkene	699.81	−632.26	−167.585	284.62
1-Phenyl-1-alkyne	527.78	−411.31	−157.723	283.09
1,1-Diphenylalkane	406.87	−245.22	−223.926	425.24
1,n-Diphenylalkane	617.38	−494.96	−216.155	441.76
1,1-Diphenyl-1-alkene	498.20	−358.25	−262.885	457.36
Phenylcyclane	776.30	−705.54	−150.209	272.57
n-Phenylmethane	576.27[a]	−377.16		

[a] In this equation n_e was used instead of $n_e + 4.4$.

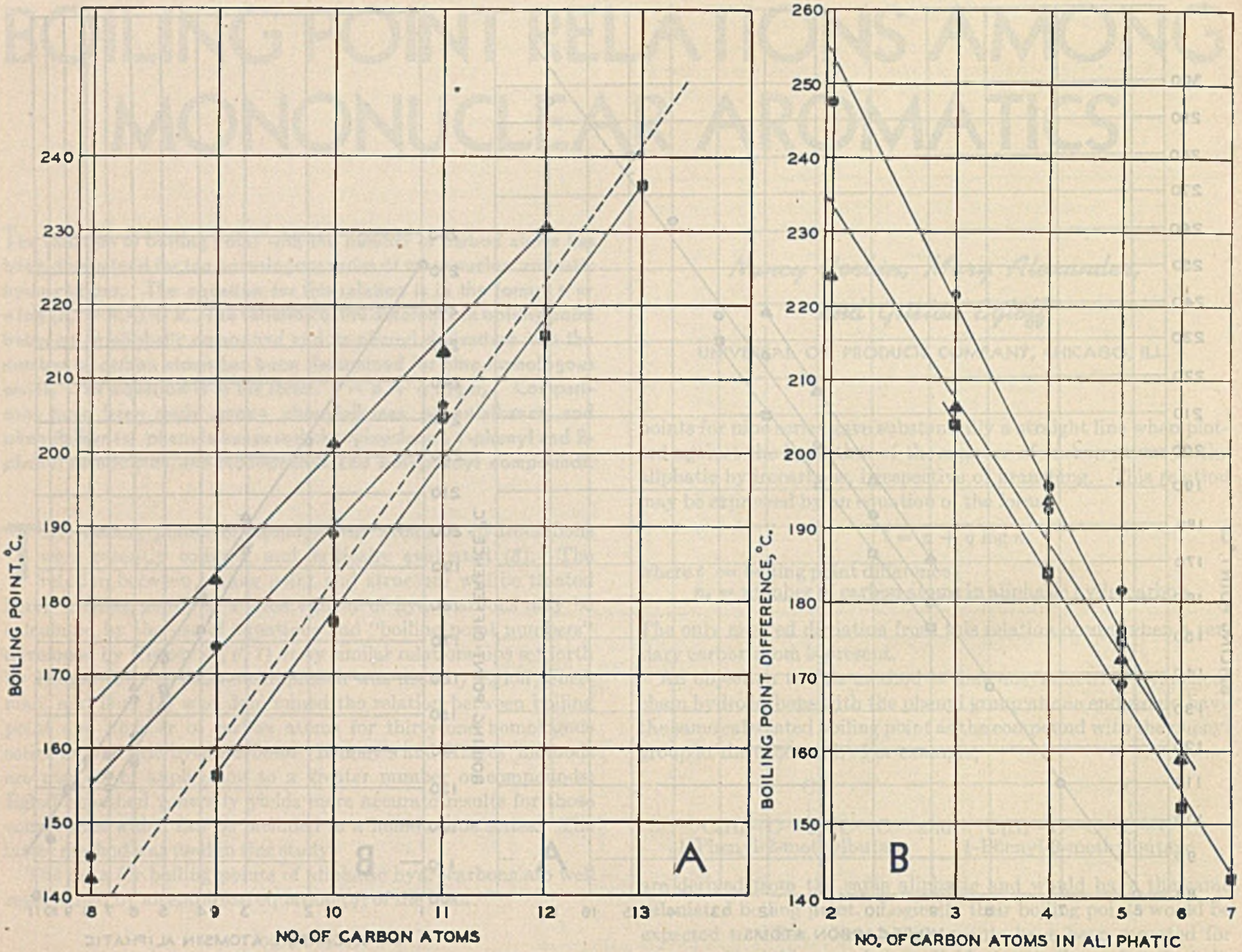


Figure 2. Boiling Points and Boiling Point Differences for: ○ 1-Phenyl-1-alkene, □ 1-Phenyl-1(n − 1)-alkene, △ 1-Phenl-1-alkyne, and - - - - - 1-Phenylalkane Series

Phenylcyclanes have higher boiling points than the corresponding phenylalkanes; the increment increases with the size of the ring (Figure 1A).

A shift of the phenyl group from the 1- to the 2-position on an alkane lowers the boiling point. The increment increases with increasing chain length (Figure 1A). Data on compounds with the phenyl group in positions other than 1- and 2- are too few to permit comparison.

Equations for boiling point increments between series were worked out by subtracting the calculated boiling points for one series from the corresponding calculated values of another series. The increments thus obtained were correlated with the number of carbon atoms by the method of least squares:

1-phenylalkane ⟶ 1-phenyl-1-alkene
$\Delta t = 207.68 - 173.01 \log (n_c + 4.4)$

1,1-diphenylalkane ⟶ 1,1-diphenyl-1-alkene
$\Delta t = 96.20 \log (n_c + 4.4) - 119.385$

1-phenylalkane ⟶ 1-phenyl-1-alkyne
$\Delta t = 231.87 - 185.03 \log (n_c + 4.4)$

1-phenyl-1-alkene ⟶ 1-phenyl-1-alkyne
$\Delta t = 23.65 - 11.56 \log (n_c + 4.4)$

1-phenylalkane ⟶ 1-phenyl-(n − 1)-alkene
$\Delta t = 10.54 - 12.69 \log (n_c + 4.4)$

1-phenylalkane ⟶ 1-phenylcyclane
$\Delta t = 63.65 \log (n_c + 4.4) - 62.60$

1-phenylalkane ⟶ 2-phenylalkane
$\Delta t = 29.52 \log (n_c + 4.4) - 24.21$

The effect of introducing phenyl groups into hydrocarbons is, of course, to raise the boiling point because of the increase in molecular weight. The increase in molecular weight resulting from addition of a phenyl group precludes the possibility of comparing a monophenyl compound with the corresponding polyphenyl compound on the basis of the total number of carbon atoms. When the boiling point increments are plotted against the logarithm of 4.4 plus the number of carbon atoms in the alkane or alkene to which the phenyl groups are attached, a straight line results (Figures 1A, 2A, and 3A). Equations for boiling point increments follow. In these equations n_c refers to the number of carbon atoms in the aliphatic chain:

1-phenylalkane ⟶ 1,1-diphenylalkane
$\Delta t = 324.23 - 237.15 \log (n_c + 4.4)$

1-phenylalkane ⟶ 1,n-diphenylalkane
$\Delta t = 276.71 - 157.79 \log (n_c + 4.4)$

1-phenyl-1-alkene ⟶ 1,1-diphenyl-1-alkene
$\Delta t = 204.48 - 108.32 \log (n_c + 4.4)$

The effect of adding a phenyl group to an aromatic compound cannot readily be compared with the effect of adding a phenyl to an aliphatic compound because the increment in the latter case is linear with respect to the logarithm of n_c, but not linear with respect to $n_c + 4.4$. Qualitatively, the effect on the boiling point of adding the first phenyl group is much greater than the effect of further addition of phenyl groups.

The data for polysubstituted benzenes are too inconsistent to be used for any quantitative relations. Only a few general con-

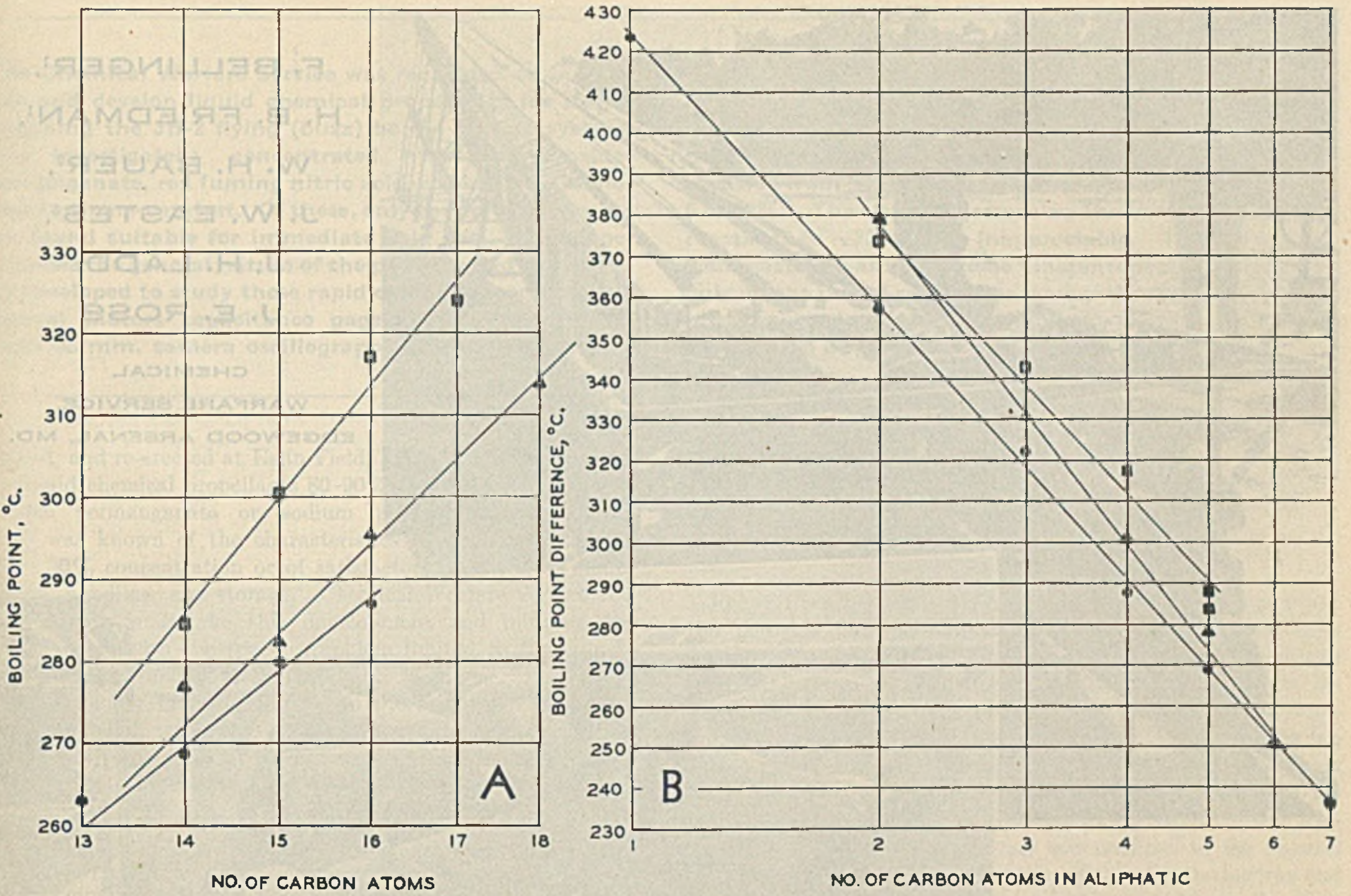


Figure 3. Boiling Points and Boiling Point Differences for: ○ 1,1-Diphenylalkane, □ 1,*n*-Diphenylalkane, and △ 1,1-Diphenyl-1-alkene Series

clusions can be drawn. For compounds of eight and nine carbon atoms, the boiling point is higher for hydrocarbons with more than one substitution than for compounds of the same molecular weight with only one substitution. For example, the xylenes have higher boiling points than ethylbenzene has. Above C_9 the boiling points are, in general, lower in disubstituted compounds than in their monosubstituted isomers. Trisubstituted compounds are, almost without exception, higher boiling than disubstituted compounds of the same molecular weight. A further increase in the number of substituents usually continues to raise the boiling point.

In the disubstituted compounds the effect on the boiling point of the relative position of the substituents is not consistent. In almost every case the meta-substituted compound has a lower boiling point than either the ortho or para derivative, but with di-*n*-propylbenzene and methylisopropenylbenzene the para compound is lower boiling than the meta. The ortho and para compounds are variable. In some instances (especially the lower-molecular-weight hydrocarbons) the ortho compound has a higher boiling point than the para; in other instances this is reversed.

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Catalytic Polymerization Unit of Universal Oil Products Company

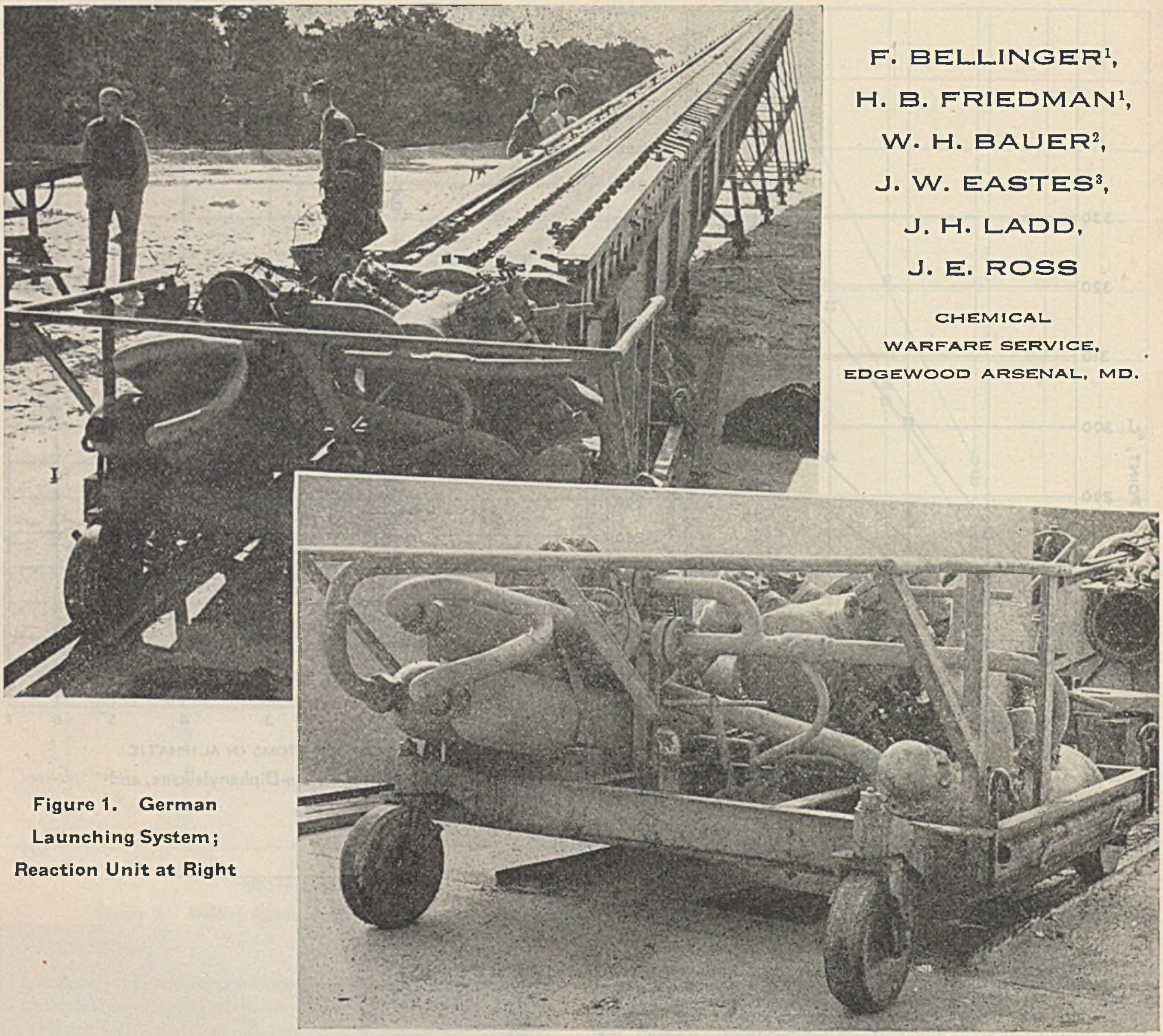

Figure 1. German Launching System; Reaction Unit at Right

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CHEMICAL PROPELLANTS

The System Hydrogen Peroxide–Permanganate

THE German "buzz bomb", so effectively used by the Germans as a weapon of destruction for an area target and as a nerve-shattering missile, has been adequately described in the press. The bomb's propelling mechanism was a 600-horsepower motor; into its hot combustion chamber, gasoline was injected continuously. The front of the motor contained a series of steel vanes, like Venetian blinds but V-shaped, which opened and closed with high frequency. In flight, the ram-jet effect of air opened the vanes and thus permitted air to enter the combustion chamber until an explosive mixture was obtained. The resulting spontaneous ignition developed pressure which closed the vanes and forced the hot combustion gases out of the rear of the motor. The reaction against the closed vanes furnished the force to propel the bomb to the target. As soon as the pressure within the motor fell below the effective pressure of the air ram, the vanes again were forced open. This cycle was repeated many times a second and developed the loud intermittent roar from which the term "buzz bomb" was obtained. Since the motor depended upon ram effect of the air, the bomb had a stalling speed of approximately 200 miles per hour. It was therefore necessary to provide a method of launching the bomb by a separate system which would impart an initial velocity greater than the stalling speed in order that the motor should function properly and accelerate the bomb to flying speed.

The responsibility of developing an American counterpart of the V-1 and a method of launching was assigned to the Army Air Forces. Research and development were expedited along several varied lines. With the invasion of the Normandy Coast a complete German launching system was captured, dismantled,

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The Chemical Warfare Service was requested to investigate and develop liquid chemical propellants for use in launching the JB-2 flying (buzz) bomb. Three systems were investigated: concentrated hydrogen peroxide–permanganate, red fuming nitric acid–aniline, and mononitromethane-catalyst. Of these, only the peroxide system was found suitable for immediate field use. This paper discusses the general nature of the problem and the methods developed to study these rapid chemical reactions. A General Motors capacitance gage–cathode ray oscillograph–35 mm. camera oscillograph recorder was used to record the pressure obtained in the chamber of a thrust motor as the chemical propellants were injected. Reaction data are presented for the hydrogen peroxide–permanganate system over a range of concentrations of hydrogen peroxide from 50 to 90% and permanganate (MnO_4^-) from 5 to 52%. The effect of decreasing the temperature of the reactants to −23° C. was inappreciable. The decomposition reaction was found to be "instantaneous", depending only on the rate of mixing the reactants; therefore smooth pressure development was possible by controlling the rate of injection of peroxide.

shipped, and re-erected at Eglin Field, Fla. The Germans used the liquid chemical propellants 80–90% hydrogen peroxide and calcium permanganate or sodium permanganate solutions. Little was known of the characteristics of hydrogen peroxide above 50% concentration or of satisfactory methods of manufacture, handling, and storage. Chemical Warfare Service was requested to undertake this development and initiated the Fred Project with the specific problem limited to the launching of the Air Forces JB-2 flying bomb.

A preliminary investigation led to the conclusion that three liquid chemical propellant systems should be investigated simultaneously—namely, hydrogen peroxide–permanganate, mononitromethane, and fuming nitric acid–aniline. This conclusion was based upon the following results of the initial investigation:

> The Germans used peroxide-permanganate and it was known to work. The German reaction unit was constructed of an unfamiliar aluminum alloy, whose inside surfaces were coated with a wax. Intelligence reports contained many rumors of "explosions" at the launching sites due to the peroxide. Plants in the United States normally produced 30% peroxide, and satisfactory production of 90% material was questionable. Practically our entire capacity for 30 and 50% material was being used for other military needs. Hence a new plant would be required for the bomb program.
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> Considerable research work had been carried out on mononitromethane at the Guggenheim Aeronautics Laboratory, at California Institute of Technology, under joint Air Forces and Ordnance contracts. The possible use of a monopropellant which could be handled like gasoline required investigation. Available production capacities were small, and a new plant to meet the demand would be required.
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> Exhaustive data on red fuming nitric acid–aniline were available, and this system or its counterpart, mixed acid–monoethylaniline, was being used in thrust motors. Production capacity was available for a large program.

As developed later, only the first system was found to be satisfactory for immediate use. The object of this series of papers is to present the methods of investigation that were developed to study these extremely rapid chemical reactions. The same methods can be used to study other chemical systems. It is hoped that generation of power by chemical propellants in the future will be applied to more constructive uses than launching a flying bomb, propelling of torpedoes and submarines, or driving gas turbines in a V-2 rocket.

NATURE OF THE PROBLEM

Military considerations of mobility and camouflage decreed that a launching ramp be as short and light in weight as practicable. Structural strength of the flying bombs was the factor limiting the degree of acceleration to which the bomb could be subjected during launching.

Army Air Forces tentatively specified an average acceleration of fifteen times gravity, 483 feet per (sec.)^2, and a maximum of $18g$. To launch the bomb at 250 miles per hour, a 150-foot ramp was required, similar to the German unit. The magnitude of the problem is then indicated by the following figures:

Length of launching travel, ft.	150
Launching speed, m.p.h.	250
Launching period, second	0.75
Instantaneous work being done at end of period, hp.	55,000
Required gas generation at end of period, cu. ft./min. (at 850 lb./sq. in.)	15,000

Figure 1 is a photograph of the German reaction unit in which the peroxide and permanganate solutions were blown from separate blow cases by high pressure (2200 pounds per square inch) air into a reaction chamber. The gaseous products developed pressures of 800 to 100 pounds behind a piston in a "cannon", 11.5 inches i.d. and 160 feet long. A steel fin on the top of the piston protruded through a narrow (0.5-inch) slot along the top of the tube and fitted into a 12° angled keyway in the belly of the bomb. A small iron sled with wooden runners supported the rear of the bomb and was confined in the channel track provided on top of the cannon. The end of the keyway and the front edge of the fin were angled 12° to hold down the front of the bomb during launching. Throughout this operation the acceleration created a moment of force around the center of gravity of the bomb. Near the end of the launching, the bomb wings created an additional upward lift.

To minimize the escape of gases through the slot, a one-inch-diameter rod was suspended by small wires beneath the slot throughout its length. The piston was grooved along the top to accommodate this rod. As the piston shot forward, the rod was pushed up by the piston against the slot and the internal pressure kept the rod in place until the piston left the barrel.

The design of the reaction unit was obviously complicated and empirical. While only one solenoid valve and two air-operated valves were used, it was not believed that the unit regulated the rate of injection to produce a uniform acceleration. However, before a design of a full scale unit could be attacked with confidence that the resulting unit would be satisfactory for field use, it was necessary to obtain the fundamental characteristics of the propellant system. The discussion is limited to the system hydrogen peroxide–permanganate.

An adequate solution to the problem had to include answers to the following questions: Could the system develop sufficient gaseous pressure rapidly and smoothly at high rates of injection? Could operating conditions be determined under which the system could be used? Would the system have acceptable latitude and sufficient safety factors? Were the various materials satisfactorily stable even under unfavorable field storage conditions? Would they be hazardous when handled by personnel? Could materials of construction be found for the use of the system and for storing and transporting the propellants?

At the time this project was initiated, commercial production of hydrogen peroxide was standardized at 30%, with 50% product made under special orders. The Buffalo Electrochemical Company developed a concentration process yielding a product which contained impurities of the same order as those in conductivity water and was, therefore, exceptionally stable. Most of the tests were made with this high purity product. Similar

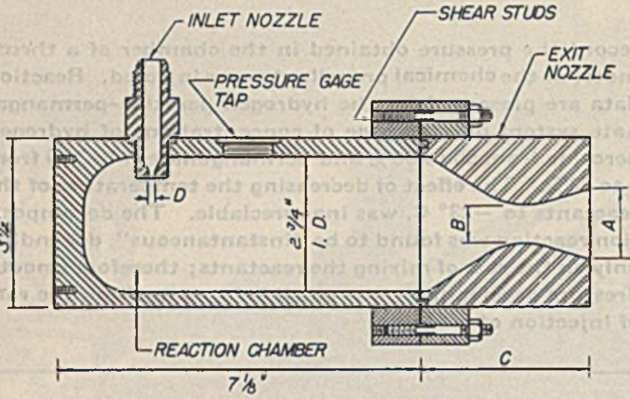

Figure 2. Thrust Motor Assembly

A. Exit diameter (of exit nozzle)
B. Throat diameter (of exit nozzle)
C. Over-all length (of exit nozzle)
D. Orifice diameter at inlet nozzle

reaction tests were made on captured German peroxide containing about 900 p.p.m. of impurities, mostly as added stabilizing agents.

Calcium and sodium permanganate solutions were obtained from the Carus Chemical Company. The calcium permanganate solution received was about 77%, based on $Ca(MnO_4)_2 \cdot 4H_2O$. For the present purpose permanganate was determined and expressed as per cent MnO_4^-, since that is the active constituent and since the solution also contained approximately 1% $NaMnO_4$.

The dangerous nature of the work made it unfeasible to start the work with full scale equipment. To study the fundamental reaction characteristics of the system hydrogen peroxide–permanganate, two types of small scale experimental equipment were used. The first was a closed, high pressure bomb in which the reactants could be rapidly mixed and the resultant pressures and temperatures observed. In contrast to this static method was a reaction chamber, commonly referred to as a thrust motor; this equipment provided for the continuous injection of reactants through inlet nozzles and the removal of products through an exhaust nozzle. Pressures developed in the thrust motor were recorded by a continuous recording arrangement.

TEST PITS

Reinforced concrete test pits were used for all runs with the thrust motors and the closed bomb. The pits consisted of two test barricades utilizing a common separating wall; both were U-shaped. They were adjoined by an instrument room. The larger barricade used for thrust motor runs was 18 feet wide and 25 feet long, with two concrete blocks to accommodate the two thrust motors and accessory equipment. The smaller barricade, approximately 10 feet square, was used for the closed bomb runs and gas impact work. The barricade walls were 18-inch concrete heavily reinforced with steel. Safety glass windows protected by steel grillwork were located in the outside walls to permit observation of the experiments. The instrument room was directly behind the barricades and had no wall in common with them. The concrete flooring of the instrument room was separated from the barricade foundation by 2 feet of earth. All connections between the instrument room and the barricades were made by 6-inch pipes overlapping 4-inch pipes. The space between the pipes was loosely packed with oakum to prevent rain from washing back into the instrument room and to maintain a vibration-free connection.

Safety features of the barricades, in addition to mechanical strength, included a fire spray system, to flood the barricade, which could be quickly operated by a valve from either inside or outside of the instrument room. The interior of the test pit was made fire resistant by covering all exposed wood with transite. Safety showers of the treadle type were located directly outside of the barricade openings. The roof of the pits was sandbagged to prevent flying missiles from endangering personnel. The safety glass windows ordinarily were not used. Instead, mirrors were placed in the barricade opening to allow indirect observation. No windows were located between the barricade and the instrument room.

CLOSED BOMB STUDIES

Reaction Rate. The early tests on this system were carried out in an Aminco superpressure bomb of 1000-ml. capacity, held in an Aminco bomb shaker and heating jacket. The shaking mechanism was removed, and a releasable stop was made to permit holding the bomb in a horizontal position. The stop had a pull wire to permit releasing the bomb from the horizontal position. This allowed a rapid rotation to the vertical position where a spring clip held it.

A glass tube, approximately 1 inch in diameter and 10 inches long, having a thin bottom, was placed horizontally in the bomb. In this position the glass tube held as much as 30 ml. of 90% peroxide. When the bomb was rotated to the vertical position, the glass tube fell to the bottom of the bomb, where the appropriate amount of $Ca(MnO_4)_2$ had been placed. This resulted in a measurable pressure rise in the bomb, which was followed by the General Motors capacitor gage to be described in the section on thrust motors. An 18–8 stainless steel liner was used to protect the carbon steel bomb proper.

Early experiments showed that the rate of pressure development had little correlation with the results of the thrust motor work. In the bomb the rate of mixing was so much slower than the rate of reaction that the mixing rate entirely governed the rate of pressure build-up. Therefore, the results are not comparable and hence of little significance.

Development of Oxygen Pressure. The use of air or other gas under high pressure was required to accomplish the injection of peroxide and permanganate in the launching of the JB-2 bombs. To have adequate amounts of the high pressure gas in the field would require considerable heavy equipment in the form of compressors and storage cylinders. A means of eliminating this amount of heavy equipment would be advantageous.

One suggestion was to produce the necessary gas pressure by the controlled decomposition of concentrated peroxide. This suggestion envisaged the slow decomposition of peroxide in a pressure reservoir, to produce oxygen under pressure and temperature conditions at which the water would be liquid. The oxygen pressure reservoir could then be used for the injection of peroxide and permanganate. The first attempts to decompose concentrated peroxide were carried out in an open 250-ml. beaker using 100 ml. of 90% peroxide and adding to it a few drops of 0.1 N $KMnO_4$; if this small amount was added without stirring, rather vigorous decomposition occurred but only in the surface layer. If the $KMnO_4$ was stirred into the peroxide, about 30 p.p.m. would cause uniform and total decomposition in about an hour.

This amount of permanganate was used in attempts to decompose peroxide in the Aminco bomb. The peroxide was placed in the bottom of a stainless steel liner in the bomb, and the $KMnO_4$ solution added to it by tilting the bomb from a near horizontal position to the vertical position; the glass bulb containing $KMnO_4$ then fell into the peroxide and broke against a steel rod. This method gave erratic results which were attributed to lack of uniform mixing. A special head for the Aminco bomb was then made for adding peroxide to the bomb at a controlled rate. The head contained a $1^1/_4$-inch stainless steel reservoir 2 feet long, connected to the inside of the bomb through the head and having a $^1/_4$-inch stainless steel needle valve at the bottom and a $^1/_2$-inch stainless steel tube at the top. By this arrangement, peroxide was added to the catalyst—$KMnO_4$, $Ca(MnO_4)_2$, MnO_2, or PbO_2—in the bomb at a rate slow enough to allow the heat of reaction to dissipate so that the gage pressure recorded was due solely to oxygen formed by decomposition of peroxide and not at all to steam pressure. The data from these experiments (Table I) show that peroxide can be decomposed at a controlled rate to give the calculated pressures. Discrepancies in observed and calculated pressures are due to the bomb being warm at the time of final reading.

Table I. Controlled Decomposition of 90% Peroxide (400 Ml.)

Run No.	Catalyst	Total Time, Min.	Pressure, Lb./Sq. In.		Bomb Temp.
			Final	Calcd.	
1	50 ml. 0.1 *N* $KMnO_4$	45	1850	1850	......
2	50 ml. 0.1 *N* $KMnO_4$	55	1835	1850	Normal
3	10 ml. $Ca(MnO_4)_2$[a]	52	2200	1785	Very hot
4	5 g. MnO_2	50	1950	1785	Warm
5	5 g. PbO_2	43	1950	1785	Warm

[a] Solution was 41% MnO_4^-.

If the peroxide reservoir became too hot, the peroxide decomposed at a rapid, violent, and dangerous rate. This is in conformity with the known fact that peroxide may "explode" at or near its normal boiling point.

THRUST MOTOR ASSEMBLY

A typical open reaction chamber or thrust motor assembly consisted of a feed pressure storage tank, blow cases to hold the test materials, quick-opening liquid control valves, and the thrust motor.

Thrust Motors. The design simulated in some respects the large launcher breech used in assisted take-off (Figure 2). The motor was made of 3$^1/_2$-inch round bar 18–8 stainless steel, type 304. The chamber proper was 2$^3/_4$ inches i.d. and 6$^1/_2$ inches long, and was designed for a bursting strength of approximately 10,000 pounds per square inch. It utilized hemispherical design at the rear of the motor and a heavy flanged connection for the exhaust nozzle. Three inlet nozzle entrances were provided in the side wall of the chamber, with two of them directly opposing each other and the third at a 45° angle to one of them. This provided flexibility in operation. Any entrances not in use were plugged. Side-entrance nozzles were utilized since they more nearly approximated the injection to be used in the larger scale work. Two pressure tap locations were placed in the side walls of the chamber between the nozzle entrance and the exhaust nozzle connection, and consisted of 1-inch diameter openings to take the General Motors capacitance gage. The nozzle entrances were $^3/_4$ inch in diameter, which permitted any desired variation in nozzle size. The flange connection for the exit nozzle was tongue-and-groove design to ensure adequate sealing with a soft copper gasket. Shear bolts held the exit nozzle to the thrust motor chamber proper and were designed to allow the exit nozzle to blow off between 2000 and 2500 pounds per square inch. This safety measure proved highly desirable in practice, since numerous explosions occurred that blew off the exhaust nozzle without any damage to the thrust motor chamber itself. The stainless steel construction of the motor had adequate corrosion resistance for all the work carried out, and showed little or no evidence of corrosion from any of the runs.

Exhaust Nozzles. Venturi type nozzles were used (Figure 2). No effort was made to introduce any cooling to the exhaust nozzle, since the runs never exceeded 2 seconds and were usually less. The nozzles showed excellent life on these short runs. The flange holding the nozzle to the thrust motor chamber was grooved to fit the corresponding tongue of the chamber. The design proved satisfactory and afforded protection to the sealing surface, with the result that no nozzle was damaged in any chamber explosion, although some of them caused the nozzle to be thrown from 50 to 200 feet.

Injection Nozzles. Design of these solid stream nozzles (Figure 2) was based on velocities of approximately 100 feet per second at the nozzle orifice. The orifice had a rounded inlet and a length of approximately its own diameter. Pressure drops through these nozzles were not measured, but were estimated to be in the neighborhood of 100 pounds per square inch at flow rates corresponding to velocities at the orifice of 100 feet per second. In comparing flow rates of two liquids entering the thrust motor at the same time, it was assumed that their volume rates of flow were directly proportional to the nozzle orifice areas. No difficulties were experienced with regard to mechanical strength of the nozzles, and no nozzle was damaged at any time. The high liquid velocities of the solid stream jets afforded good mixing with the jets impinging on each other at an angle of 135°. This angle prevented the stream from entering the opposing nozzle.

Blow Cases. The blow cases used to contain the liquids tested were constructed of 18–8 stainless steel. Two sizes were constructed; the larger, used for the concentrated peroxide, had a total capacity of approximately 800 ml. It was constructed of 3-inch, schedule 80, 18–8 stainless steel pipe with welding cap ends and was designed to have a bursting pressure in excess of 8000 pounds per square inch. Vertical baffles were welded inside to prevent vortexing of the liquid during the rapid emptying of the blow case. The design was satisfactory, but small amounts of liquid were held up in the blow case and line which resulted in a mist or foglike flow at the end of a run. The small blow case, used for the permanganate, had a total capacity of approximately 90 ml.; it was constructed of 1-inch, schedule 80, 18–8 stainless steel pipe with welding cap ends. No baffles were used since the diameter was small enough so that vortexing would not be serious. The only change required was to enlarge the inlet fitting to $^1/_2$-inch Army-Navy Standard Fitting as a result of loading difficulties.

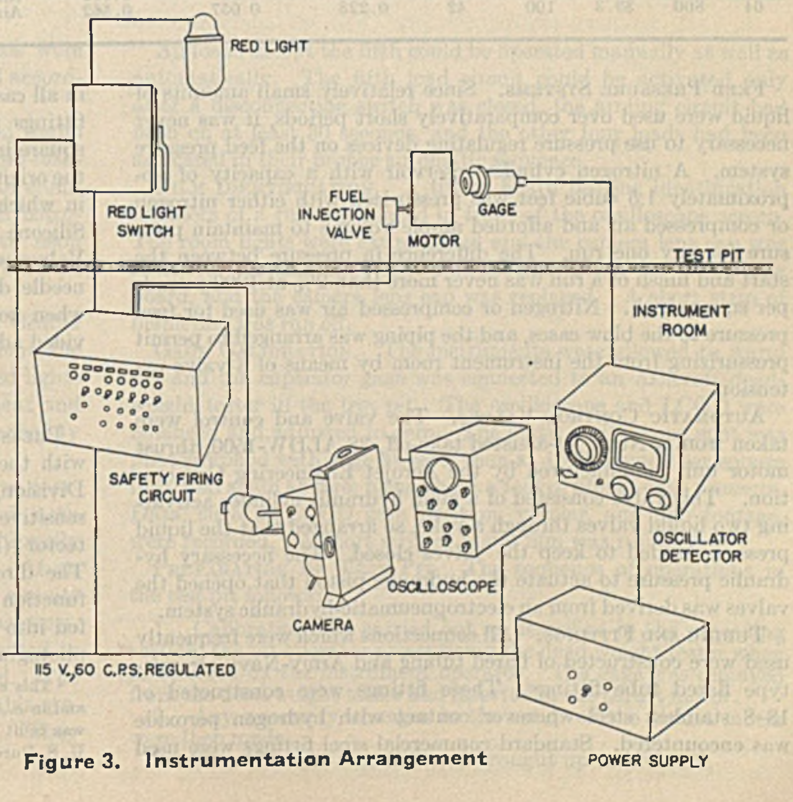

Figure 3. Instrumentation Arrangement

Table II. Effect of Variables on Results

Run No.	Peroxide		Permanganate		Nozzles, Inches			Gas	Pressures, Lb. per Sq. In.			Time, Seconds			
	Ml.	%	Ml.	%	Peroxide	Permanganate	Exhaust		On blow-case	IASP	FASP	SSP	ESP	EI	DSI
3	200	90	50	52	0.080	0.025	0.258	N_2	950	570	780	0.06	1.25	1.40	1.19
5	250	90	25	52	0.180	0.057	0.562	N_2	900	650	780	0.05	0.28	0.59	0.23
6	250	90	25	52	0.180	0.057	0.562	N_2	900	680	700	0.05	0.29	0.57	0.24
7	500	90	50	52	0.254	0.080	0.795	N_2	900	520	500	0.05	0.38	0.69	0.33
8	500	90	50	52	0.254	0.080	0.795	N_2	900	560	500	0.05	0.42	0.72	0.37
9	750	90	75	52	0.254	0.080	0.795	N_2	900	550	550	0.06	0.63	0.79	0.57
11	750	90	75	52	0.254	0.080	0.795	N_2	900	550	550	0.06	0.68	0.82	0.62
12	750	90	75	52	0.254	0.080	0.795	N_2	900	550	500	0.06	0.63	0.80	0.57
13	750	90	75	52	0.254	0.080	0.795	N_2	900	550	520	0.06	0.65	0.81	0.50
14	750	90	75	52	0.254	0.080	0.795	N_2	900	500	550	0.06	0.67	0.87	0.61
15	750	90	75	52	0.254	0.080	0.795	N_2	900	550	550	0.06	0.64	0.78	0.58
16	750	90	75	52	0.254	0.080	0.795	N_2	900	550	550	0.06	0.64	0.78	0.58
17	750	90	75	52	0.254	0.080	0.795	N_2	900	550	550	0.06	0.63	0.74	0.57
18	750	90	75	52	0.254	0.080	0.795	N_2	1500	800	900	0.05	0.23	0.39	0.18
19	750	90	75	35	0.254	0.080	0.795	N_2	900	550	500	0.06	0.66	0.75	0.60
20	750	90	75	35	0.254	0.080	0.795	N_2	900	550	500	0.06	0.66	0.73	0.60
21	750	90	75	35	0.254	0.080	0.795	N_2	900	600	550	0.05	0.65	0.68	0.68
22	750	70	75	35	0.254	0.080	0.795	N_2	900	550	500	0.05	0.46	0.67	0.41
23	750	70	75	35	0.254	0.080	0.795	N_2	870	525	475	0.05	0.43	0.73	0.38
24	750	70	75	52	0.254	0.080	0.795	N_2	900	575	500	0.05	0.37	0.71	0.32
25	750	70	75	52	0.254	0.080	0.795	N_2	900	550	500	0.05	0.33	0.68	0.28
27	750	90	37.5	35	0.254	0.080	0.795	N_2	900	600	550	0.05	0.57	0.68	0.52
28	750	90	37.5	32	0.254	0.057	0.795	N_2	880	600	600	0.05	0.55	0.65	0.50
29	750	90	37.5	35	0.254	0.057	0.795	N_2	900	550	550	0.05	0.67	0.77	0.62
30	750	70	37.5	35	0.254	0.057	0.795	N_2	910	550	500	0.05	0.32	0.58	0.27
31	750	71	37.5	35	0.254	0.057	0.795	N_2	900	550	500	0.05	0.31	0.55	0.26
33	750	90	75	52[a]	0.254	0.080	0.795	N_2	900	600	550	0.04	0.58	0.79	0.54
34	750	90	75	52[b]	0.254	0.080	0.795	N_2	900	600	600	0.04	0.59	0.78	0.55
37	750	89.5	75	41	0.254	0.080	0.795	Air	1000	566	500	0.06	0.18	0.26	0.13
38	750	89.5	75	41	0.254	0.080	0.795	Air	1000	587	472	0.04	0.50	0.66	0.46
39	750	89.5	75	41	0.254	0.080	0.795	Air	1000	598	448	0.07	0.47	0.88	0.40
40	750	89.5	75	41	0.254	0.080	0.795	Air	1000	610	560	0.07	0.69	0.83	0.62
41	750	89.5	75	41	0.254	0.080	0.795	Air	800	529	541	0.07	0.67	0.86	0.60
42	750	89.5	75	41	0.254	0.080	0.795	Air	1200	706	706	0.07	0.17	0.58	0.11
43	750	89.5	75	41	0.254	0.080	0.795	Air	1000	623	659	0.08	0.19	0.65	0.11
44	750	89.3	75	42	0.254	0.080	0.795	Air	1000	693	671	0.10	0.36	0.79	0.26
45	750	89.3	75	42	0.254	0.080	0.795	Air	1000	625	625	0.08	0.34	0.83	0.26
46	750	89.3	75	42	0.254	0.080	0.795	Air	1000	591	579	0.03	0.44	0.76	0.41
47	750	89.3	75	42	0.254	0.080	0.795	Air	975	638	625	0.03	0.43	0.83	0.40
48	750	89.3	75	42	0.254	0.080	0.562	Air	1200	941	1000	0.10	0.69	1.06	0.59
49	750	89.3	75	42	0.254	0.080	0.795	Air	1200	678	744	0.04	0.26	0.72	0.22
50	750	89.0	75	42	0.254	0.080	0.795	Air	1200	710	750	0.01	0.24	0.81	0.23
51	800	89.3	50	42	0.228	0.057	0.795	Air	1200	680	680	0.02	0.27	0.79	0.25
53	800	89.3	50	42	0.228	0.057	0.562	Air	1200	920	930	0.02	0.68	1.07	0.66
54	800	89.3	50	42	0.228	0.057	0.562	Air	1200	880	920	0.05	0.59	1.09	0.55
55	800	89.3	25	42	0.228	0.057	0.562	Air	1200	850	930	0.05	0.71	0.97	0.66
56	800	89.3	10	42	0.228	0.057	0.562	Air	1150	840	880	0.05	0.71	0.94	0.66
57	800	89.3	80	42	0.228	0.057	0.562	Air	1200	920	990	0.05	0.68	1.10	0.63
58	800	89.3	125	42	0.228	0.057	0.562	Air	1200	910	940	0.04	0.72	1.05	0.68
59	800	82	100	42	0.228	0.057	0.562	Air	1200	870	940	0.05	0.67	1.04	0.62
60	800	72	100	42	0.228	0.057	0.562	Air	1200	820	860	0.05	0.61	0.93	0.57
61	800	62	100	42	0.228	0.057	0.562	Air	1200	800	820	0.05	0.52	0.86	0.47
62	800	51.3	100	42	0.228	0.057	0.562	Air	1200	730	810	0.05	0.46	0.74	0.41
63	800	89.3	100	52	0.228	0.057	0.562	Air	1200	930	960	0.02	0.77	1.22	0.76
64	800	89.3	100	42	0.228	0.057	0.562	Air	1200	860	930	0.02	0.79	1.17	0.77

Feed Pressure Systems. Since relatively small amounts of liquid were used over comparatively short periods, it was never necessary to use pressure regulating devices on the feed pressure system. A nitrogen cylinder reservoir with a capacity of approximately 1.5 cubic feet was pressurized with either nitrogen or compressed air and afforded ample volume to maintain pressure for any one run. The difference in pressure between the start and finish of a run was never more than 2% at 1200 pounds per square inch. Nitrogen or compressed air was used for feed pressure to the blow cases, and the piping was arranged to permit pressurizing from the instrument room by means of a valve extension.

Automatic Control Valves. The valve and control were taken from a Navy jet-assisted take-off, 38 ALDW-1500, thrust motor unit manufactured by the Aerojet Engineering Corporation. This valve consisted of a main hydraulic cylinder activating two liquid valves through a yoke, so arranged that the liquid pressure tended to keep the valves closed. The necessary hydraulic pressure to actuate the hydraulic piston that opened the valves was derived from an electropneumatic-hydraulic system.

Tubing and Fittings. All connections which were frequently used were constructed of flared tubing and Army-Navy aircraft-type flared tube fittings. These fittings were constructed of 18-8 stainless steel wherever contact with hydrogen peroxide was encountered. Standard commercial steel fittings were used in all cases where corrosion resistance was not necessary. These fittings proved adequate at pressures up to 2000 pounds per square inch and permitted quick assembly and disassembly after the original tubing had been flared and made up. For connections in which there was danger of contact with hydrogen peroxide, Silicone grease was used in place of standard pipe lubricants. Valves were of forged or stainless steel, and were globe, gate, or needle design as required. Bar-stock needle valves were used when no liquid flows were encountered, since these valves provided adequate mechanical strength.

INSTRUMENT DESIGN AND OPERATION

Pressure Recording. Reaction pressures were measured with the indicator equipment[4] made by Research Laboratories Division, General Motors Corporation. It consisted of a pressure-sensitive element (capacitor gage), a link-coupled oscillator detector (LCOD), and its link-coupled power supply (LCPS). The direct-current output from the LCOD is a direct linear function of the pressure applied to the gage. This output was fed into a cathode-ray oscilloscope, and the resulting trace was photographed on 35-mm. motion picture film. General Elec-

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[4] This equipment is described in detail in the GMC Instruction Manual, and in *S.A.E. Journal* [52, 534–56 (1944)]. The pressure-sensitive element was built by General Motors according to the design of B. H. Sage of the U. S. Bureau of Mines Explosives Laboratory.

TABLE II (*Continued*)

Run No.	Peroxide		Permanganate		Nozzles, Inches			Gas	Pressures, Lb. per Sq. In.			Time, Seconds			
	Ml.	%	Ml.	%	Peroxide	Permanganate	Exhaust		On blow-case	IASP	FASP	SSP	ESP	EI	DSI
65	800	89.3	100	35	0.228	0.057	0.562	Air	1200	870	920	0.02	0.78	1.15	0.76
66	800	89.3	100	25	0.228	0.057	0.562	Air	1200	880	920	0.02	0.76	1.10	0.74
67	800	89.3	100	15	0.228	0.057	0.562	Air	1200	860	910	0.02	0.71	1.06	0.69
68	800	89.3	100	5	0.228	0.057	0.562	Air	1200	840	870	0.02	0.60	0.96	0.58
69	800	72	100	52	0.228	0.057	0.562	Air	1200	800	820	0.02	0.41	0.90	0.39
70	800	72	100	41	0.228	0.057	0.562	Air	1200	810	820	0.02	0.37	0.83	0.35
71	800	72	100	35	0.228	0.057	0.562	Air	1200	810	820	0.02	0.41	0.87	0.39
72	800	72	100	25	0.228	0.057	0.562	Air	1200	810	820	0.02	0.39	0.86	0.37
73	800	72	100	15	0.228	0.057	0.562	Air	1200	810	820	0.02	0.43	0.83	0.41
74	800	72	100	5	0.228	0.057	0.562	Air	1200	770	760	0.02	0.51	0.96	0.49
75	800	89.3	100	41	0.228	0.057	0.562	Air	1200	840	930	0.02	0.92	1.26	0.90
76	800	89.3	100	41	0.228	0.057	0.562	Air	1200	840	930	0.02	0.94	1.24	0.92
77	800	89.3	100	41	0.228	0.057	0.562[c]	Air	1200	780	830	0.02	0.82	1.27	0.81
78	800	89.3	100	41	0.228	0.057	0.562[c]	Air	1200	875	1040	0.02	0.70	1.16	0.69
79	800	89.3	100	50[d]	0.228	0.057	0.562	Air	1200	920	930	0.03	0.77	1.21	0.73
80	800	89.3	100	25[d]	0.228	0.057	0.562	Air	1200	920	965	0.02	0.70	1.18	0.68
81	800	89.3	100	50[d]	0.228	0.057	0.562	Air	1200	920	980	0.02	0.77	1.21	0.75
82	800	89.3	100	41[d]	0.228	0.057	0.562	Air	1200	860	980	0.02	0.73	1.21	0.71
83	800	89.3	100	41[d]	0.228	0.057	0.562	Air	1200	920	960	0.02	0.81	1.17	0.79
84	800	89.3	100	25[d]	0.228	0.057	0.562	Air	1200	890	980	0.03	0.75	1.18	0.72
85	800	89.3	100	41	0.228	0.057	0.562	Air	1200	920	960	0.01	0.79	1.21	0.78
86	800	89.3	100	41	0.228	0.057	0.562	Air	1400	960	980	0.01	0.58	0.95	0.57
87	800	89.3	100	41	0.228	0.057	0.562	Air	1200	910	930	0.01	0.73	1.19	0.72
88	800	89.3	100	41	0.228	0.057	0.562	Air	1000	790	820	0.01	0.88	1.28	0.87
89	800	89.3	100	42	0.228	0.057	0.562	Air	800	620	700	0.02	1.16	1.51	1.14
90	800	89.3	100	42	0.228	0.057	0.562	Air	600	490	510	0.01	1.54	1.93	1.53
91	800	89.3	100	41	0.228	0.057	0.562[c]	Air	1200	870	890	0.03	0.74	1.10	0.72
92	800	89.3	100	41	0.228	0.057	0.562[c]	Air	1200	810	780	0.03	0.74	1.13	0.71
93	800	70	100	41	0.228	0.057	0.562[c]	Air	1200	720	780	0.04	0.33	0.66	0.29
94	800	70	100	41	0.228	0.057	0.562[c]	Air	1200	760	820	0.07	0.47	0.91	0.40
95	800	89.4	100	41	0.228	0.057	0.562	Air	1000	770	850	0.01	0.91	1.20	0.90
96	800	89.4	100	41	0.228	0.057	0.562	Air	1200	880	910	0.03	0.83	1.20	0.80
97	800	73	100	41	0.228	0.057	0.562	Air	1200	780	780	0.03	0.44	0.91	0.41
98	800	73	100	41	0.228	0.057	0.562	Air	1200	760	710	0.03	0.52	0.80	0.49
99	680	73	100	41	0.228	0.057	0.562	Air	1200	745	715	0.02	0.44	0.77	0.42
100	800	75.1	100	41	0.228	0.057	0.562	Air	1200	815	755	0.02	0.52	0.96	0.50
101	800	75.1	100	41	0.228	0.057	0.562	Air	1200	805	785	0.03	0.51	0.99	0.48
102	520	75.1	100	41	0.228	0.057	0.562	Air	1200	795	825	0.03	0.22	0.72	0.19
103	800	89.7	400	41	0.228	0.080	0.562	Air	1200	850	895	0.01	0.83	1.16	0.84
104	800	89.7	400	41	0.228	0.080	0.562	Air	1200	860	935	0.03	0.85	1.16	0.82
105	800	48.4	400	41	0.228	0.080	0.562	Air	1200	675	715	0.06	0.29	0.77	0.23
106	800	48.4	400	41	0.228	0.080	0.562	Air	1200	615	640	0.01	0.24	0.70	0.23
108	800	50.2	400	52	0.228	0.080	0.562	Air	1200	675	645	0.08	0.48	0.85	0.40
109	800	50.2	400	52	0.228	0.080	0.562	Air	1200	740	670	0.05	0.45	0.74	0.41
110	800	89.7	400	52	0.228	0.080	0.562	Air	1200	905	830	0.04	0.88	1.18	0.84
111	800	89.7	360	52	0.228	0.080	0.562	Air	1200	880	970	0.04	0.84	1.15	0.80
112	800	89.7	800	41	0.228	0.161	0.562	N_2	1200	890	960	0.01	0.89	1.32	0.88
113	800	89.7	800	41	0.228	0.161	0.562	N_2	1200	840	880	0.02	0.85	1.32	0.83
114	800	50.4	800	41	0.228	0.161	0.562	N_2	1200	750	860	0.02	0.21	0.95	0.19
115	800	50.4	800	41	0.228	0.161	0.562	N_2	1200	720	760	0.03	0.28	0.91	0.24
116	660	50.2	82	41	0.228	0.057	0.562	Air	1000	...	...	...	...	...	...

[a] pH = 0.7. [b] pH = 9.55. [c] Cold run. [d] Sodium permanganate.

tric type CRO-5-S and DuMont type 208 oscilloscopes were used. A special input terminal and switch were installed according to directions given in the GMC Instruction Manual.

The best available continuous camera was the General Radio type 651-AE oscillograph recorder, although several old-fashioned movie cameras were also used after modification to eliminate the intermittent film motion and shutter action. The instrument arrangement is shown in Figure 3. A $^1/_{25}$-watt neon lamp, operated at 60 cycles per second put the time base on all films.

SAFETY AND COORDINATION. After all personnel had cleared from the danger area of the test pit, the red light circuit in the test pit was turned on manually. This circuit posted red lights all around the test area to warn that firing was imminent and provided power for the coil circuit of the arming relay in the safety firing circuit.

The rapid sequence of operations during each test was coordinated by the safety firing circuit (Figure 4). This unit activated five load circuits in rapid succession, with an arbitrarily adjusted time interval between successive load circuits. At an adjustable time after activation of the fifth load, all load circuits were automatically deactivated and the entire unit was reset. The automatic deactivation and resetting could be prevented to allow any particular test to continue indefinitely if desired. The safety firing circuit was designed for general use, and in this system only the third and fourth load circuits were active. They operated the camera and fuel injection valve, respectively.

All loads except the fifth could be operated manually as well as automatically. The fifth load circuit could be activated only after a disconnecting switch was closed, the arming circuit had been on at least 30 seconds, and the other four loads had been activated in their proper automatic sequence.

FILM IDENTIFICATION. A titling board bearing identification numbers of a run was placed in front of the oscilloscope screen. The room lights were extinguished and the camera lens cap was removed. A flashlight spot was flashed briefly on the titling board, and the camera lens cap was replaced. A short strip of blank film was run off.

GAGE CALIBRATION. The instruments were allowed to warm up, and the capacitor gage was connected to an Ashcroft deadweight tester in the test pit. The oscilloscope and LCOD were balanced and adjusted to zero. The static oscilloscope spot was photographed with gage at zero, then at 1000 pounds per square inch, and again at zero, using about a foot of film at each pressure. Data, such as LCOD gain position, vernier, and film footage, were recorded. A short strip of blank film was run off.

PREPARATION OF TEST PIT. The sequence of operations in the test pit follows:

1. Calibration was carried out as described in the preceding section, the pit operator pressurizing the dead weight tester when so directed by the instrument operator. The gage was removed from the dead weight tester and inserted in the thrust motor.
2. Any necessary changes in the setup of the thrust motor were then made.
3. The drive gas reservoir was brought up to pressure.

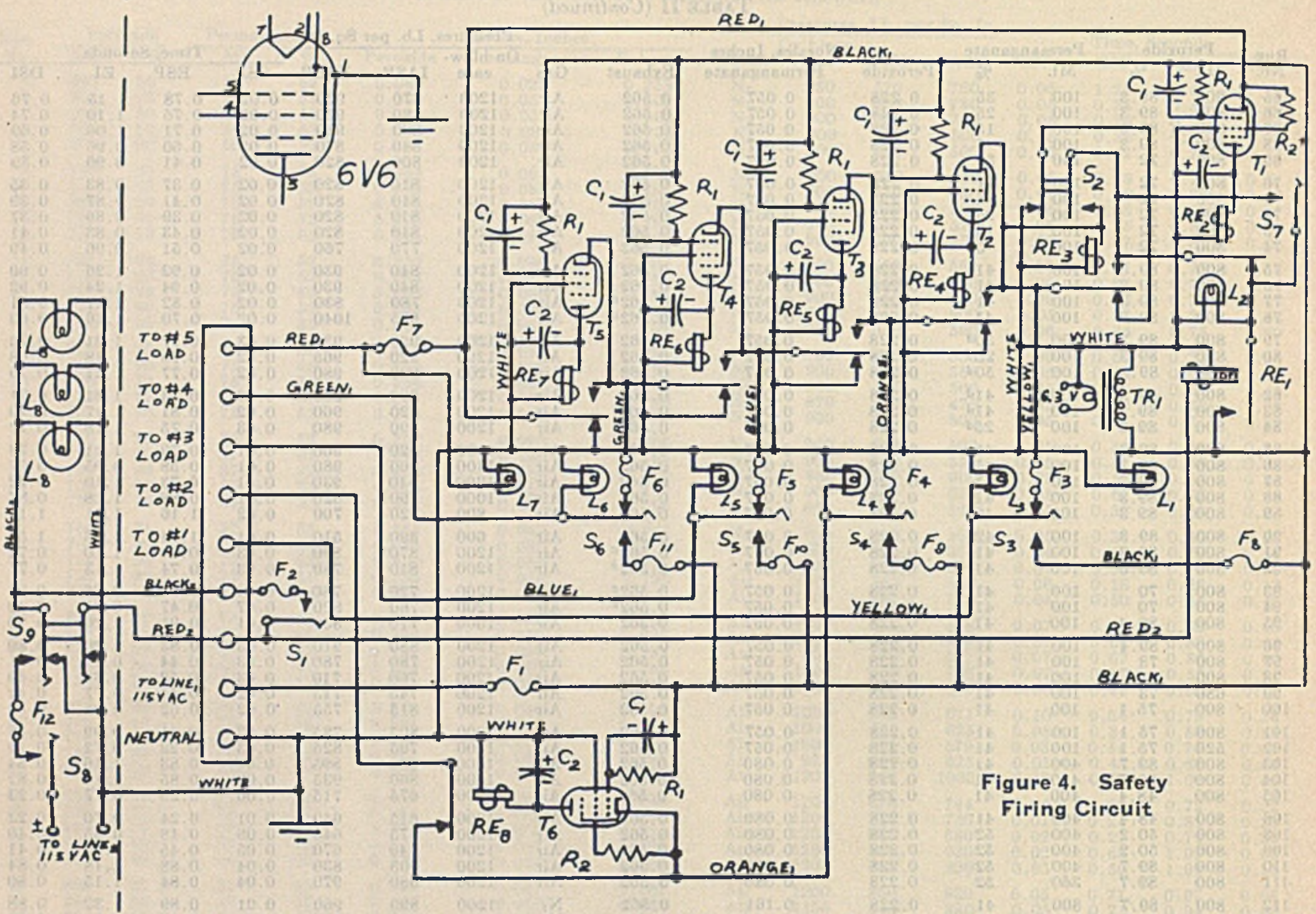

Figure 4. Safety Firing Circuit

4. The blow cases were disconnected, filled, and reconnected.
5. The vent valve between blow case and main gas drive valve was closed.
6. All personnel cleared the pit. The pit operator, upon leaving the pit, turned on the red light circuit and blew the warning whistle.
7. Firing was then carried out as described in the following section. Then the vent valve was opened when the pit was first entered.
8. The capacitor gage was removed from the motor, cooled, washed under a stream of water, dried, and placed in the dead weight tester. (Care was taken to see that the electrical connection was not wet during cleaning.)

Firing. The following was the firing sequence:

1. After the red lights came on and the warning whistle blew, the arming switch on the safety firing circuit was closed.
2. After a 30-second delay and after the officer in charge of the test pit opened the main drive gas valve and closed the necessary disconnecting switches in the instrument room, firing could proceed.
3. Room lights were extinguished, and the camera lens cap was removed. The starter switch on the safety firing circuit was pressed, and the run continued automatically.
4. When the run was completed, the camera cap was replaced, lights were turned on, and a short strip of blank film was run off.
5. The fuel injection valve was reopened manually to blow air through the combustion chamber and thus flush out any residual gases in the motor. The disconnecting switches were opened, main drive gas valve was closed, red lights were turned off, and outside observers were notified that the pit could be reentered.
6. The film was again identified as described in the section on Film Identification.

Results and Conclusions. Under all conditions of injection the initiation of the reaction was spontaneous and rapid. The power developed was characterized by a smooth rise within 0.01–0.02 second to operating pressures as high as 1000 pounds per square inch. This pressure was maintained during the entire period of injection.

Table II lists data of all runs. Various runs were selected to illustrate the effect of altering certain variables.

Figure 5 presents typical pressure-time curves. It shows the normal types of curves expected—a short preliminary irregular trace, followed by a rapid rise to maximum height, a long flat part corresponding to sustained injection, and a final tail-off region. This last region is, in general, sharply marked although in no case is the fall to final chamber pressure as rapid as the initial surge to full operating pressure. This is doubtless due to the injection of a mist or spray of peroxide from the residual liquid remaining in the blow case after the main bulk of the liquid has been injected. Below each curve is a broken line which constitutes the time base. The dashes were caused by the alternate flashes of the two filaments of a neon lamp operating on 60-cycle current; hence each flash corresponds to $^1/_{120}$ second. Figure 5 shows the relation between the heights and durations of maximum pressure using 90, 70, and 50% peroxide, respectively. The maximum pressure is higher and its duration longer, the higher the concentration of peroxide.

To characterize the various runs and to analyze the data obtained from them, it was necessary to define certain values which have been measured on the film strips: The initial maximum pressure (IMP) was taken as the value of the pressure when it had reached a steady state. The initial average sustained pressure (IASP) was taken as the average pressure during the first part of the run, after full pressure had been reached. The final average sustained pressure (FASP) was the average pressure

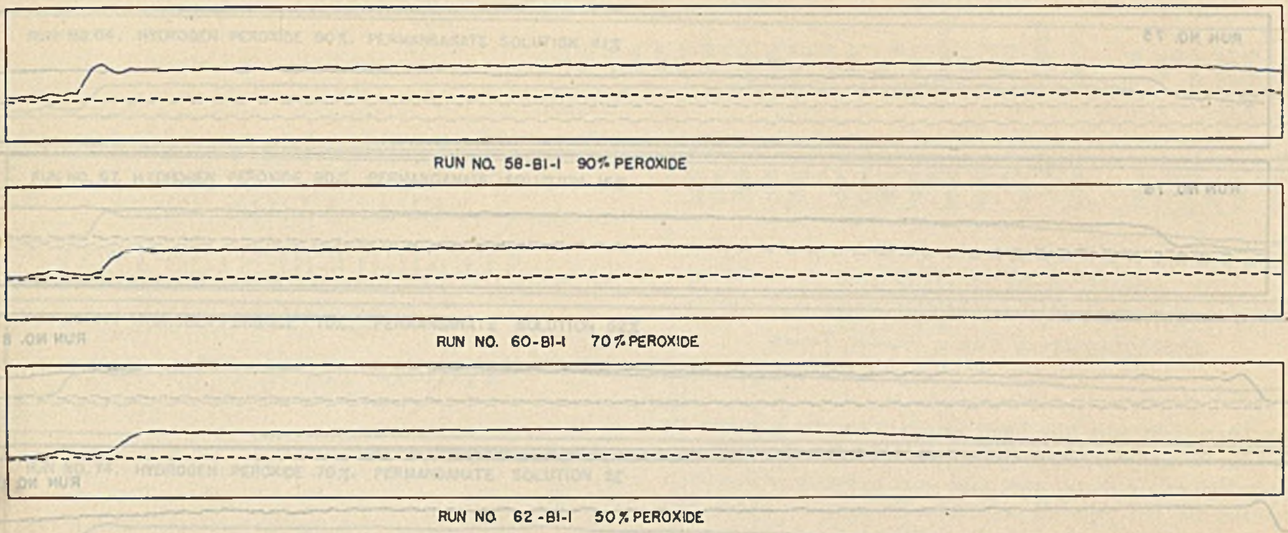

Figure 5. Typical Operating Curves to Show Effect of Different Concentrations of Hydrogen Peroxide

near the end of the run, before the pressure had begun to fall off markedly.

In many runs IASP and FASP were nearly identical. Yet it was necessary to define these terms to provide for certain runs which showed a distinctly lower or higher pressure during the second half of the run.

The start of injection (SI) is defined as the time at which the first rise in pressure was noted. The start of sustained pressure (SSP) was taken as the time at which IMP was reached. The end of sustained pressure (ESP) is the time at which the FASP had fallen to approximately 90% of its value near the end of a run, and after which the pressure falls off in a regular manner.

Table III. Pressure Development in Thrust Motors at Various Input and Efflux Rates

Run No.	Nozzle Diameter, In. H_2O_2 inlet	Nozzle Diameter, In. MnO_4^- inlet	Nozzle Diameter, In. Exhaust	Volume, Ml. H_2O_2	Volume, Ml. MnO_4^-	Pressure, Lb./Sq. In. IASP	Pressure, Lb./Sq. In. FASP	Time, Sec. DSI	Time, Sec. DI
Section *A*[a]									
3	0.080	0.025	0.26	200	50	570	780	1.19	1.34
5	0.180	0.057	0.56	250	25	650	680	0.23	0.54
6	0.180	0.057	0.56	250	25	680	700	0.24	0.52
7	0.254	0.084	0.80	500	50	520	500	0.33	0.64
8	0.254	0.080	0.80	500	50	560	500	0.37	0.67
9	0.254	0.080	0.80	750	75	550	550	0.57	0.73
11	0.254	0.080	0.80	750	75	550	550	0.64	0.74
Section *B*[b]									
51	0.228	0.057	0.80	800	50	680	680	0.28	0.79
53	0.228	0.057	0.56	800	50	920	930	0.66	1.05
54	0.228	0.057	0.56	800	50	880	920	0.55	1.04
Section *C*[c], Blowcase Pressure 880 Lb. N_2 per Sq. In.									
9–17 (av.)	0.254	0.080	0.80	750	75	540	540	0.59	0.68
Section *C*[c], Blowcase Pressure 1420 Lb. N_2 per Sq. In.									
18	0.254	0.080	0.80	750	75	850	900	0.23	0.34
Section *D*[d], Chamber Length 6.5 In.									
64	0.228	0.057	0.56	800	100	860	930	0.76	1.14
85	0.228	0.057	0.56	800	100	920	960	0.77	1.17
87	0.228	0.057	0.56	800	100	910	970	0.71	1.19
Section *D*[d], Chamber Length 15.5 In.									
75	0.228	0.057	0.56	800	100	840	930	0.92	1.26
76	0.228	0.057	0.56	800	100	840	930	0.94	1.24

[a] Propellant 90% H_2O_2, catalyst 52% MnO_4^-; blowcase pressure 880 lb. N_2 per sq. in.; chamber length 6.5 in.

[b] Propellant 90% H_2O_2, catalyst 41% MnO_4^-; vol. H_2O_2/vol. MnO_4^- = 16/1; blowcase pressure 1140 lb. air per sq. in.; chamber length 6.5 in.

[c] Propellant 90% H_2O_2, catalyst 52% MnO_4^-; chamber length 6.5 in.

[d] Propellant 90% H_2O_2, catalyst 41% MnO_4^-; vol. H_2O_2/vol. MnO_4^- = 16/1; blowcase pressure 1140 lb./sq. in. In section *D* the ratio of rates of injection of peroxide to permanganate was 16/1 because all of the peroxide entered within the time the first half of the permanganate entered.

In certain cases ESP is difficult to determine with accuracy, since it tapers off gradually; in those instances some arbitrary choice must be used. In most cases, however, this quantity is easy to fix since it is registered as a sharp break in the curve.

The end of injection (EI) is the time at which the pressure curve flattens out and becomes the trace of the gas pressure of the injection system. The duration of sustained injection (DSI) was calculated as the difference between ESP and SSP. These terms are illustrated in Figure 6.

The films were read as follows: The film strip was placed on a sheet of millimeter graph paper on top of a pane of glass which was illuminated from below by an electric light. The vertical displacement between the calibration lines corresponding to zero and 1000 pounds per square inch given by the dead weight tester was read in millimeters. This value, multiplied by 100 and divided by the corresponding height for each item IMP, IASP, and FASP, gave the pressures. The number of dashes, $^1/_{120}$ second each, divided by 120, gave the time in seconds for SSP, ESP, DI, and DSI.

Table III illustrates the effect of differences in chamber pressure, injection pressure, injection rate, and chamber length. The chamber length was increased by means of a 9-inch extension on the thrust motor.

Table IV illustrates the operating conditions obtained when the hydrogen peroxide concentration was varied from 50 to 90%; variations do not affect the manner of power development but determine only its magnitude per unit mass of propellant injected. Figure 5 gives pressure curves illustrating these runs.

Under similar conditions for a series of runs, the reaction proceeds with remarkable reproducibility. Section *A*, Table V, shows a series of runs made under identical conditions, along with the measured results and the normal reproducibility expected. Sections *B* and *C* show two pairs of duplicate runs; curves are reproduced in Figure 7.

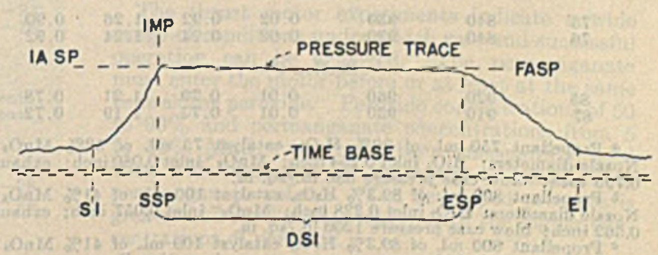

Figure 6. Definition of Values Measured on Film Strips

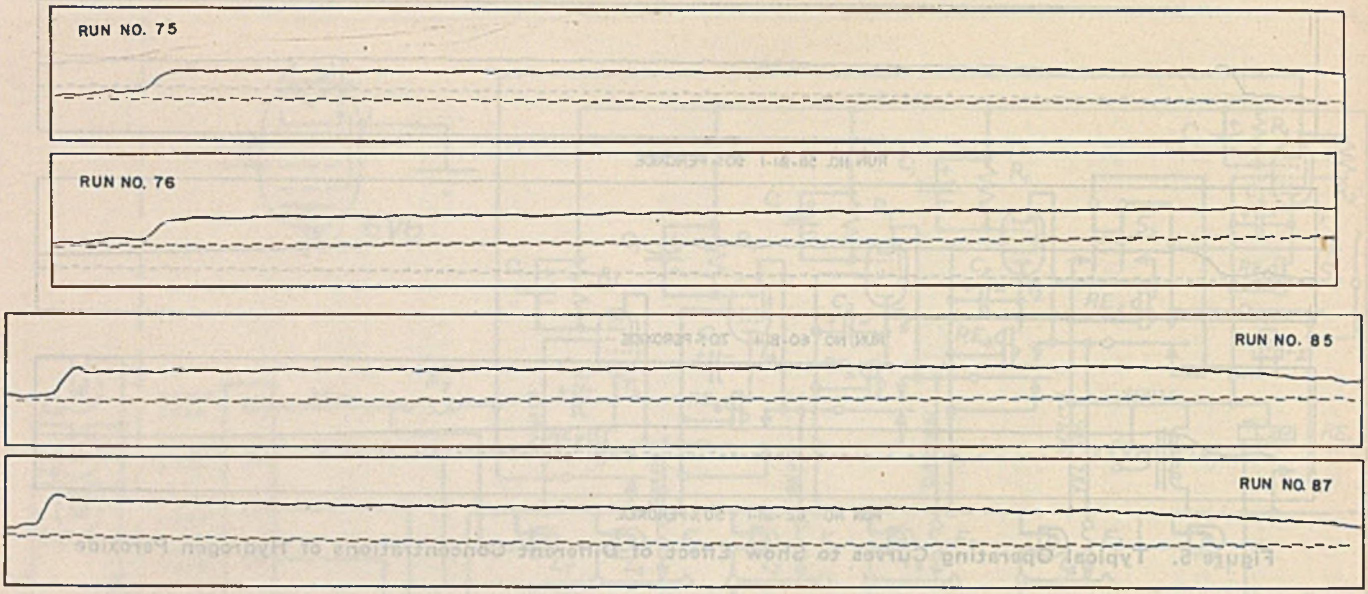

Figure 7. Reproducibility of Duplicate Runs (Compare Run 75 with 76, 85 with 87)

An extreme range of permanganate concentrations and of ratios of propellant to catalyst is permissible and provides adequate safety factors for field use (Table VI and Figure 8). Section *C*, Table VI, shows no noticeable difference in runs in which the pH of the calcium permanganate solution was varied over the wide range from 0.7 to 9.55. Interruption in the flow of either reactant is without dangerous effect, as section *B* shows. A constant ratio of propellant to catalyst was maintained, while the duration of flow of each liquid was controlled by altering the quantity of liquids loaded in the blow cases. It is essential, however, that the permanganate solution precede, or at least arrive simultaneously with, the peroxide to prevent explosions.

Table VII shows the effect of cooling the reactants. There is a slight but scarcely noticeable decrease in pressure, and no shortening of the cold runs as compared to those at ambient temperature. The important point is that the cold runs were not inhibited; this corresponds to successful launchings. Any minor differences could well be due to increased viscosities and densities of the liquids at the lowered temperatures. Thus, the sys-

TABLE IV. PRESSURE DEVELOPMENT IN THRUST MOTORS AT VARIOUS PEROXIDE CONCENTRATIONS

(Propellant, 800 ml. of H_2O_2 solution; catalyst, 100 ml. of 41% MnO_4^-; propellant catalyst ratio = 16/1; blow case pressure 1140 lb./sq. in. Nozzle diameters: H_2O_2 inlet 0.228 inch; MnO_4^- inlet 0.057 inch; exhaust 0.562 inch)

Run No.	Concn. H_2O_2, %	Pressure, Lb./Sq. In.		Time, Sec.		Av. Sustained Pressure × DSI
		IASP	FASP	DSI	DI	
58	90	910	940	0.68	1.05	63
59	80	870	940	0.62	1.04	56
60	70	820	860	0.57	0.93	48
61	60	800	820	0.47	0.68	38
62	50	730	810	0.41	0.74	31

TABLE V. REPRODUCIBILITY OF REACTION CHARACTERISTICS IN THRUST MOTORS

Run No.	Pressure, Lb./Sq. In.		Time, Seconds			
	IASP	FASP	SSP	ESP	EI	DSI
Section *A*[a]						
9	550	550	0.06	0.63	0.79	0.57
11	550	550	0.06	0.68	0.82	0.62
12	550	500	0.06	0.63	0.80	0.57
13	550	520	0.06	0.65	0.81	0.59
14	500	550	0.06	0.67	0.87	0.61
15	550	550	0.06	0.64	0.78	0.58
16	550	550	0.06	0.64	0.78	0.58
17	550	550	0.06	0.63	0.74	0.57
Av.	540	540	0.06	0.65	0.80	0.59
Section *B*[b]						
75	840	930	0.02	0.92	1.26	0.90
76	840	930	0.02	0.94	1.24	0.92
Section *C*[c]						
85	920	960	0.01	0.79	1.21	0.78
87	910	930	0.01	0.73	1.19	0.72

[a] Propellant 750 ml. of 90% H_2O_2, catalyst 75 ml. of 52% MnO_4^-; Nozzle diameters: H_2O_2 inlet 0.254 inch; MnO_4^- inlet 0.080 inch; exhaust 0.795 inch; blow case pressure 880 lb./sq. in.

[b] Propellant 800 ml. of 89.3% H_2O_2, catalyst 100 ml. of 41% MnO_4^-. Nozzle diameters: H_2O_2 inlet 0.228 inch; MnO_4^- inlet 0.057 inch; exhaust 0.562 inch; blow case pressure 1200 lb./sq. in.

[c] Propellant 800 ml. of 89.3% H_2O_2, catalyst 100 ml. of 41% MnO_4^-; nozzle diameters and blowcase pressure same as in section *B*.

TABLE VI. EFFECT OF CATALYST CONCENTRATION AND VOLUME ON PRESSURE DEVELOPMENT IN THRUST MOTORS

Run No.	Permanganate	Pressure, Lb./Sq. In.		Time, Sec.	
		IASP	FASP	DSI	DI
Section *A*[a], H_2O_2 Concentration 90%					
63	52% MnO_4^-	930	960	0.74	1.19
64	40.6	860	930	0.75	1.14
65	35	870	920	0.76	1.13
66	25	880	920	0.73	1.07
67	15	870	910	0.69	1.04
68	5	840	870	0.57	0.92
Section *A*[a], H_2O_2 Concentration 70%					
69	52% MnO_4^-	800	820	0.39	0.88
70	40.6	810	820	0.34	0.81
71	35	810	820	0.39	0.85
72	25	810	820	0.37	0.84
73	15	810	820	0.41	0.81
74	5	870	760	0.49	0.94
Section *B*[b]					
58	125 ml.	910	940	0.68	1.05
57	80	920	980	0.63	1.10
54	50	880	920	0.55	0.94
55	25	850	930	0.66	0.97
56	10	840	880[c]	0.66	0.94
Section *C*[d]					
33	0.7 pH	600	550	0.54	0.79
9–17 (av.)	5.0	540	550	0.59	0.80
34	9.55	600	600	0.54	0.78

[a] 800 ml. of H_2O_2, 100 ml. of MnO_4^-. Nozzle diameters: H_2O_2 inlet 0.228 inch; MnO_4^- 0.057 inch; exhaust 0.56 inch; blow case pressure 1140 lb./sq. in.; chamber length 6.5 inches.

[b] 800 ml. of 90% H_2O_2; MnO_4^- concentration, 41%; nozzle diameters, blow case pressure, and chamber length same as *A*.

[c] Pressure oscillations, 350 lb./sq. in. amplitude after start.

[d] 800 ml. of 90% H_2O_2, 100 ml. of 52% MnO_4^-. Nozzle diameters: H_2O_2 inlet 0.254 inch; inlet MnO_4^- 0.080 inch; exhaust 0.80 inch; blow case pressure 880 lb. N_2 per sq. in.

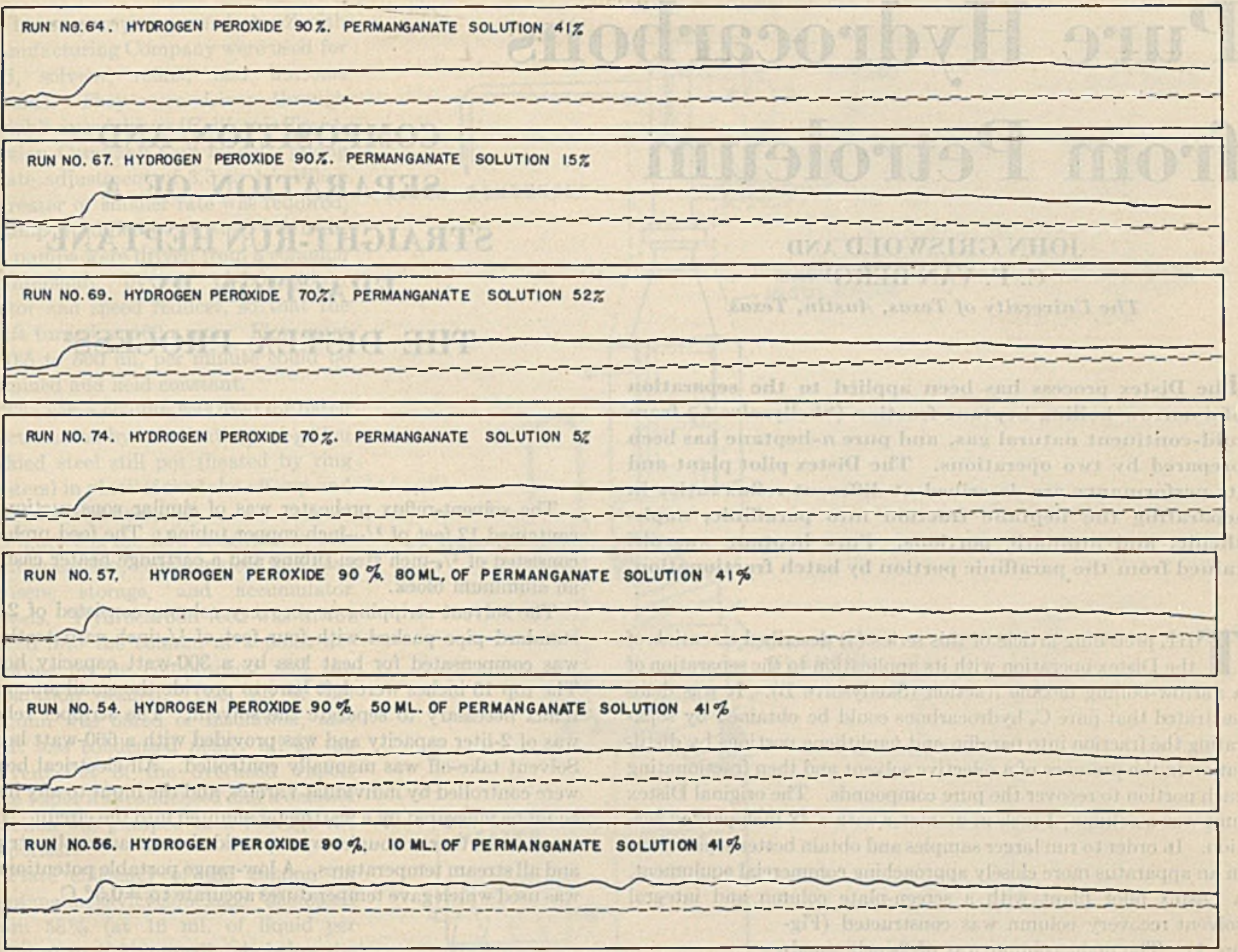

Figure 8. Effect of Catalyst Concentration and Volume on Pressure Development in Thrust Motors

tem permits of operation at low temperatures. In one run bits of luting compound from a threaded joint fell into the peroxide blow case, which caused the peroxide to boil. The run was carried out to note the effect of the elevated temperature. The run proceeded satisfactorily and was indistinguishable from other runs with like concentrations.

Table VII. Effect of Cooling the Reactants

(All runs used same injection and exhaust nozzles throughout, 1200 lb. air pressure on blow cases, 100 ml. of 41% MnO_4^-, 800 ml. of H_2O_2)

Run No.	Concn. of H_2O_2, %	Pressure, Lb./Sq. In. IASP	FASP	Av. of IASP and FASP	Time, Sec. SSP	ESP	EI	DSI	Temp., ° C. H_2O_2	MnO_4^-
				Section *A*						
77	89.3	782	828	805	0.02	0.82	1.27	0.80	12	12
78	89.3	875	1038	957	0.02	0.70	1.16	0.68	9	9
91	89.3	872	892	880	0.03	0.74	1.10	0.71	1	−23
92	89.3	806	782	782	0.03	0.74	1.13	0.71	1	−18
				(Comparable Normal Temperature Runs)						
85	89.3	920	960	940	0.01	0.79	1.21	0.78	Ambient	
96	89.3	879	912	895	0.03	0.83	1.20	0.80	Ambient	
				Section *B*						
93	70	723	782	753	0.04	0.33	0.66	0.29	−28	−28
94	70	762	822	792	0.07	0.47	0.91	0.40	−28	−28
				(Normal Temperature Run)						
70	72	810	820	815	0.02	0.37	0.83	0.35	Ambient	

A series of runs on 73% peroxide, made by concentrating 35% technical grade, showed no distinguishable differences.

A series was run to determine the effect of a large excess of calcium permanganate solution. Eight hundred milliliters of peroxide were used, varying in concentration from 48.4 to 89.7%. The permanganate was either 41 or 52%, and 400 to 800 ml. were used. The runs were directly comparable to the normal runs for the amounts and concentrations of peroxide used, except that a large quantity of unused permanganate, in the form of a purple cloud, issued from the exhaust nozzle.

Runs were carried out to determine whether nitrogen could be used instead of air pressure on the blow cases; no difference was found.

CONCLUSIONS

The thrust motor experiments indicate a wide range of conditions under which safe and successful operation can be achieved. The permanganate must enter the motor before or at least at the same time as the peroxide. Peroxide concentrations of 50 to 90% and permanganate concentrations from 5 to 52% MnO_4^- ion have been successfully used with wide variation in the ratio of peroxide to permanganate volume. The developed pressure is greater and its duration longer with the higher concentrations of peroxide.

Released by authority of the Chief, Chemical Warfare Service.

Pure Hydrocarbons from Petroleum

COMPOSITION AND SEPARATION OF A STRAIGHT-RUN HEPTANE FRACTION BY THE DISTEX PROCESS[2]

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C. F. VAN BERG[1]
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The Distex process has been applied to the separation of a narrow-boiling heptane fraction (Skellysolve C) from mid-continent natural gas, and pure *n*-heptane has been prepared by two operations. The Distex pilot plant and its performance are described at different reflux ratios in separating the heptane fraction into paraffinic, naphthenic, and aromatic portions. Pure heptane was obtained from the paraffinic portion by batch fractionation.

THE preceding article of this series (*4*) described essentials of the Distex operation with its application to the separation of a narrow-boiling hexane fraction (Skellysolve B). It was demonstrated that pure C_6 hydrocarbons could be obtained by separating the fraction into paraffin and naphthene portions by distillation in the presence of a selective solvent and then fractionating each portion to recover the pure compounds. The original Distex unit was a column, 1 inch in diameter with a 48-inch packed section. In order to run larger samples and obtain better separations in an apparatus more closely approaching commercial equipment, a Distex pilot plant with a screen-plate column and integral solvent recovery column was constructed (Figure 1). The main column was of 2-inch standard pipe and had 150 screen plates (called "column 2" in an earlier article, *5*). Details of the columns and heaters are shown in Figure 2.

The main column consisted of six sections of twenty-five plates each. It was wrapped first with Fiberglas tape, then wound with six heating sections of Nichrome wire strung through Fiberglas tubing and insulated with standard pipe lagging. Each heating element had a capacity of about 200 watts and was controlled by an individual Variac. An iron-constantan thermocouple was mounted at the center of each section, projecting to the interior of the column. Each section also included a manometer connection at its top and a feed or takeoff connection at its center.

Figure 2 shows the column as used for solvent operation. The bottom take-off cup was equipped with a sight glass. An air-actuated low-range flowmeter was adapted to the use of a level controller. When a reboiler was employed, the column tended to surge, or flood and drain. This difficulty was eliminated by a hydrocarbon vaporizer consisting of a coil of 5 feet of $^{1}/_{8}$-inch o.d. steel tubing mounted in a steam chamber. The outlet temperature was controlled by adjusting the steam pressure.

The solvent-reflux preheater was of similar construction but contained 12 feet of $^{3}/_{16}$-inch copper tubing. The feed preheater consisted of $^{1}/_{8}$-inch steel tubing and a cartridge heater cast into an aluminum block.

The solvent stripping or recovery column consisted of 2-inch standard pipe packed with four feet of $^{1}/_{8}$-inch card teeth. It was compensated for heat loss by a 300-watt capacity heater. The top 15 inches were left bare to provide the small amount of reflux necessary to separate the solvent. The stripper reboiler was of 2-liter capacity and was provided with a 660-watt heater. Solvent take-off was manually controlled. All electrical heaters were controlled by individual Variacs, and the input to any heater could be measured by a wattmeter shunted into the circuit. Iron-constantan thermocouples were provided to measure the stripper and all stream temperatures. A low-range portable potentiometer was used which gave temperatures accurate to ±0.5° C.

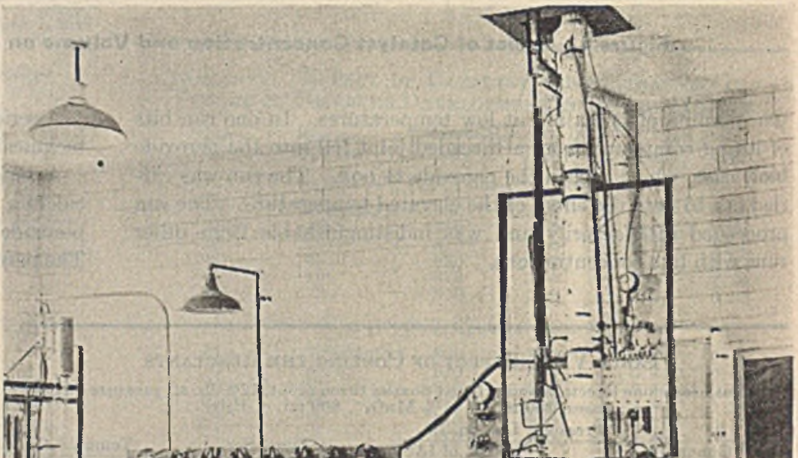

Figure 1. Distex Pilot Plant

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[2] Earlier articles in this series appeared in Volume 35, pages 117–19, 247–51, 854–7 (1943), Volume 36, pages 1119–23 (1944), and Volume 38, pages 61–6 (1946).

Viscose gear pumps made by Zenith Manufacturing Company were used for feed, solvent, reflux, and bottoms streams. They were driven through variable-speed drives (California Transmission Company Cub model), giving a rate adjustment of 3.3 to 1. When a greater or smaller rate was required, a pump of a different capacity was used. All pumps were driven from a common countershaft by a $^1/_6$-horsepower motor and speed reducer, so that the shaft turned at 100 r.p.m. Flow rates of 0.5 to 500 ml. per minute could be obtained and held constant.

The same column was used for batch fractionation by substituting a 4-gallon welded steel still pot (heated by ring heaters) in place of the take-off cup and bottoms vaporizer.

Figure 3 is the flow diagram for solvent operation, showing steel pipe condensers, storage, and accumulator vessels. Hydrocarbon feed was introduced into the column at a point depending on its composition and the separation desired. The top of the column was bared of insulation, and heat loss condensed nearly all of the solvent out of the overhead vapor. The vapor was condensed and a definite fraction was pumped back through the vaporizer.

Plate efficiency of the column on heptane-methylcyclohexane decreased from 58% (at 16 ml. of liquid per minute) to 40% immediately below the flood point of 140 ml. per minute, as reported previously (*5*). Plate efficiency tests for Distex operation using same hydrocarbons in approximately 80 mole % aniline are summarized in Table I. Top and bottom samples from the 150-plate column were so nearly pure heptane and methylcyclohexane that they could not be analyzed with sufficient accuracy for plate computation of the entire column. Samples taken from the fiftieth and hundredth trays and analyzed by the method reported previously (*4*) gave plate efficiencies of 28 to 30%, which is about two thirds of the value for the hydrocarbons alone. It is interesting to note that the flood point of the column (as measured by liquid rate) was not decreased for the solvent operation. The hydrocarbon capacity is much lower in the solvent operation.

OPERATIONAL CONSIDERATIONS

The Distex operation on a pilot plant scale is difficult because all flow rates and temperatures must be maintained constant to obtain satisfactory separation. As noted, all streams were pumped and means were provided for close control of temperatures by electrical and steam heaters. A pressure differential

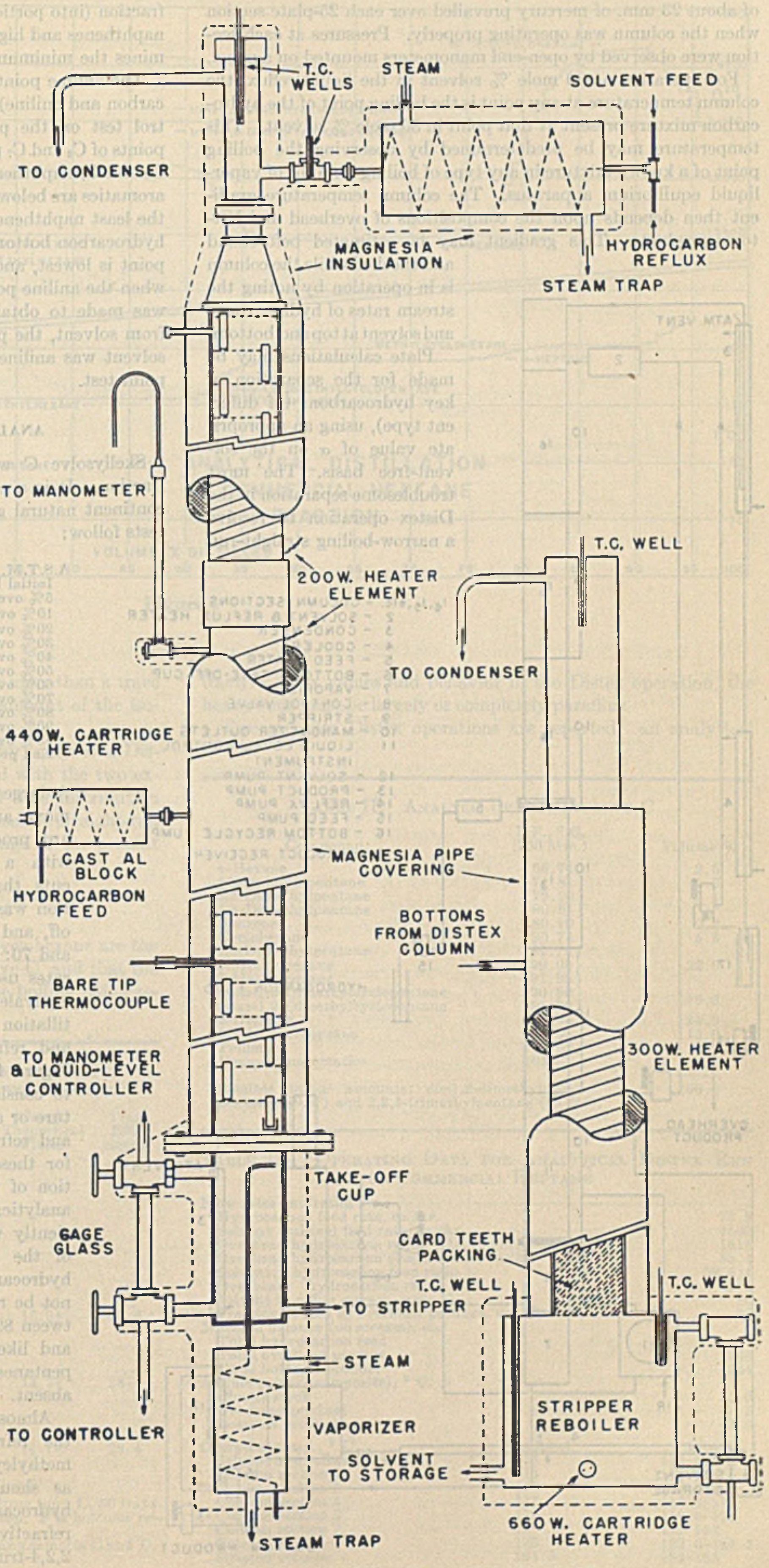

Figure 2. Distex Column and Stripper Detail

of about 23 mm. of mercury prevailed over each 25-plate section when the column was operating properly. Pressures at each section were observed by open-end manometers mounted on a panel.

For operation at 80 mole % solvent in the liquid reflux, the column temperature at any point is the boiling point of the hydrocarbon mixture present at that point in 80 mole % solvent. This temperature may be predetermined by observing the boiling point of a known mixture in any type of boiling-point or of vapor-liquid equilibrium apparatus. The column temperature gradient then depends upon the compositions of overhead and bottoms products. This gradient may be estimated beforehand and checked while the column is in operation by noting the stream rates of hydrocarbons and solvent at top and bottom.

Plate calculations may be made for the separation of key hydrocarbons (of different type), using an appropriate value of α on the solvent-free basis. The most troublesome separation in the Distex operation to resolve a narrow-boiling straight-run fraction (into portions according to type) is between low-boiling naphthenes and higher-boiling paraffins. This separation determines the minimum hydrocarbon reflux ratio as discussed later.

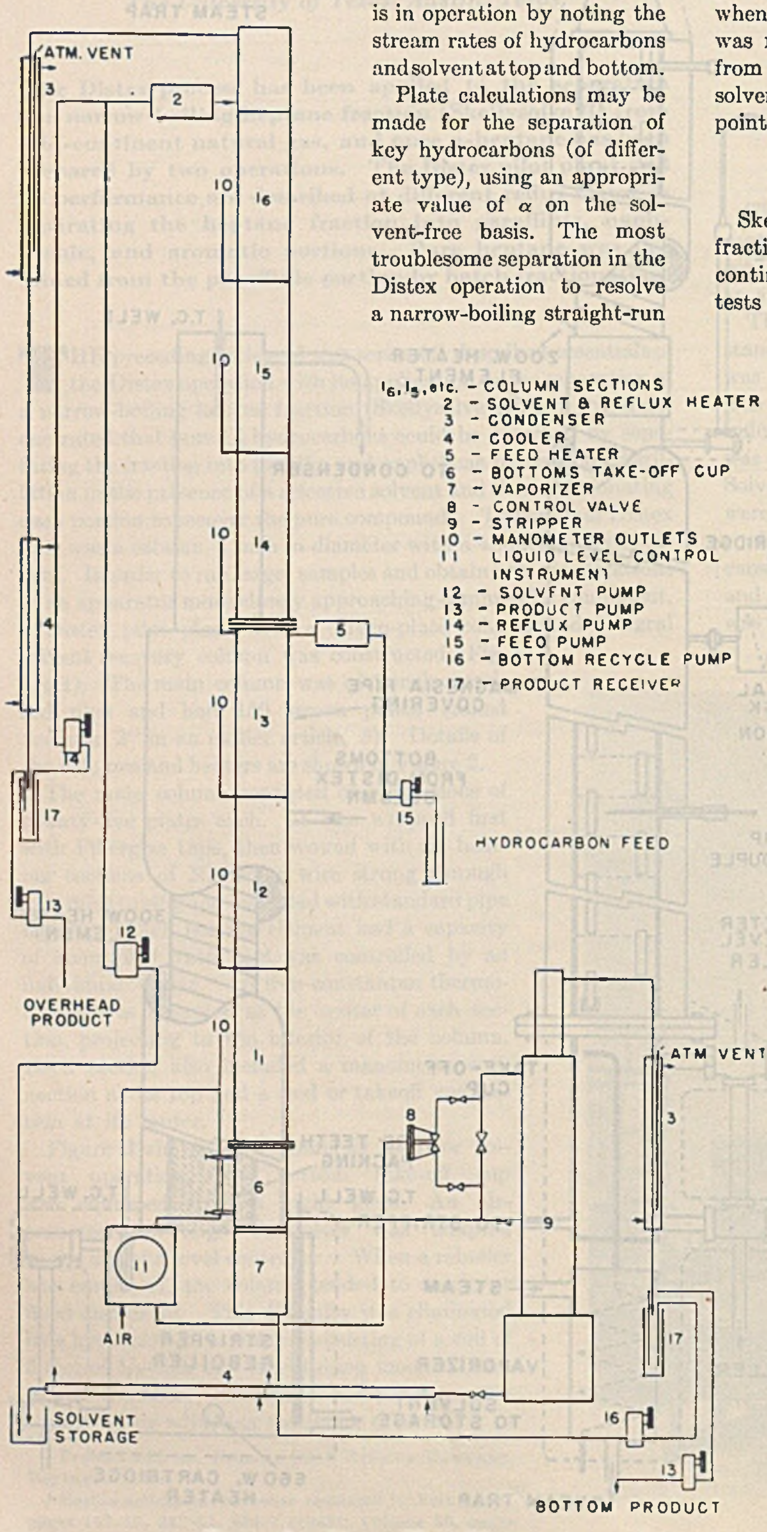

Figure 3. Distex Flow Diagram

The aniline point temperature (using equal volumes of hydrocarbon and aniline) is easily determined, and was used as a control test on the performance of the Distex column. Aniline points of C_6 and C_7 paraffins range from 68° to 78° C., those of the C_6 and C_7 naphthenes are between 31° and 48° C., and those of aromatics are below −30° C. The Distex overhead then contains the least naphthene when its aniline point is highest, the Distex hydrocarbon bottoms contains the least paraffin when its aniline point is lowest, and the column gives the best type separation when the aniline point spread is greatest. Although no attempt was made to obtain primary Distex products completely free from solvent, the products contained only traces, and since the solvent was aniline, there was no interference with the aniline point test.

ANALYSIS OF HEPTANE FRACTION

Skellysolve C was selected as the narrow-boiling heptane fraction. It is a commercial product manufactured from mid-continent natural gas by the Skelly Oil Company. Inspection tests follow:

A.S.T.M. distillation, ° F.		Recovery, %	99.0
Initial b.p.	190	Residue %	0.8
5% over	194	Loss, %	0.2
10% over	195	n_D^{20}	1.40127
20% over	196	Gravity, °A. P. I.	63.2
30% over	196.5	Aniline point, ° C.	55.0
40% over	198	Bromine No.	< 0.1
50% over	198.5		
60% over	199.5		
70% over	200		
80% over	202		
90% over	204		
95% over	207		
End point	233		

A large sample was nitrated to determine and remove aromatics, using National Bureau of Standards procedure (*2*). A 200-ml. portion was fractionated with a 11-mm. diameter Heligrid column into cuts that averaged 0.7% of the charge. Operation was total reflux with intermittent sample take-off, and reflux ratios averaged 30:1 at the plateaus and 70:1 at the temperature breaks. At the boiling rates used, the column contained more than sixty equivalent theoretical plates. Results of this distillation with temperatures corrected to 760 mm. and refractive indices of the cuts are plotted on Figure 4. Analysis of the data, assuming each cut to consist of a pure hydrocarbon or a binary mixture or a binary group, and assuming boiling points and refractive indices linear with volume fractions for these mixtures and groups, gave the composition of the material as reported in Table II. The analytical column did not resolve the mixture sufficiently well at several points to permit calculation of the analysis with respect to every individual hydrocarbon; 2,2- and 2,4-dimethylpentanes could not be resolved. The three isoheptanes boiling between 89° and 92° C. must be reported as a group, and likewise the *trans*-1,2- and 1,3-dimethylcyclopentanes. 1,1-Dimethylcyclopentane appears to be absent.

Almost 20% of the stock distilled between the refractive index plateaus of *n*-heptane and methylcyclohexane; this separation is not so sharp as should have been obtained. There are two hydrocarbons of intermediate boiling points and refractive indices—*cis*-1,2-dimethylcyclopentane and 2,2,4-trimethylpentane (iso-octane)—neither of which has been isolated from petroleum (*3*). Of these, the

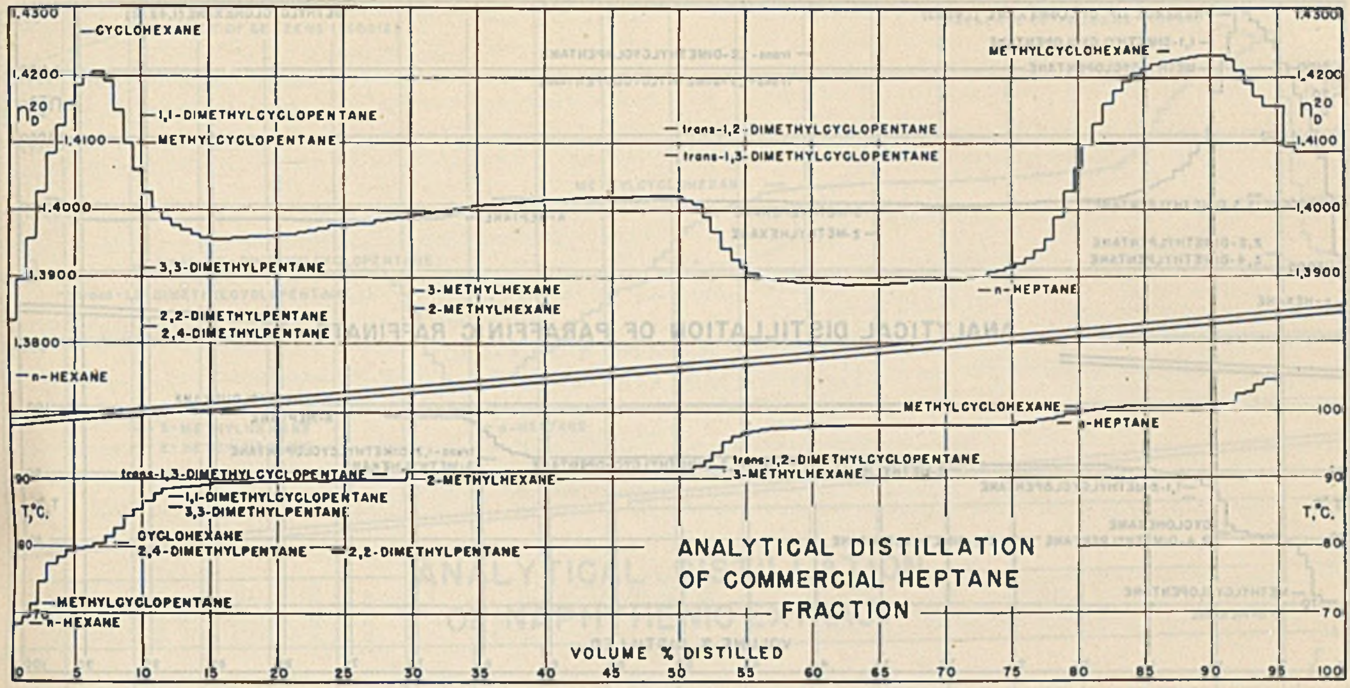

Figure 4

refractive index of the naphthene is too high for more than a trace to be present, but it is believed that a small amount of the isooctane is present in this stock.

The analysis given in Table II is confirmed by analyses of Distex fractions reported later in this article, and with the two exceptions noted, the hydrocarbons present and their distribution are in accord with Bureau of Standards analyses of straight-run naphthas (*3*) when the source and boiling range of the present stock are taken into consideration.

DISTEX PILOT PLANT TESTS

Table II shows that *n*-heptane and methylcyclohexane are the two most abundant hydrocarbons in Skellysolve C, and that the stock contains at least 44% cyclics. From the boiling point–refractive index values and behavior in the Distex operation, the heavy ends must be largely or completely paraffins.

Two separate Distex operations are reported: an analytical

TABLE I. PLATE EFFICIENCY OF COLUMN FOR DISTEX OPERATION ON *n*-HEPTANE–METHYLCYCLOHEXANE–ANILINE

Distex Run No.	Total Liquid Rate (Solvent + Reflux), Cc./Min.	Sample[a]	*n*-Heptane in Sample, Mole %	Calcd. Theoretical Plates	Tray Efficiency
8	140	A	> 99.5	...	...
		B	99.0	...	...
		E	0.59	...	...
		F	< 0.5	...	...
9	140	A	> 99.5	...	...
		B	> 99.5	...	...
		E	1.2	...	...
		F	0.5	...	...
11	140	A	> 99.5	...	...
		C	98.24	15.3[b]	30.6
		D	24.6	...	...
		F	< 0.5	...	...
12	90	A	> 99.5	...	...
		C	97.5	14.2[b]	28.4
		D	24.7	...	...
		F	< 0.5	...	...
13	90	A	> 99.5	...	...
		C	99.2	14.7[b]	29.4
		D	52.9	...	...
		F	< 0.5	...	...

[a] Sample A is overhead reflux; B is taken 25 trays from top; C, 50 trays from top; D, 100 trays from top; E, 125 trays from top; F is bottoms recycle material.

[b] Calculated from Fenske equation for total reflux using samples C and D. α for 80 mole % aniline = 1.4.

TABLE II. ANALYSIS OF SKELLYSOLVE C

Compound	B.P., ° C. (760 Mm.)	Volume %
n-Hexane	68.74	2.5
Methylcyclopentane	71.81	1.3
2,2-Dimethylpentane	79.20	0.5
2,4-Dimethylpentane	80.51	
Benzene	80.10	0.2
Cyclohexane	80.74	5.5
2,3-Dimethylpentane	89.79	22.9
2-Methylhexane	90.05	
3-Methylhexane	91.95	
trans-1,3-Dimethylcyclopentane	90.80	19.3
trans-1,2-Dimethylcyclopentane	91.90	
n-Heptane	98.43	24.9
Methylcyclohexane	100.93	15.0
Toluene	110:62	2.7
Heavy nonaromatics	105+	5.2
Possible minor amounts: *cis*-1,2-dimethylcyclopentane (99.3°) and 2,2,4-trimethylpentane (99.24°).		100.0

TABLE III. OPERATING DATA FOR ANALYTICAL DISTEX RUN FOR COMMERCIAL HEPTANE

Flow rates and ratios		
Hydrocarbon feed rate, cc./hr.		76.8
Solvent (aniline) feed rate, cc./hr.		4500
Overhead hydrocarbon reflux rate, cc./hr.		1615
Overhead hydrocarbon product rate, cc./hr.		38.4
Solvent: hydrocarbon feed ratio		58.6:1
Overhead: hydrocarbon reflux ratio		42:1
Solvent in reflux stream, mole %		80
Fraction of feed as overhead product, vol. %		50
Material balance (on stream), cc.		
Total hydrocarbon feed		551
Total overhead product		266
Total bottoms product		264
Aniline points (composite), ° C.		
Charge stock		55.0
Overhead product		67.5
Bottoms product		43.5
Operating temp., ° C.	Predicted	Actual
Solvent and reflux stream	113	112–114.5
Column section 6	113	112–113.5
Column section 5	115	114–116
Column section 4	117	116.5–118
Column section 3	119	118.5–120
Column section 2	121	121–122
Column section 1	123	122.5–124.5
Stripper reboiler	184.5	184–185

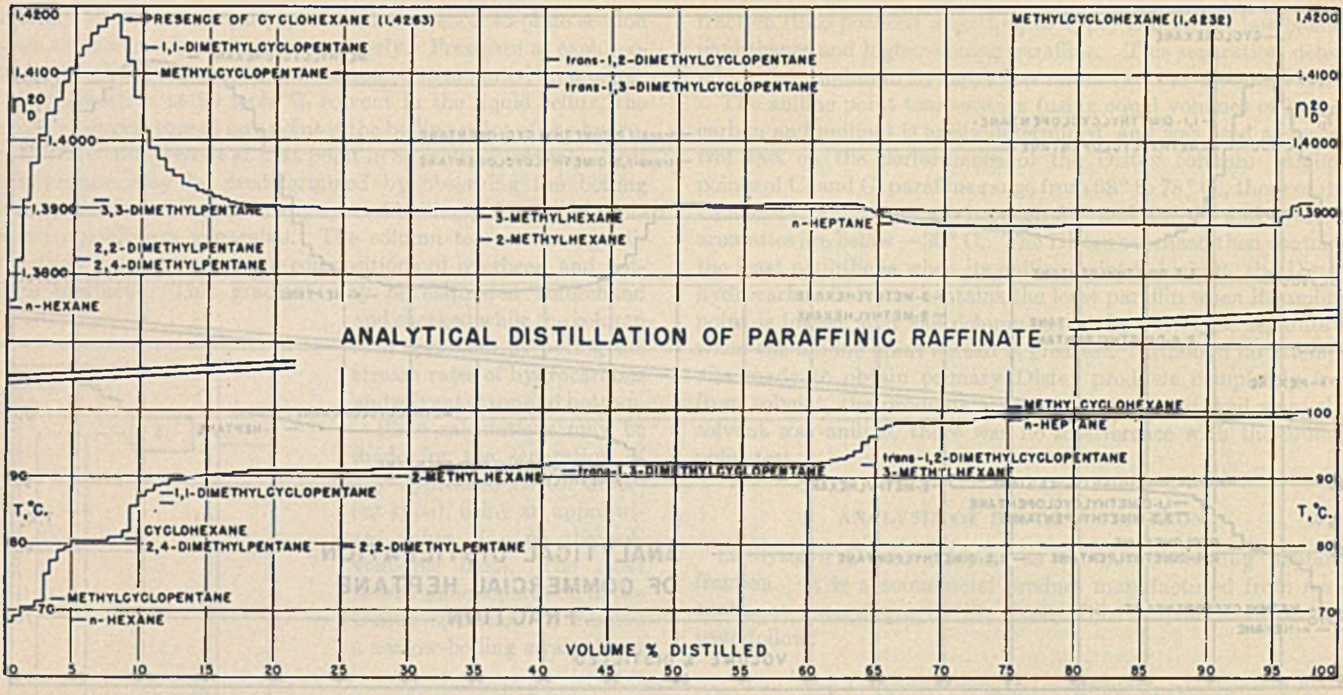

Figure 5

run at a hydrocarbon reflux ratio ($L:D$) of 42:1, and a pilot-plant run of much longer duration at a hydrocarbon reflux ratio of 10:1, both on the original stock. The naphthenic extract from the latter operation was rerun under different operating conditions to remove the toluene. Both runs were conducted with a split of approximately 50% overhead and a concentration of 80 mole % aniline in the reflux.

Analytical Run. The pilot plant was brought on stream, and fractions were collected after flow rates and temperatures were steady. The operating conditions are given in Table III. The predicted temperatures were obtained from an experimental boiling point of the Skellysolve C in 80 mole % aniline (118° C.) and an assumed 10° C. temperature gradient between top and bottom of the column. The solvent-reflux stream was preheated to the predicted column top temperature. The predicted stripper reboiler temperature is the boiling point of aniline.

Figures 5 and 6 show analytical distillations of overhead and bottoms on the Heligrid column by the technique described earlier. Analyses of the fractions and calculation of the composition of the original stock from them are given in Table IV. Comparison of the two analyses indicates a possible mechanical loss of n-hexane during the Distex operation, a lower total n-heptane content and a higher total methylcyclohexane content than in the original analysis, and percentages of other compounds in fair agreement.

As expected, the Distex operation segregated paraffins into the overhead and naphthenes into the bottoms, although the boiling range of the stock is too wide to permit complete separation according to type[3].

Table IV. Analytical Distillations of Distex Products and Composition of Heptane Fraction

Constituents	Paraffinic Raffinate, Vol. %	Naphthenic Extract, Vol. %	Original Stock[a], Vol. %
n-Hexane	1.4	0	0.70
Methylcyclopentane	2.5	0	1.25
2,2-Dimethylpentane	2.6	0	1.30
Cyclohexane	7.7	0	3.85
Benzene	0	0.5	0.25
1,1-Dimethylcyclopentane	0	0	0
2-Methylhexane + 3-methylhexane	46.4	0	23.2
trans-1,2- + *trans*-1,3-Dimethylcyclopentane	5.9	33.2	19.55
n-Heptane	32.0	11.8	21.90
Methylcyclohexane	0	36.5	18.25
Toluene	0	5.9	2.95
Octane paraffins	1.5	12.1	6.8
	100.00	100.00	100.00

[a] Composite results of Distex analysis.

Table V. Distex Pilot Plant Run

	Operation 1[a]	Operation 2[b]	
Flow rates and ratios			
Hydrocarbon feed rate, cc./hr.	330[c]	360[d]	
Solvent (aniline) feed rate, cc./hr.	4,500	4500	
Overhead hydrocarbon reflux rate, cc./hr.	1,800	1800	
Overhead hydrocarbon product rate, cc./hr.	181.5	325	
Solvent: hydrocarbon feed ratio	13.6:1	12.5:1	
Overhead: hydrocarbon reflux ratio	10:1	5.5:1	
Solvent in overhead reflux, mole %	80	80	
Fraction of feed in overhead product, vol. %	55	90	
Material balance, cc.			
Total hydrocarbon feed	29,885	7195	
Total overhead product	10,275	6490	
Total bottoms product	8,569	650	
Total rejected	11,041	...	
Aniline points (composite), ° C.			
Charge stock	55.0	46.2	
Overhead product	63.8[e]	51.5	
Bottoms product	46.2[f]	27.0	
Operating temp., ° C.		Predicted	Actual
Solvent and reflux stream	...	125	123–125
Column section 6	...	125	125–127
Column section 5	...	127	126–129
Column section 4	...	129	127–130
Column section 3	...	131	128–131
Column section 2	...	133	131–134
Column section 1	...	135	134–136
Stripper reboiler	...	184.5	184.0–184.5

[a] Separation of stock into paraffinic and naphthenic fractions.
[b] Elimination of toluene from naphthenic fraction.
[c] Skellysolve C.
[d] Naphthenic fraction.
[e] Optimum more than 62° C.
[f] Optimum less than 48° C.

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[3] From the collective work done to date, it is known that the relative volatility on the solvent-free basis of paraffins to naphthenes decreases as the boiling point of the paraffin approaches and rises above that of the naphthene. For C_6 to C_8 hydrocarbons in 80 mole % aniline, the relative volatility of a paraffin to a naphthene reverses (crosses and falls below unity) when the paraffin boils somewhere between 5° and 15° C. higher than the naphthene.

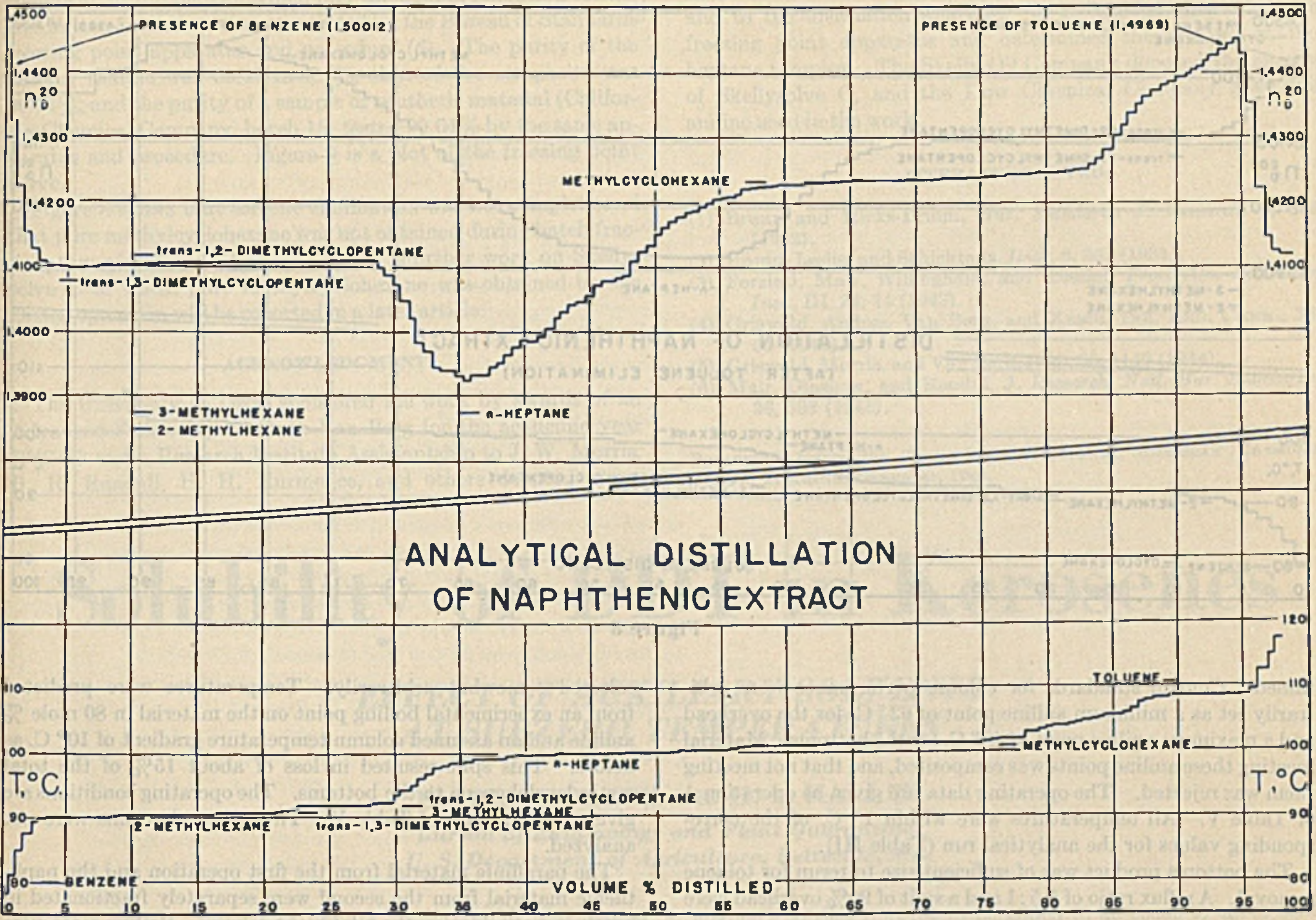

Figure 6

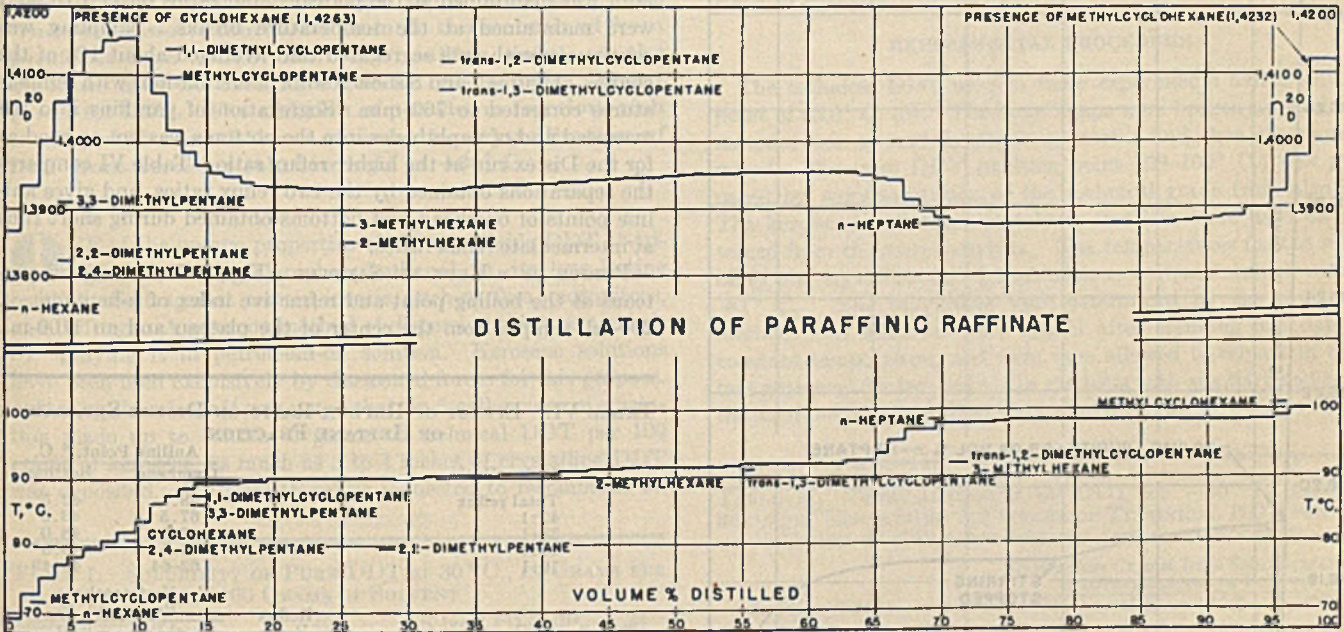

Figure 7

The overhead contained 16% naphthenes, all of the methylcyclopentane and cyclohexane, 15% of the higher-boiling dimethylcyclopentanes, and none of the methylcyclohexane. All of both benzene and toluene were found in the bottoms, and the *n*-heptane and higher-boiling paraffins were distributed. Some heptane in the bottoms was anticipated, since the stock contains about 56% paraffins whereas only 50% of the material was taken overhead.

Pilot Plant Run. The reflux ratio of 42:1 is higher than may be desired for a commercial operation. A run lasting 125 hours was made at a reflux ratio of 10:1, during which about 30 liters of the stock were charged and a split of 55% overhead was main-

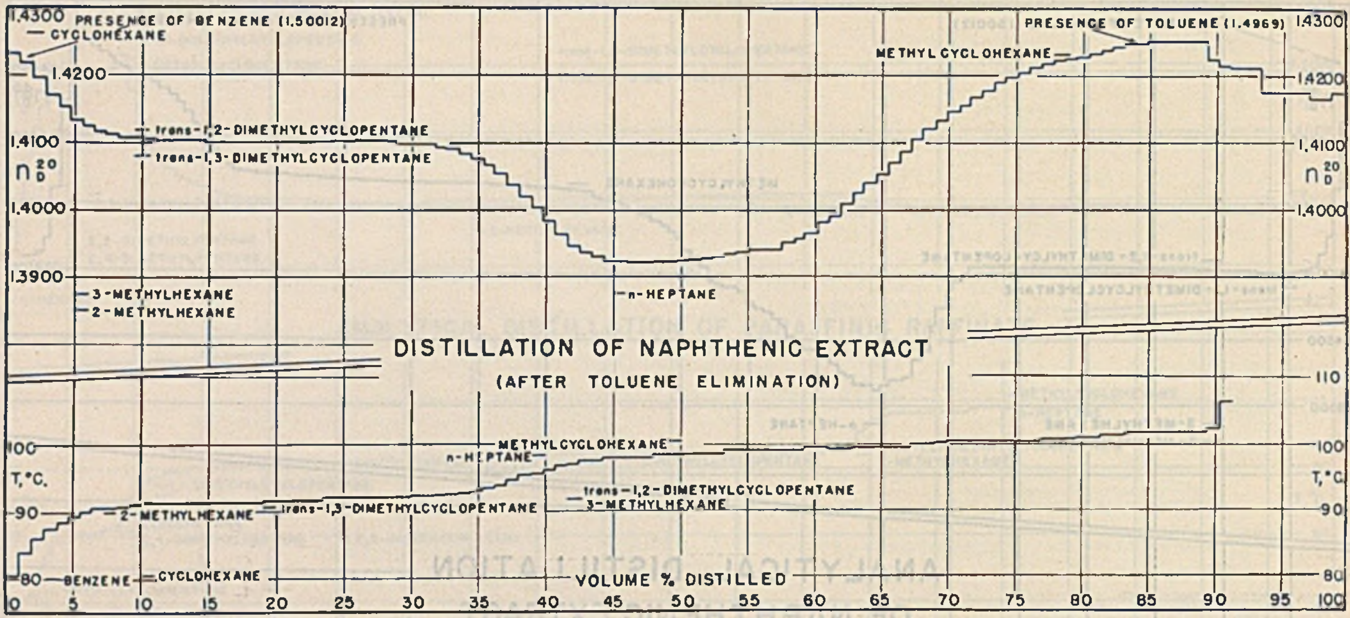

Figure 8

tained. Control standards for column performance were arbitrarily set as a minimum aniline point of 62° C. for the overhead and a maximum aniline point of 48° C. for the bottoms. Material meeting these aniline points was composited, and that not meeting them was rejected. The operating data are given as operation 1 of Table V. All temperatures were within 1° C. of the corresponding values for the analytical run (Table III).

The bottoms product was of sufficient size to rerun for toluene removal. A reflux ratio of 5.5:1 and a split of 90% overhead were selected somewhat arbitrarily. Temperatures were predicted from an experimental boiling point on the material in 80 mole % aniline and an assumed column temperature gradient of 10° C. as before. This split resulted in loss of about 15% of the total methylcyclohexane to the bottoms. The operating conditions are given as operation 2 of Table V. The toluene bottoms were not analyzed.

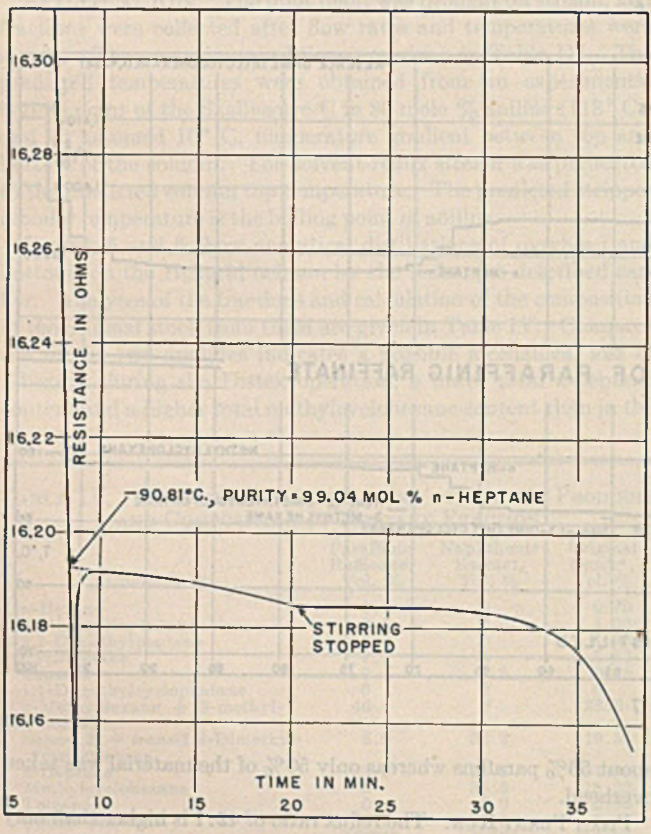

Figure 9. Freezing Point Determination of Purity of Composite *n*-Heptane Sample

Freezing point of pure *n*-heptane is −90.62° C. (*1*)

The paraffinic material from the first operation and the naphthenic material from the second were separately fractionated in batch operations using the pilot plant column. Boiling rates were between 90 and 140 ml. per minute. A minimum reflux ratio of 30:1 was maintained at the plateaus, and ratios of 55:1 to 90:1 were maintained at the temperature breaks. Sampling was continuous with cuts segregated that averaged about 1% of the charge. Figures 7 and 8 show results of distillations with temperatures corrected to 760 mm. Segregation of paraffins into the overhead and of naphthenes into the bottoms was not so good as for the Distex run at the higher reflux ratio. Table VI compares the separations obtained by the two reflux ratios, and gives aniline points of overhead and bottoms obtained during short runs at intermediate reflux ratios.

Purity of *n*-Heptane Samples. Figure 7 shows good plateaus at the boiling point and refractive index of *n*-heptane. A 200-ml. sample from the center of the plateau and an 1100-ml.

Table VI. Effect of Reflux Ratio on Distex Separation of Heptane Fraction

Reflux Ratio	Aniline Point, ° C. Overhead	Aniline Point, ° C. Bottoms
Total reflux	68.5	42.5
42:1	67.5	43.5
33:1	67.0	48.0
20:1	66.5	48.5
10:1	62–64	48–49

Distributed Constituents[a]	Reflux Ratio	Hydrocarbons Recovered, % Overhead	Hydrocarbons Recovered, % Bottoms
trans-1,2- + *trans*-1,3-Dimethylcyclopentane	10:1	49.5	50.5
	42:1	15.7	84.3
n-Heptane	10:1	73.5	26.5
	42:1	74.0	26.0
Methylcyclohexane	10:1	4.80	95.2
	42:1	0	100.0
C_7 paraffins	10:1	8.1	91.9
	42:1	22.0	78.0

[a] Compounds appearing in both overhead and bottom fractions.

composite of the plateau which had the boiling point and refractive index of pure heptane were tested by the Bureau of Standards freezing point apparatus and procedure (*6*). The purity of the 200-ml. sample was 99.47 mole %, that of the composite was 99.04%, and the purity of a sample of synthetic material (California Chemical Company, batch 15) tested 99.64% by the same apparatus and procedure. Figure 9 is a plot of the freezing point curve.

Figure 8 shows that toluene elimination was not complete and that pure methylcyclohexane was not obtained during batch fractionation of the naphthenic material. Further work on Skellysolve C in which pure methylcyclohexane was obtained by the Distex operation will be reported in a later article.

ACKNOWLEDGMENT

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Solubility of DDT in Kerosenes

EFFECT OF AUXILIARY SOLVENTS AT SUBZERO TEMPERATURES

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The solubilities of technical and pure DDT in a number of kerosenes over the range +30° to −30° C. have been determined. Kerosenes obtained from naphthenic-base crude oils dissolve more DDT than do those obtained from paraffinic-base crude oils. The aniline point of the kerosene may be used as a general guide to its solvent power for DDT. The addition of petroleum fractions rich in alkylated naphthalenes retards the crystallization of DDT from kerosene solution held at −30° C.

ONE of the unique properties of the insecticide DDT [1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] is its long-lasting residual effect against certain insects, such as flies, mosquitoes, and bedbugs. A common method of dispersing this insecticide is by spraying it in petroleum-oil solution. Kerosene solutions have been used extensively by the armed forces for this purpose.

During the winter it was noted that, in 5-gallon cans of a solution made up to contain 5 grams of technical DDT per 100 grams of kerosene, as much as 3 to 4 inches of crystalline DDT was deposited. We were therefore requested to recommend an auxiliary solvent that might be added to kerosene to effect complete solution at −30° C., and also to study the solubility of DDT in kerosene obtained from various sources.

EXPERIMENTAL PROCEDURE

The technical DDT used in these experiments had a setting point of 93.0° C. (*3*). The large lumps were broken up, and the material was ground lightly in a mortar and then thoroughly mixed. The pure DDT (melting point 108–109° C.) was prepared by recrystallization of the technical grade from alcohol. The kerosenes and other petroleum fractions were used as obtained from the manufacturers. The temperatures for the solubility and crystallization determinations were maintained within ±1° C. The solubilities were determined by the synthetic method. All solutions were seeded after standing one day at constant temperature, and were then allowed to remain in contact with seed for two days. In the tests with auxiliary solvents, the solutions were seeded at the end of seven days.

TABLE I. SOLUBILITY OF PURE DDT at 30° C., IN GRAMS PER 100 GRAMS OF SOLVENT

Amsco solvent G[a]	40	Solvent PD 544B[a]	45
Aro-Sol (151-B)[a]	49	Solvent PD 544C[a]	39
Benzene	85	Solvesso No. 1[b]	52
Deobase[b]	6	Solvesso No. 2[b]	50
Diisopropylbenzene	22	Solvesso No. 3[b]	40
Heavy aromatic naphtha[a]	48	Toluene	80
Culicide oil[a]	48	Ultrasene[b]	6
Methyl ethyl ketone	100	Velsicol AR-50[a]	53
Monomethylnaphthalene	63	Velsicol AR-60[a]	49
Solvent PD 544A[a]	40	Xylene	64

[a] An alkylated naphthalene fraction.
[b] A petroleum fraction.

TABLE II. CRYSTALLIZATION OF DDT AT −30° C. FROM A SOLUTION CONTAINING 5.0 GRAMS OF TECHNICAL DDT PER 100 GRAMS OF KEROSENE PLUS AN AUXILIARY SOLVENT

	Days before Crystn. from Soln. Containing Auxiliary Solvent as Follows:			
Auxiliary Solvent	5%	10%	15%	20%
Diisopropylbenzene	3	3	3	3
Heavy aromatic naphtha	6	6	23	NC[a]
Methyl ethyl ketone	..	2	...	2
Monomethylnaphthalene	7	20	NC	NC
Solvent PD 544B	6	10	21	NC
Solvent PD 544C	6	6	13	13
Solvesso No. 1	1	1	2	2
Solvesso No. 2	2	2	2	2
Solvesso No. 3	6	6	6	6
Xylene	2	3	3	8

[a] No crystallization during a minimum period of 3 weeks.

SOLUBILITY RESULTS

To keep fire hazards at a minimum, solvents of high flash point and good solvency for DDT were sought. Table I shows the solubility of DDT in some of the solvents tested. Preliminary experiments had indicated that the ability to retard crystallization of DDT at −30° C. from a solution containing kerosene mixed with an auxiliary solvent did not depend alone upon the solubility of DDT in the auxiliary solvent. Thus, xylene and monomethylnaphthalene dissolve almost the same amount of DDT, but the results in Table II show that xylene afforded little retardation of crystallization whereas monomethylnaphthalene prevented crystallization for more than three weeks. When commercial grades of solvents containing alkylated naphthalenes were used, they were found to have the same effect. Naphthalene itself did not retard crystallization.

Table III. Crystallization of DDT at −30° C. from Solution Containing 5 Grams of Technical DDT, 85 Grams of Kerosene, and 15 Grams of Auxiliary Solvent

	Days before Crystn. from Soln. Containing Kerosene from Various Sources						
Auxiliary Solvent	A (naphthenic source)	B (paraffinic source)	C (midcontinent source)	D[a]	E[a]	F[a]	G (local purchase)
Amsco solvent G	17	2	11	4	6	7	10
Aro-Sol (151-B)	NC[b]	6	18	10	10	15	12
Heavy aromatic naphtha	NC	2	8	2	6	8	9
Solvent PD 544A	NC	11	NC	11	17	14	NC
Solvent PD 544B	NC	5	17	9	14	11	11
Solvent PD 544C	NC	2	14	2	6	4	10
Velsicol AR-50	NC	2	14	8	8	8	20

[a] Kerosenes D, E, and F were supplied by the Quartermaster Corps, as representative of solvents currently used in the manufacture of residual sprays.
[b] No crystallization during a minimum period of 3 weeks.

Table IV. Solubility of DDT in Kerosene at Various Temperatures

Kerosene	Aniline Point, ° C.	Solubility, Grams per 100 Grams of Solvent: 30° C. Tech.	30° C. Pure	20° C. Tech.	20° C. Pure	0° C. Tech.	0° C. Pure	−20° C. Tech.	−20° C. Pure	−30° C. Tech.	−30° C. Pure
A (naphthenic source)	48.1	20	12	12	9	7	5	4	3	3	2
B (paraffinic source)	70.4	11	8	8	6	4	3	2	1	1	0.5
C (midcontinent source)	63.0	16	12	9	8	4	3	4	2	3	1
D (Quartermaster Corps)	69.1	13	8	8	6	4	3	3	2	2	1
E (Quartermaster Corps)	67.3	15	10	9	7	5	3	3	2	2	1
F (Quartermaster Corps)	67.3	15	10	9	7	5	3	3	2	2	1
G (local purchase)	63.5	17	11	10	8	6	4	3	2	2	1

Solvesso No. 1 and Velsicol AR-50 dissolve about the same amount of DDT, but when these solvents were mixed with kerosene, Velsicol AR-50 retarded crystallization for a much longer period. Solvesso No. 1 contains a considerable proportion of monocyclic aromatic hydrocarbons, whereas Velsicol AR-50 is rich in alkylated naphthalenes. Since the commercial solvents containing alkylated naphthalenes were found to delay crystallization, a series of this type was tested against kerosenes from various sources. Table III gives the results.

A similar set of experiments was made with Culicide oil. A black, amorphous deposit separated in each case as soon as the solution was cooled to −30° C. No deposition of DDT could be observed in any of the mixtures during a minimum period of three weeks.

The kerosene used in the preparation of these sprays is commonly required to meet Federal Specification VV-K-211a (*2*). Since this specification covers only a burning test, flash point, distillation end point, sulfur content, and color, it is possible for a wide variation in composition to occur. Inasmuch as aliphatic hydrocarbons are poorer solvents for DDT than are aromatic hydrocarbons, we expected that the kerosenes derived from paraffinic-base crude oil would be poorer solvents for DDT than kerosenes derived from naphthenic-base crude oil. Table IV indicates that as much as 50% more DDT may be dissolved in naphthenic-base kerosene than is possible in a paraffinic-base kerosene.

The rather large difference in solubility between technical and pure DDT shown in Table IV is due to the fact that technical DDT contains approximately 70 to 75% of the active *p,p'*-isomer, the remainder consisting chiefly of a less active isomer, 1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane (*4*). This *o,p'*-isomer is much more soluble in hydrocarbons than is DDT itself. For this reason the technical DDT chosen for these determinations contained a maximum of the active *p,p'*-isomer consistent with current production practices. This means a difference of about 5 to 6% of *p,p'*-isomer between the material used and the standard required by the armed forces (*3*). Accordingly, the solubility figures given for the technical DDT should be viewed as minimum values, with higher solubilities indicated for DDT containing less of the *p,p'*-isomer.

Inasmuch as the aniline point is frequently used as a measure of the content of aromatic hydrocarbons in petroleum fractions (*1*), this value was determined for the kerosenes (Table IV) and for mixtures of two of the kerosenes with auxiliary solvents (Table V). In general it has been found that the solubility of DDT increases as the aniline point decreases. This conclusion is further supported by the low solubility of DDT in kerosenes refined to remove unsaturated hydrocarbons. Thus, Deobase (aniline point, 80.0° C.) and Ultrasene (aniline point, 79.8° C.) both dissolve only 6 grams of pure DDT per 100 grams of solvent at 30° C.

Although the aniline point of a kerosene can be used to indicate the solubility of DDT, it cannot be used to measure the retardation in crystallization of DDT. This is shown in Table V, where the aniline points are given for two kerosenes containing 15% of an auxiliary solvent. In both cases the mixture containing the xylene shows the lowest aniline point, but this mixture is ineffective in retarding the crystallization of DDT (Table II).

Table V. Aniline Points (° C.) of Mixtures of Kerosene with 15% of an Auxiliary Solvent

Auxiliary Solvent	Kerosene G	Kerosene F
Amsco solvent G	56.7	59.6
Aro-Sol (151-B)	54.2	59.0
Heavy aromatic naphtha	54.7	58.4
Solvent PD 544A	57.7	59.6
Solvent PD 544B	53.6	59.6
Solvent PD 544C	55.7	56.6
Velsicol AR-50	55.4	57.7
Xylene	51.9	54.9

ACKNOWLEDGMENT

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Dielectric Heating of Granular Materials

ALUMINUM AND SILICON OXIDES

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The heating rates of alumina and silica grains in an alternating electric field were measured as a function of particle size. The pertinent dielectric properties of these grains were measured as a function of frequency and particle size. The frequency range was 10 to 30 megacycles. The average diameter of the alumina was 0.103 to 2.04 mm., and of the silica, 0.65 to 9.00 mm. The effect of surrounding the grains with dielectrics other than air was determined. The dielectric loss factor and heating rate of granular alumina increase with particle size throughout the size range covered, 2.04-mm. particles heating approximately twenty times as fast as 0.103-mm. particles. The same direction of change is evident in the heating rate of pure silica, 3.50-mm. particles heating about twice as fast as 0.65-mm. particles. In the case of silica, the heating rate is practically constant for sizes larger than 3.50 mm. Increasing the dielectric constant of the medium surrounding the particles increases the heating rate of the particles themselves, over and above any increase in energy pickup due to the loss within the added dielectric. The heating rates of the several sizes of alumina, both dry and surrounded by liquid dielectrics, are readily correlated with the loss factors.

THE application of dielectric heating to industrial heating problems is increasing rapidly. To date most of the applications have been in the heating or heat treating of solid shapes (*1*, *3*, *4*, *7*, *8*). A notable exception is the use of dielectric heating in the dewatering of penicillin (*6*). Because of the unique features of this method of heating, it has seemed advisable to investigate its use in heating masses of discontinuous material such as represented by catalyst beds and liquid-solid mixtures. In the present work an impure alumina (94.21% Al_2O_3, 3.26% TiO_2, 1.16% SiO_2, 0.83% Fe_2O_3, 0.47% MnO, and 0.07% CaO), silica (99.9% SiO_2), and ordinary brown river sand of unknown composition were used in granular form. As pointed out recently (*2*), this field is sufficiently new that the accumulation of data and rules is of prime importance if results obtained later are to be properly interpreted. The authors hope that the present work and subsequent reports on other kinds of granulated materials may serve as a guide to those interested in the use of the dielectric method.

In the course of preliminary experiments on the heating of sands in a high-frequency electric field, it was found that apparently anomalous results were always obtained unless the sand was rather closely graded as to size. This observation led to an effort to correlate the dielectric properties of materials with particle size. In an effort to account for the observed fact that, with a particular oxide larger particles absorb energy from such a field at a higher rate than do smaller particles, a parallel series of determinations was made with alumina in which the granules were immersed in a liquid medium. The same phenomenon was observed; in addition, it was found that, when the dielectric constant of the medium surrounding the solid particles was increased, the rate of energy absorption by the solid itself was materially increased. These results are given in detail and, for alumina, correlate with measured values of dielectric constant and power factor.

ELECTRICAL MEASUREMENTS

Heating rates were determined by placing the particular material to be tested in one compartment of the three-compartment Mycalex cell shown in Figure 1. This cell was sealed to one of the electrodes with polystyrene. The compartment was filled level without packing, and the second electrode placed on top. The cell was 2 inches deep, and the electrodes were flat iron plates, 7 × 10 inches. For the frequency used (20 megacycles), this size was such a small fraction of one wave length that there was little possibility of voltage gradients across the plate. This point was checked with an electrostatic voltmeter, and the voltage found to be constant at all points on the electrodes. Mercury-glass thermometers were inserted through the side walls as shown so that the bulbs were centrally located. Blank experiments with the cells empty and the thermometers in place showed no measurable heating of the thermometer in the longest time interval used in later experiments. When determining temperature rises with material in the cells, temperatures were read at regular intervals after current was shut off. These readings were continued until the temperature began to fall from the maximum value obtained. This maximum in all cases persisted for several minutes and was never more than a few degrees above the temperature recorded at the time the current was shut off. In all cases the maximum temperature was used in calculating heating rates.

Because of the difficulty of calibrating a high-voltage radio-frequency voltmeter and the effect of the voltmeter impedance on circuit tuning, it was felt necessary to use a method of operation which would give accurate comparative results without knowledge of the exact voltage used in successive experiments. The voltage when the dry materials were heated ranged from 5000 to 7000 volts. The method adopted was as follows: The three cells were filled with different materials, and the temperature rise was determined after application of the field for a measured length of time. In the case of alumina all runs lasted one minute. Because of the much smaller heating rates obtained with silica, a longer interval was sometimes used with this material. In no case did the maximum temperature exceed 120° C. The total energy absorbed was then calculated from the temperature rise, heat capacity, and weight of material present. The product of these three quantities is designated "heating rate" and has the units of heat input per unit time—B.t.u. per minute. This is to be differentiated from the rate of increase in temperature (° C. per minute) which takes no account of the weight of material present. The latter value offers a convenient rough measure of heating rates since the weights differed only slightly and the heat capacity not at all. The three determinations made simultaneously are obviously comparable since there were no voltage gradients across the electrodes. Any one of these values may now be used as a reference and the others expressed as a ratio of their own value to that of the reference material. By suitable repetition and overlapping, it was thereby possible to express all heating rates in terms of a single standard value. Actually, in the case of the alumina results, which are somewhat more complete than the others, each different size of alumina was run three

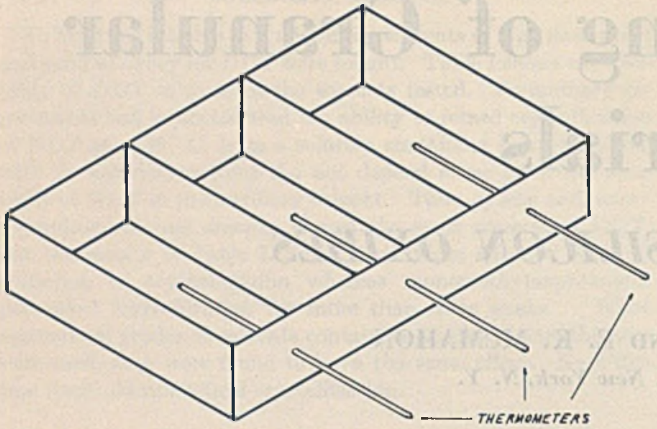


Figure 1. Mycalex Cell for Heating Measurements

different times without removing it from the cell. It was thus compared through three different pairs of sizes. A check on the approximate constancy of the voltage was also obtained in this way since the heating rates for a given size were very nearly the same in all cases.

In a few experiments, particularly those presented in Table IV, it was necessary to determine relative voltages as accurately as possible. A specially built electrostatic voltmeter was calibrated at 60 cycles, and theoretically the calibration is independent of frequency. The matter of meter lead inductance, however, raises some doubt as to the absolute value of the recorded voltages. For any given setup the voltages recorded were reproducible to ±12.5 volts. Since all measurements were made at the same frequency and with the same meter leads, the relative voltages appear to be quite accurate and the absolute values are probably not seriously in error.

For all heating rate determinations the compartments were filled by pouring the material into the compartment until it was filled level. In no case was it purposely packed more tightly than natural filling would cause. Since there was the possibility that packing might have some effect over and above that due to the variation in the amount of material present, measurements of dielectric constant and power factor were made with loose and compacted alumina; comparison of these results shows a small effect of packing. However this effect is so small that accidental differences in packing would result in negligible effects; in any case the direction of change of heating rate as a function of particle size is not changed. In those runs in which the air was replaced by an oil, the oil was added slowly after filling as before and the mixture allowed to stand until all air had been displaced.

Since water has a uniquely high dielectric loss factor, the question of the effect of adsorbed moisture naturally arose. Samples heated after normal handling around the laboratory showed no difference from the same samples heated immediately after a 12–15 hour oven treatment at 125–150° C. Even though this treatment may have left some moisture in and on the particles, the amount present would have been changed markedly; in any event the effect of moisture would have caused a change in heating rate with particle size in a direction opposite to that found.

The measurements of K and tan δ were made with a type 160-A Boonton Q-meter, using a cell (Figure 2) consisting of two circular polished disks 3.75 inches in diameter, mounted in a Pyrex tube with polystyrene cement. An opening in the glass wall between the plates was provided to facilitate filling and cleaning the cell. For measurements on dry grains, the space between the plates was filled with the granules with as little packing as possible. For measurements on mixtures of oil and granular material, the cell was filled as for the dry measurements, and oil was then added until all air was removed. All measurements were made at 25° C.

Resistivity was determined by measuring resistance R, in ohms, of the glass cell filled with the material. The value of RA/d was then calculated and designated as the resistivity, ρ. The measurements were made with an RCA Junior Voltohmyst.

Particle sizes were determined from sieve analyses. For alumina the supplier's standard analyses were used (5). In the case of silica and brown sand, a set of Tyler Standard screens was used. The one exception was the 20–30 mesh silica which was sized with U. S. Standard sieves.

The oils used were a refined white mineral oil and pure castor oil.

Results. Values of K, tan δ, and loss factor of alumina, both dry and in oil as measured on the Q-meter, and relative heating rates are given in Table I. They are shown as a function of particle size with frequency as a parameter in Figures 3 to 6, inclusive. Similar data for silica, brown sand, white mineral oil, and castor oil are presented in Table II. The data for silica and brown sand were not plotted for reasons given later.

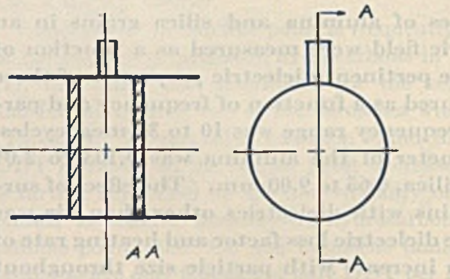


Figure 2. Cell for Measuring Dielectric Properties with Q-Meter

Table I. Q-Meter and Heating Results for Alumina

Material (Loosely Packed)	Grit No.	Av. Diam., Mm.	Frequency, Mc.	K	Tan δ	Loss Factor	Relative Loss Factor	Relative Heating Rate	Approx. Temp. Rise, ° C./Min.
Dry alumina grains	10	2.04	12	4.41	0.068	0.300	0.97		
		2.04	20	4.68	0.066	0.309	1.00	1.00	56
		2.04	30	4.68	0.073	0.342	1.11		
	12	1.71		...	...	...	..		
		1.71	20	...	...	...	..	0.91	52
		1.71		...	...	...	..		
	16	1.21	12	4.13	0.040	0.165	0.53		
		1.21	20	4.32	0.043	0.186	0.60	0.62	38
		1.21	30	4.37	0.048	0.210	0.68		
	24	0.730	12	3.78	0.020	0.076	0.24		
		0.730	20	4.04	0.026	0.105	0.34	0.34	21
		0.730	30	4.23	0.032	0.136	0.44		
	30	0.610		...	...	...	...		
		0.610	20	...	...	...	...	0.29	18
		0.610		...	...	...	...		
	36	0.520		...	...	...	...		
		0.520	20	...	...	...	...	0.25	15
		0.520		...	...	...	...		
	46	0.370	12	3.19	0.010	0.032	0.10		
		0.370	20	3.65	0.014	0.051	0.17	0.17	12
		0.370	30	3.77	0.016	0.060	0.19		
	120	0.103	12	2.77	0.002	0.005	0.02		
		0.103	20	3.23	0.002	0.006	0.02	0.03	4
		0.103	30	3.09	0.003	0.009	0.03		
Alumina grains in mineral oil	10	2.04	12	6.77	0.122	0.827	2.68	..	..
		2.04	20	7.18	0.110	0.790	2.56	2.5	..
		2.04	30	7.32	0.122	0.893	2.89	...	..
	16	1.21	12	6.50	0.068	0.442	1.43	..	..
		1.21	20	6.59	0.071	0.466	1.51	1.4	..
		1.21	30	6.95	0.078	0.540	1.75	..	..
	24	0.730	12	5.95	0.047	0.277	0.90	..	..
		0.730	20	6.48	0.048	0.325	1.05	0.77	..
		0.730	30	6.23	0.052	0.325	1.05	..	..
Alumina grains in castor oil	10	2.04	12	9.15	0.154	1.41	4.57	..	..
		2.04	20	9.43	0.157	1.48	4.78	..	..
		2.04	30	9.93	...	...	...	..	..
	16	1.21	12	8.92	0.113	1.01	3.27	..	..
		1.21	20	9.38	0.124	1.16	3.75	..	..
		1.21	30	9.65	...	...	...	..	..
	24	0.730	12	7.70	0.077	0.592	1.91	..	..
		0.730	20	8.00	0.087	0.697	2.26	..	..
		0.730	30	8.70	0.111	0.970	3.14	..	..

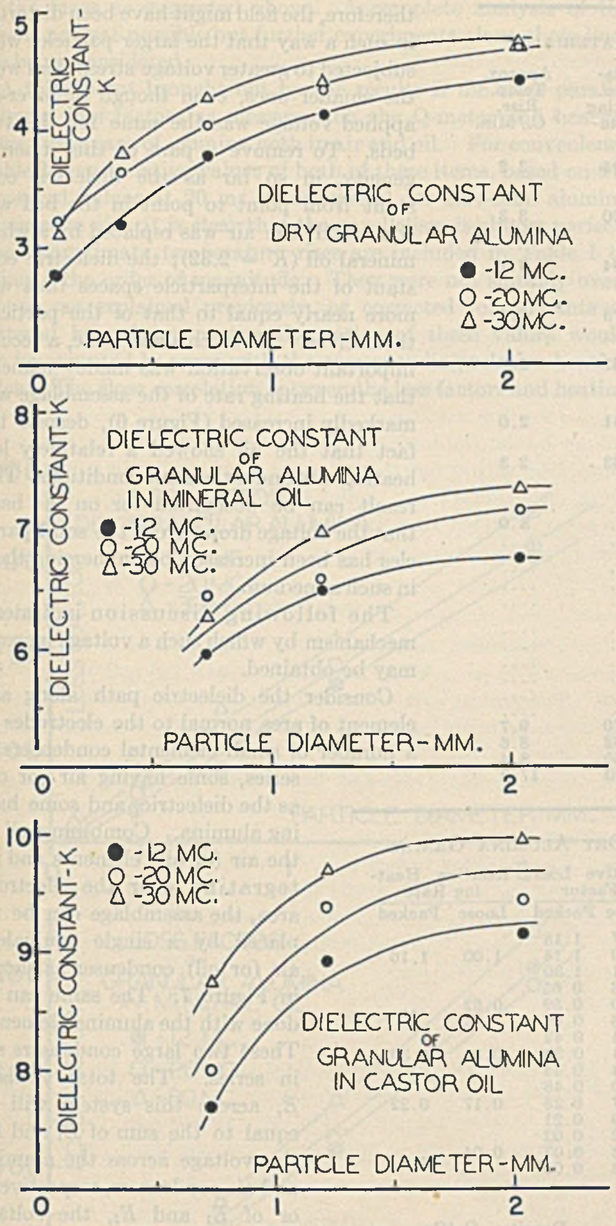


Figure 3. Dielectric Constants

Table III shows the results obtained when measurements were made with the Q-meter and in the dielectric field on loosely and tightly packed alumina. The packed material was as tightly packed as possible, and the bulk densities are shown.

The actual heating rates of two pairs of grains as a function of voltage are given in Table IV. Resistance data on some of the various dry materials used are presented in Table V.

RESULTS WITH ALUMINA

The first observation to be made was the large change in heating rate with particle size. The fact that the larger material heated more rapidly than the smaller is somewhat surprising and, indeed, was first thought to be a spurious result. Several factors might cause an apparent variation in heating rate with particle size, which are not due to the differences in particle size, or are only secondary results of these differences. In the earliest experiments each sample was heated alone, and there was the possibility that the voltage applied to the larger sizes was always greater than that applied to the smaller sizes. The technique described was adopted to avoid this possibility and, except for slightly better self-consistency, there was no change in the effect.

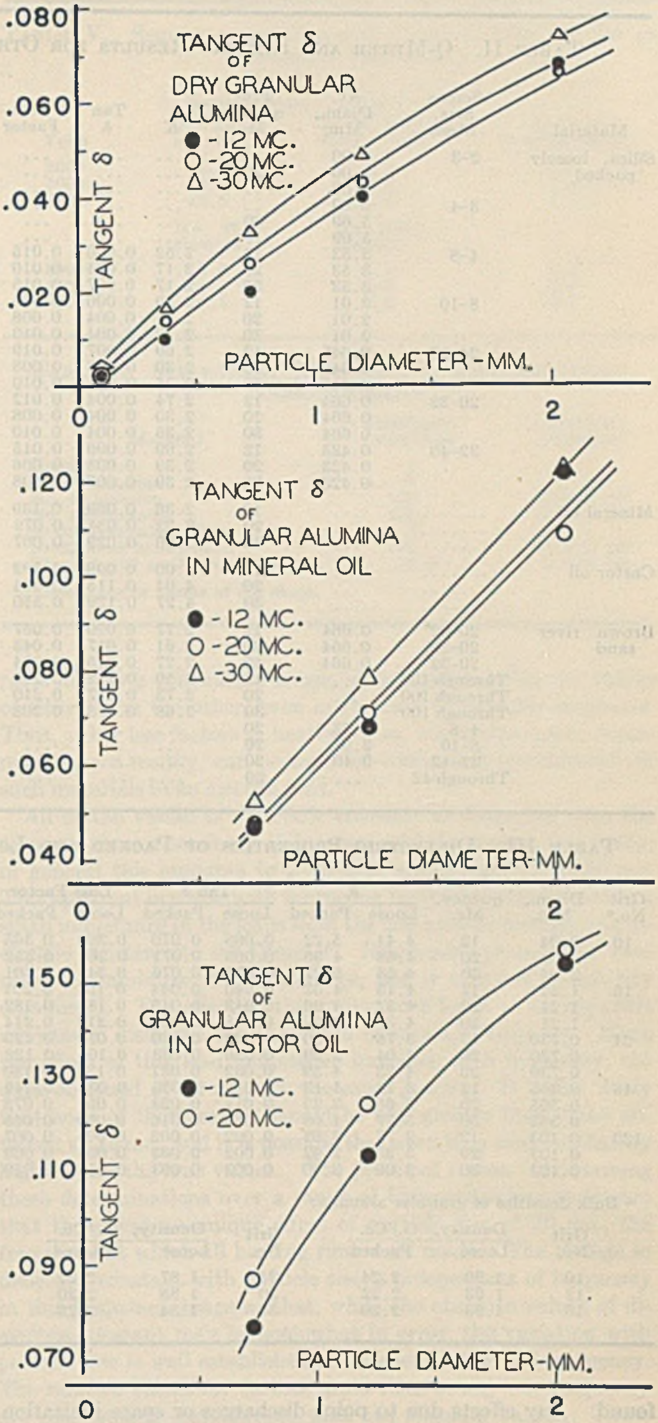


Figure 4. Value of Tangent δ

Data reported here were obtained with this method. A second possible extraneous cause of the observed effect was a difference in the amount of adsorbed moisture. Any reasonable hypothesis seemed to indicate that effects due to adsorbed water would result in a more rapid energy absorption in the smaller particles, since water absorbs energy readily from an electric field and more of it should be present on the smaller particles. Nevertheless, the point was checked experimentally and no effect of moisture was found. The third possibility was that the result might be due to an ordinary ohmic resistance effect, but again it appeared that the resistance of the smaller-particle beds should be less than that of the larger-particle beds. This point was also checked (Table V), and no resistance effect in a direction to account for the higher heating rates of the larger particles was

Table II. Q-Meter and Heating Results for Other Materials

Material	Screen Size, Mesh	Av. Diam., Mm.	Frequency, Mc.	K	Tan δ	Loss Factor	Relative Heating Rate	Approx. Temp. Rise, ° C./Min.
Silica, loosely packed	2–3	9.00	..	...	...	...		
		9.00	20	...	...	...	0.94	3.2
		9.00	..	...	...	...		
	3–4	5.69	..	...	...	...		
		5.69	20	...	...	...	1.00	3.3
		5.69	....	...	...	...		
	4–8	3.53	12	2.52	0.006	0.015		
		3.53	20	2.17	0.004	0.010	0.94	3.1
		3.53	30	2.17	0.007	0.016		
	8–10	2.01	12	2.39	0.006	0.015		
		2.01	20	2.17	0.004	0.008	0.73	2.1
		2.01	30	2.22	0.004	0.010		
	24–28	0.645	12	2.69	0.007	0.019		
		0.645	20	2.30	0.003	0.008	0.51	2.0
		0.645	30	2.35	0.004	0.010		
	20–32	0.664	12	2.74	0.004	0.012		
		0.664	20	2.30	0.004	0.008	0.51	2.0
		0.664	30	2.35	0.004	0.010		
	32–40	0.423	12	2.69	0.006	0.015		
		0.423	20	2.39	0.003	0.006	0.63	2.3
		0.423	30	2.39	0.003	0.008		
Mineral oil	....	...	12	2.36	0.059	0.139	...	....
	....	...	20	2.32	0.034	0.079	...	8.0
	....	...	30	2.36	0.029	0.067	...	....
Castor oil	....	...	12	4.00	0.098	0.392	...	....
	....	...	20	4.04	0.115	0.464	...	....
	....	...	30	4.27	0.129	0.550	...	....
Brown river sand	20–32	0.664	12	2.77	0.020	0.057	...	....
	20–32	0.664	20	2.61	0.017	0.043	...	....
	20–32	0.664	30	2.27	0.015	0.034	...	....
	Through 100	...	12	2.59	0.112	0.290	...	....
	Through 100	...	20	2.73	0.077	0.210	...	....
	Through 100	...	30	2.68	0.078	0.208	...	....
	4–8	3.53	20	...	...	...	0.70	9.7
	8–10	2.01	20	...	...	...	0.62	8.6
	32–42	0.40	20	...	...	...	0.56	8.4
	Through 42	...	20	...	...	...	1.00	17.9

Table III. Dielectric Properties of Packed and Loose Dry Alumina Grains

Grit No.[a]	Av. Diam., Mm.	Frequency, Mc.	K		Tan δ		Loss Factor		Relative Loss Factor		Relative Heating Rate	
			Loose	Packed	Loose	Packed	Loose	Packed	Loose	Packed	Loose	Packed
10	2.04	12	4.41	5.22	0.068	0.070	0.300	0.365	0.97	1.18		
	2.04	20	4.68	4.96	0.066	0.071	0.309	0.352	1.00	1.14	1.00	1.16
	2.04	30	4.68	5.27	0.073	0.076	0.342	0.401	1.11	1.30		
16	1.21	12	4.13	4.57	0.040	0.044	0.165	0.201	0.53	0.65		
	1.21	20	4.32	3.96	0.043	0.046	0.186	0.182	0.60	0.59	0.62	...
	1.21	30	4.37	4.27	0.048	0.050	0.210	0.214	0.68	0.69		
24	0.730	12	3.78	4.30	0.020	0.030	0.076	0.129	0.24	0.42		
	0.730	20	4.04	3.69	0.026	0.033	0.105	0.122	0.34	0.39	0.34	0.39
	0.730	30	4.23	4.39	0.032	0.031	0.136	0.136	0.44	0.44		
46	0.365	12	3.19	4.13	0.010	0.036	0.032	0.149	0.10	0.48		
	0.365	20	3.65	3.39	0.014	0.023	0.051	0.078	0.17	0.25	0.17	0.22
	0.365	30	3.77	4.08	0.016	0.016	0.060	0.065	0.19	0.21		
120	0.103	12	2.77	3.61	0.002	0.002	0.005	0.007	0.02	0.02		
	0.103	20	3.23	2.92	0.002	0.003	0.006	0.009	0.02	0.03	0.04	...
	0.103	30	3.09	3.60	0.003	0.003	0.010	0.010	0.03	0.03		

[a] Bulk densities of granular alumina:

Grit No.	Density, G./Cc.		Grit No.	Density, G./Cc.		Grit No.	Density, G./Cc.	
	Loose	Packed		Loose	Packed		Loose	Packed
10	1.99	2.24	24	1.87	2.22	46	1.81	2.16
12	1.93	2.22	30	1.88	2.20	120	1.64	1.84
16	1.93	2.20	36	1.84	2.20			

found. Any effects due to point discharges or space ionization are ruled out for two reasons: First, the results obtained from Q-meter measurements at 0–5 volts are in good agreement with those obtained at 5000–7000 volts; second, when the upper electrode was separated from the particle bed so that the latter could be observed, the same particle size effect was found but there was no visible or audible discharge apparent. For the alumina, detailed analyses for iron, titanium, and silica showed no regular variation in any constituent with grain size. Some variation existed, but it was completely random relative to particle size. The analysis given in the first paragraph is an average, supplied by the manufacturer, and is included to show the magnitude and kind of impurities involved.

Having thus eliminated causes other than dielectric heating as the origin of the variation of heating rate with particle size, it appeared that this result must arise from some direct effect of particle size on the imposed field. The particle beds were macroscopically inhomogeneous, both physically and electrically; therefore, the field might have been distorted in such a way that the larger particles were subjected to greater voltage stress than were the smaller ones, even though the over-all applied voltage was the same for the two beds. To remove a part of this inhomogeneity, in so far as the dielectric constant from point to point in the bed was concerned, the air was replaced by a white mineral oil ($K = 2.32$); the dielectric constant of the interparticle spaces thus was more nearly equal to that of the particles themselves. When this was done, a second important observation was made—namely, that the heating rate of the assemblage was markedly increased (Figure 6), despite the fact that the oil showed a relatively low heating rate under the same conditions. This result can be accounted for on the basis that the voltage drop across the solid particles has been increased by immersing them in such a medium.

The following discussion indicates a mechanism by which such a voltage increase may be obtained.

Consider the dielectric path along any element of area normal to the electrodes as a number of small elemental condensers in series, some having air (or oil) as the dielectric, and some having alumina. Combining all of the air (or oil) elements and integrating over the electrode area, the assemblage can be replaced by a single equivalent air (or oil) condenser as shown in Figure 7. The same can be done with the alumina elements. These two large condensers are in series. The total voltage, E, across this system will be equal to the sum of E_1 and E_2, the voltage across the alumina and air condensers, respectively, or of E_1 and E_3, the voltage across the oil condenser. When the applied voltage is held constant, therefore, $E_1 + E_2$ will be equal to $E_1 + E_3$. The voltage division between any two condensers in series varies inversely as the capacities. Replacing air with mineral oil will increase the capacity of this part of the system because of the increase in dielectric constant; as a result, E_1/E will be greater when the alumina is in series with oil than when it is in series with air. Since the energy dissipated in any material is proportional to the square of the voltage across it and since the alumina represents the high-loss part of the system, this shift in voltage distribution will result in a greater over-all loss when the alumina is immersed in mineral oil than when it is present in air. Table I shows that a further increase in dielectric constant of the medium (castor oil $K = 4.04$) results in a further increase in the loss factor of the assemblage as measured by the Q-meter. Anticipating a relationship which will be brought out later, this increase predicts a corresponding increase in heating rate.

From Figure 6 it is apparent that the ratio between heating rates of any two particle sizes has been changed by changing the surrounding medium. It thus appears that the effect of particle size on heating rate is associated with the electrical inhomogeneity of the mass as suggested above. A complete analysis of the case is not yet possible but further experiments along these lines are being considered.

A third point brought out by the results is the close parallel between loss factors as measured on the Q-meter and heating rates in the case of alumina both in air and oil. For convenience Table I gives relative values of both of these items, based on the measured values at 20 mc. (megacycles) for 2.04-mm. alumina particles in air; it is clear that the parallelism is almost perfect. The approximate temperature rises are included in Table I to indicate the order of magnitude. They were not suitably overlapped, as explained previously, or corrected for amounts of material heated; consequently, ratios of these values would not be expected to agree with the corresponding relative heating rates. The close correlation between the loss factors and heating rates affords a convenient means of determining relative values of either from the other, even in the case of granular materials. Thus, either loss factors or heating rates, whichever can be determined more readily, can be used for comparing the behavior of such materials in an electric field.

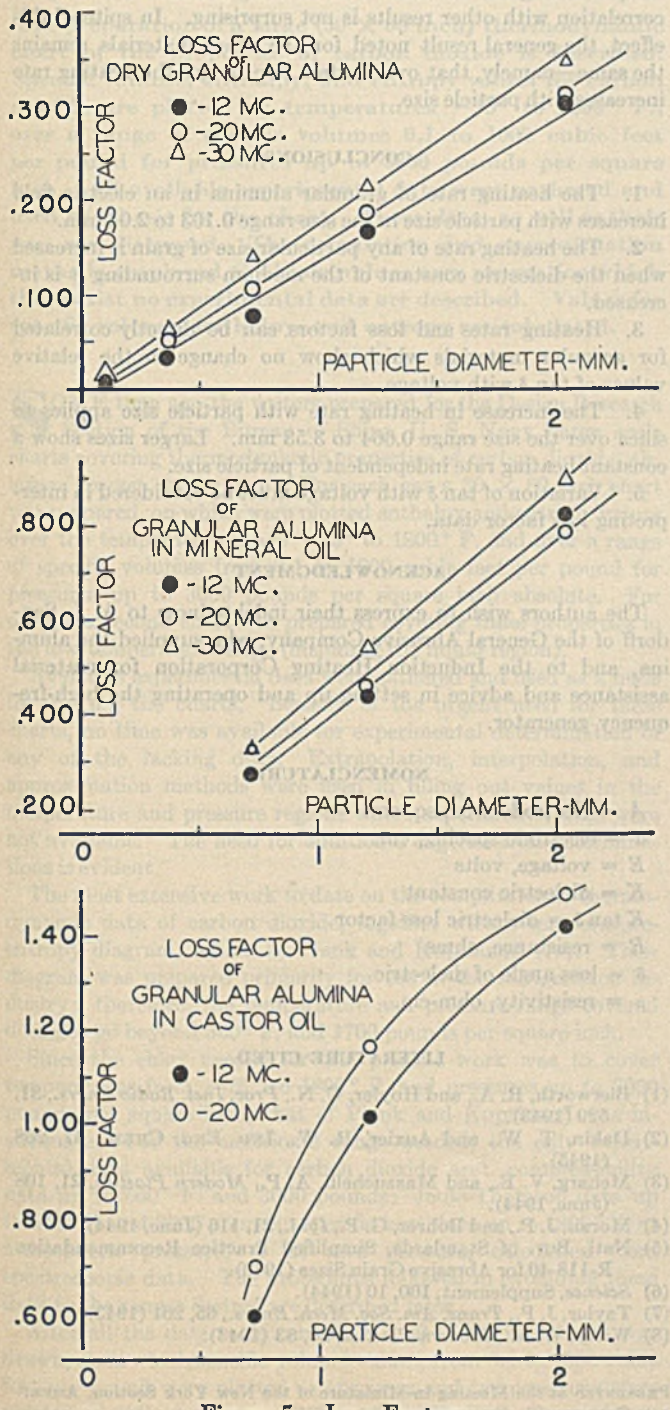


Figure 5. Loss Factors

TABLE IV. SIMULTANEOUS HEATING RATES OF TWO GRAINS AT DIFFERENT VOLTAGES

Volts	Heating Rate, ° C./Min.: No. 46 alumina	Heating Rate, ° C./Min.: 20–32 mesh brown sand	Ratio of Heating Rates
2000	1.5	1.9	1.3
3000	3.8	5.3	1.4
5750	10.5	17.5	1.7
	No. 46 alumina	No. 120 alumina	
3900	6.6	1.3	5.0
6700	19.0	4.0	4.8
8000	27.5	5.6	5.0

TABLE V. SIXTY-CYCLE RESISTANCE AND RESISTIVITY OF VARIOUS GRAINS

Material	Resistance, Megohms	Resistivity, Ohm-Cm.
Empty	[a]	...
No. 10 alumina	[a]	...
No. 46 alumina	900	23.9 × 10^9
No. 120 alumina	400	10.7 × 10^9
20–30 mesh white silica	[a]	...
20–32 mesh brown sand	570	15.2 × 10^9
Through 100 mesh brown sand	18.8	0.5 × 10^9

[a] Resistance in excess of 10^9 ohms.

All of the values of dielectric constant as measured with the Q-meter show a tendency to increase with increasing frequency; in general this amounts to 2–15% in going from 12 to 30 mc. This apparent increase with increasing frequency may be due to a small inductance in the leads from the cell used in determining dielectric constants to the Q-meter. Reasonable precautions were taken to minimize this inductance, but it was not completely eliminated. The effect of this inductance leads to an apparent increase in dielectric constant with increasing frequency. Since the effect of this lead inductance increases with frequency, the data obtained at 12 mc. are the most precise. It seems likely that none of these values should be any greater than those obtained at 12 mc., and it is possible that even they may be slightly higher than the true values. The principal reason for obtaining these determinations over a range of frequencies was to ensure that there was no unique effect of particle size at 20 mc., the frequency at which all heating runs were made. The change in dielectric constant with particle size is independent of frequency in this frequency range so that, while the absolute values of dielectric constant may be somewhat in error, the variation with particle size is well established as independent of the frequency. The relative values for various grain sizes at any one frequency are considerably more precise than the absolute values. These same considerations apply to the precision of tan δ.

SILICA AND BROWN SAND

The results obtained with silica are less complete than those reported for alumina. While certain anomalies do appear in these data, the general result that over certain size ranges the heating rate increases with the size is confirmed. With silica the further result that, above a particular size (3.50 mm. in this case), the heating rate becomes independent of particle size is also evident. The reason for the slight increase in relative heating rate in the case of the smallest size of silica used is not evident at present, and further work in this range is being done. It is possible that it may be associated with heating of the Mycalex cell as mentioned later. Several difficulties were encountered in the work on silica. First, the heating rates were very low and the values obtained are somewhat less accurate; heat losses

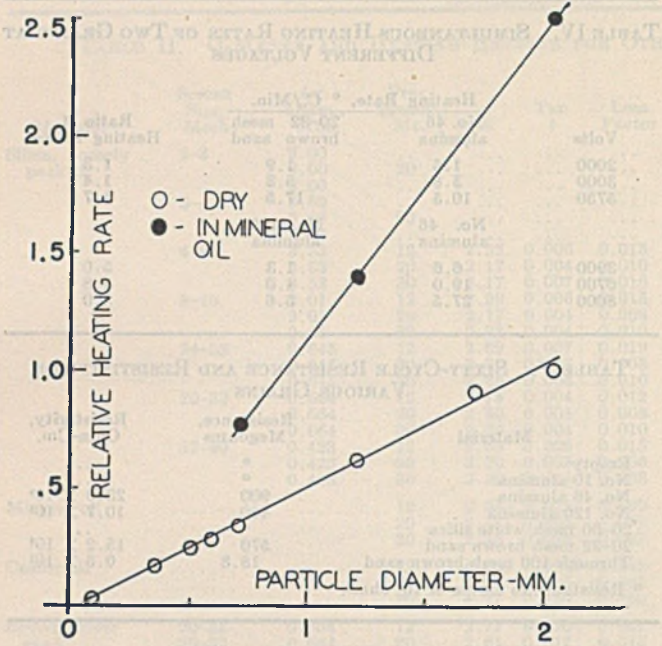
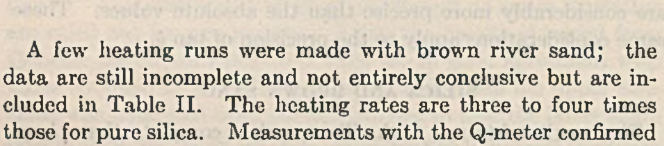


Figure 6. Relative Heating Rates of Granular Alumina at 20 Mc.

increased because the runs had to be longer in order to obtain sufficiently large temperature rises. Second, the Mycalex cell is not a perfect dielectric; while the rate of heating of the cell is negligible compared to the rates obtained with alumina, it may be of some importance in the case of the slower heating silica. Finally, the determination of power factors as low as those in Table II for silica is difficult with the Q-meter, and no great reliance can be put on the values tabulated. In general, power factors determined on the Q-meter are in considerable doubt when the values lie below 0.01. Consequently, no correspondence between loss factors and heating rates is evident in the case of silica. That such a correspondence exists, just as in the case of alumina, seems certain, and it is only the uncertainty in the measuring method that prevents its appearance.



A. **Hypothetical series arrangement of condenser elements along a line normal to electrode**

B. **Equivalent series arrangements of element *A* integrated over electrode area**

Figure 7. Arrangement of Condenser

A few heating runs were made with brown river sand; the data are still incomplete and not entirely conclusive but are included in Table II. The heating rates are three to four times those for pure silica. Measurements with the Q-meter confirmed the fact that the loss factors were also considerably greater. However, a comparison between the heating rate at 20 mc. of 20–32 mesh brown sand (loss factor = 0.043) and that of No. 46 alumina (loss factor = 0.051), both at 5750 volts, showed that brown sand heated 1.7 times more rapidly than alumina. Based on the loss factors as determined by the Q-meter, this ratio should have been 0.84. The heating rate measurements in Table IV were made at a series of voltages, and the ratio mentioned decreases linearly with the voltage in the range covered. Linear extrapolation to zero voltage gives a ratio of 1.08 instead of 0.84 as predicted by the Q-meter measurements in which the sample was subjected to a stress of from 0–5 volts.

A similar check was made of the relative heating rates of No. 46 and 120 alumina at three widely different voltages. The ratio between these rates (Table IV) is independent of voltage in the range covered.

Resistivity was determined (Table V), and that of brown sand was found to be much less than that of any of the other materials, most of which showed essentially infinite resistance at 60 cycles.

The best evidence that the resistivity of the alumina contributed but little to the relations noted is given by the fact that the heating rate increased with grain size. If the resistance losses were the determining factor, the smaller grains, having the lowest mass resistance, would have heated more rapidly than the larger grains.

The relatively low resistance of the brown sand, due probably to the iron oxide content as indicated by the color, makes it unique among the materials here investigated and lack of good correlation with other results is not surprising. In spite of this effect, the general result noted for the other materials remains the same—namely, that over certain size ranges the heating rate increases with particle size.

CONCLUSIONS

1. The heating rate of granular alumina in an electric field increases with particle size in the size range 0.103 to 2.04 mm.
2. The heating rate of any particular size of grain is increased when the dielectric constant of the medium surrounding it is increased.
3. Heating rates and loss factors can be directly correlated for granular materials which show no change in the relative values of $\tan \delta$ with voltage.
4. The increase in heating rate with particle size applies to silica over the size range 0.664 to 3.53 mm. Larger sizes show a constant heating rate independent of particle size.
5. Variation of $\tan \delta$ with voltage must be considered in interpreting loss factor data.

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NOMENCLATURE

A = electrode area, sq. cm.
d = electrode spacing, cm.
E = voltage, volts
K = dielectric constant
$K \tan \delta$ = dielectric loss factor
R = resistance, ohms
δ = loss angle of dielectric
ρ = resistivity, ohm-cm.

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Thermodynamic Properties of Gases

CARBON DIOXIDE

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The preparation of a large (30 × 80 inch) thermodynamic chart of the properties of carbon dioxide is described. Specific volume, enthalpy, and entropy values for carbon dioxide are plotted at temperatures −75° to 1800° F., over a range of specific volumes 0.1 to 1000 cubic feet per pound for pressures up to 3000 pounds per square inch. All available experimental data were gathered and used as a basis for the chart. These data, as well as their use, are discussed. The calculation and approximation methods employed to obtain values over ranges for which there exist no experimental data are described. Values for specific volume, enthalpy, and entropy are tabulated.

SOME time ago the writers prepared for the Design Research Section of the Bureau of Ships, U. S. Navy, large scale charts covering thermodynamic properties of carbon dioxide, air, argon, oxygen, and steam. For each gas a 30 × 80 inch chart was prepared, on which were plotted enthalpy and entropy values over the temperature range −75° to 1800° F. and over a range of specific volumes from 0.1 to 1000 cubic feet per pound for pressures up to 3000 pounds per square inch absolute. For oxygen a second chart was prepared covering these properties in the low-temperature range (including the liquid region).

Available experimental data were gathered and used as a basis for making the charts. Because of the urgent need for these charts, no time was available for experimental determination of any of the lacking data. Extrapolation, interpolation, and approximation methods were used in filling out values in the temperature and pressure regions where experimental data were not available. The need for additional experimental determinations is evident.

The most extensive work to date on the compilation of thermodynamic data of carbon dioxide, together with a temperature-entropy diagram, is that of Plank and Kuprianoff (*16*). Their diagram was prepared primarily for use in the refrigeration industry; therefore, the temperature and pressure range covered does not go beyond 300° F. and 1700 pounds per square inch.

Since the chart needed for the present work was to cover temperatures from −75° to 1800° F. and pressures up to 3000 pounds per square inch, that of Plank and Kuprianoff was inadequate. For the additional range needed, the only experimental data available for carbon dioxide are: compressibility data up to 500° F. and 3000 pounds; Joule-Thomson data up to 575° F. and 3000 pounds; specific heat data up to 1800° F. at atmospheric pressure, or at zero pressure, calculated from spectroscopic data. The procedures followed in extending these data to the ranges desired are described later.

After all the data were compiled, a 30 × 80 inch chart was drawn, upon which specific volume values, from 0.1 to 1000 cubic feet per pound were plotted as abscissas and temperatures were plotted as ordinates from −75° to 1800° F., in the form of constant pressure, enthalpy, and entropy lines. Figure 1 is a small scale drawing of this chart, which contains only a few lines to indicate the form followed.

In the temperature and pressure range for which experimental data were available, the properties can be read from the large chart with an accuracy within the limits of error of the data. The various properties can be read from the chart over the temperature and pressure ranges for which experimental data are lacking, with a maximum error of not over 5% at the highest pressures; the error is less than 2% at pressures below 1500 pounds per square inch.

The specific volume, enthalpy, and entropy values for the entire temperature and pressure range covered by the chart are presented in Tables I to VII.

SPECIFIC VOLUME CALCULATIONS

Various equations of state, which are modifications of the familiar equation $PV = NRT$, have been derived for representing P-V-T relations of gases under conditions at which their behavior deviates from that of a perfect gas. In general, these equations are complicated and necessitate laborious calculations in practical use. Furthermore, for accurate work they are generally limited to the pressure and temperature range in which experimental compressibility data exist so that the needed constants can be obtained. Dodge (*4*) reviews the various general equations of state which have been proposed thus far.

Plank and Kuprianoff (*16*) derived a fairly simple equation of state for calculating specific volumes of carbon dioxide which follows the experimental data in the superheated vapor region with an average deviation of less than 1%:

$$v = 0.2437\frac{T}{P} - \frac{1.32 + 1.3794 \times 10^{-3}P}{\left(\frac{T}{180}\right)^{10/3}} \tag{1}$$

A general equation of state may be written

$$Pv = ZRT \tag{2}$$

where Z, the compressibility factor, is a function of pressure, temperature, and the nature of the gas. Values of Z at any temperature and pressure can be calculated from compressibility (Pv) data and substituted in Equation 2 for the desired P-V-T relation calculations.

However, values of Z for different gases are most readily correlated by plotting Z for various gases at the same reduced pressures and temperatures. Compressibility factor charts (graphs of $Z = Pv/RT$ against reduced pressures for various values of reduced temperatures) have been drawn for many gases (*5, 8, 12, 20*).

Experimental compressibility data for carbon dioxide are available up to approximately 500° F. over the entire pressure range covered by this work (up to 3000 pounds per square inch) (*1, 10, 13, 14, 15, 17*).

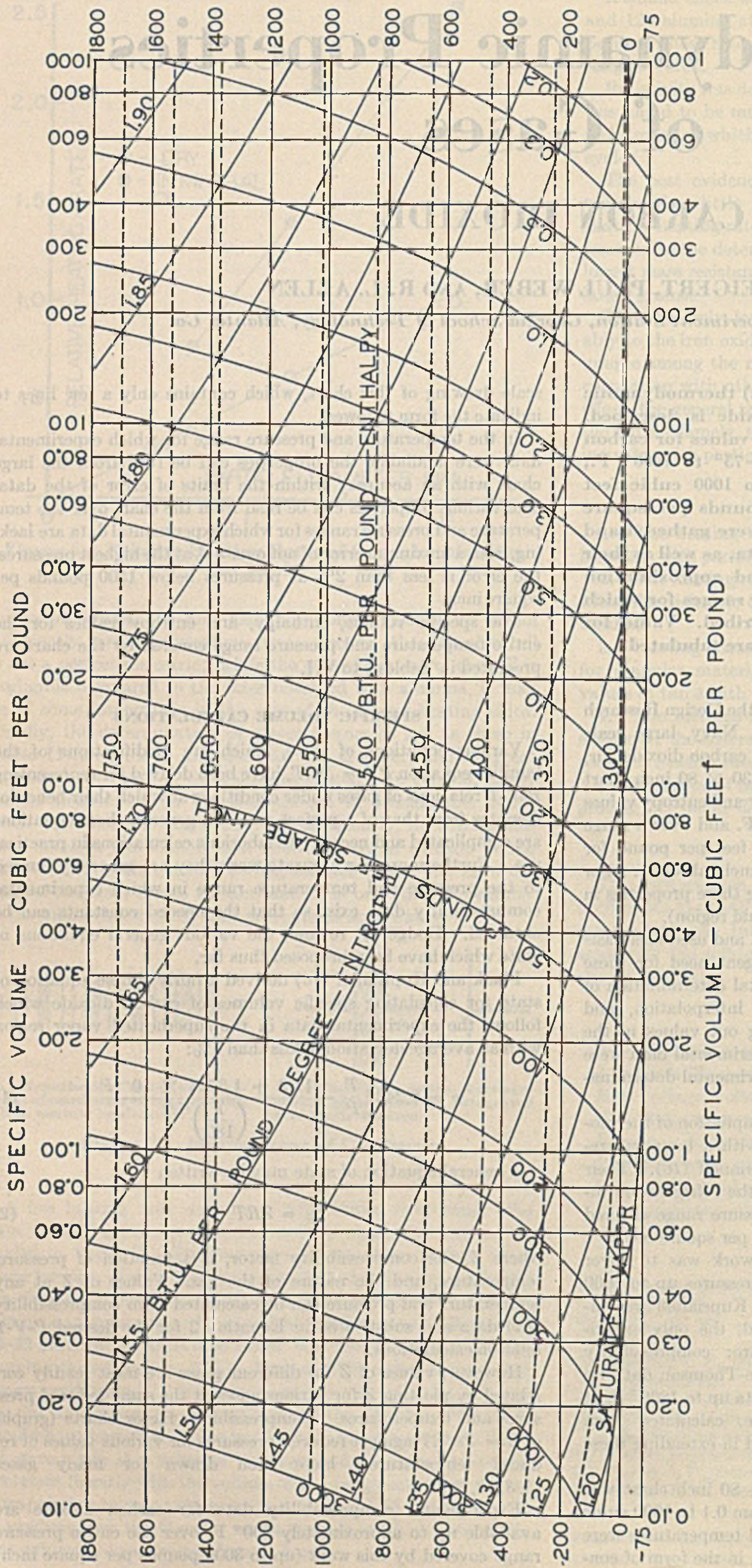

Figure 1. Temperature-Log Specific Volume Chart for Carbon Dioxide

Specific volume values for saturated carbon dioxide vapor based on data by Plank and Kuprianoff (*16*) were tabulated by Quinn and Jones (*17*) over the temperature range from −70° F. up to the critical point.

COMPRESSIBILITY FACTOR CHART

Compressibility factors for carbon dioxide were calculated from all the experimental (Pv) data available and plotted on a large scale graph. Figure 2 is a small scale drawing of this chart containing only a few lines; the solid lines represent values based on experimental data available for carbon dioxide.

Compressibility factors above 500° F. were based on averaged data for nitrogen, air, argon, carbon monoxide, ethylene, methane, and propane at similar reduced temperatures and pressures. The dotted line in Figure 2 shows compressibility factors at T_R = 4.1287 (1800° F. for carbon dioxide) based on these averaged data. Similar lines for the other temperatures above 500° F. were drawn on the large scale chart.

Compressibility factors were also plotted against temperatures for various pressures (Figure 3). The solid lines represent experimental data for carbon dioxide, and the dotted lines show Z values based on averaged data from the other gases at corresponding reduced conditions. Extrapolation was used along with the Z value averages for other gases in connecting the dotted lines with the solid lines. From the large scale compressibility factor charts (Figures 2 and 3), values were obtained for use in calculating the specific volumes for carbon dioxide in the superheated vapor region.

The maximum values of reduced temperature and reduced pressure for carbon dioxide covered by this work are T_R = 4.1287 and P_R = 2.8. At these same maximum reduced conditions the experimental compressibility factors for all the other gases thus far reported are less than 1.05. The value for carbon dioxide at these same conditions, as read from the charts represented by Figures 2 and 3, is approximated to be 1.01. Thus it is likely that the maximum error in the estimated values for compressibility factors for carbon dioxide, upon which specific volume calculations were based, is within 4% at 3000 pounds per square inch and 1800° F. At lower temperatures and/or lower pressures the probable errors are less (Figure 3).

HEAT CAPACITY AND LATENT HEAT

A critical survey of the literature on heat capacity data for carbon dioxide was made by Leduc (*11*). Quinn and Jones (*17*) discussed these data as well as later work published through 1935.

Sweigert and Beardsley (*19*) derived Equation 3 based on spectroscopic data for calculating the specific heat of carbon dioxide at zero pressure:

$$C_p = 16.2 - \frac{6.53 \times 10^3}{T} + \frac{1.41 \times 10^6}{T^2} \qquad (3)$$

Comparison of values obtained by Equation 3 with experimentally determined C_p values as reported in the literature (*7*) shows that the former are somewhat higher than those calculated by Leduc (*11*) from available experimental data. Only the experimental C_p data by Eucken and Lüde (*6*) are in fairly good agreement with values obtained by Equation 3. However, Eucken and Lüde did not report data above 400° F.

It was believed that heat capacity values based on spectroscopic data would be more accurate than the experimentally determined C_p data because of more precise measurements possible with the former measurements which are independent of high temperatures. Therefore, Equation 3 was used in this work where a heat capacity relation at zero pressure was needed.

Only fragmentary data on experimental heat capacities are available for carbon dioxide at pressures above 1 atmosphere. Jenkin and Pye (*9*) determined heat capacities at various temperatures up to 90° F. and pressures up to 47 atmospheres. Eucken and Mücke (*7*) determined C_p values at 780° F. and 5.8 atmospheres and also at 1100° F. and 8.6 atmospheres. Workman (*21*) determined heat capacities at 63 atmospheres for temperatures up to 212° F.

Thus, except for purposes of checking, these experimental heat capacity data at higher pressures were of

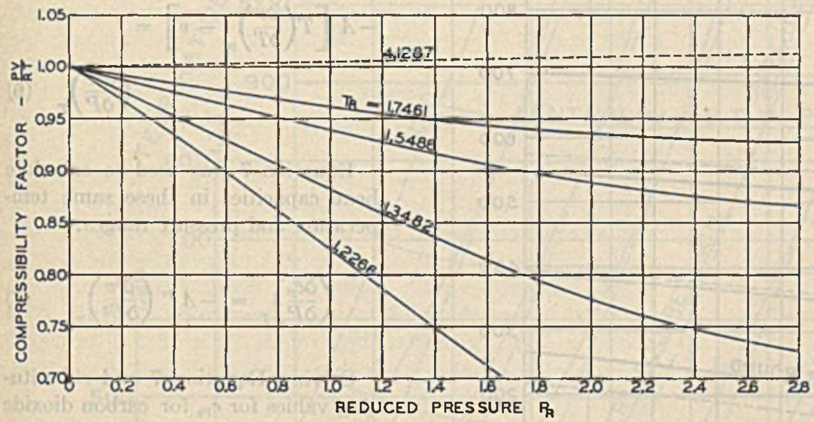

Figure 2. Compressibility Factor Chart for Carbon Dioxide

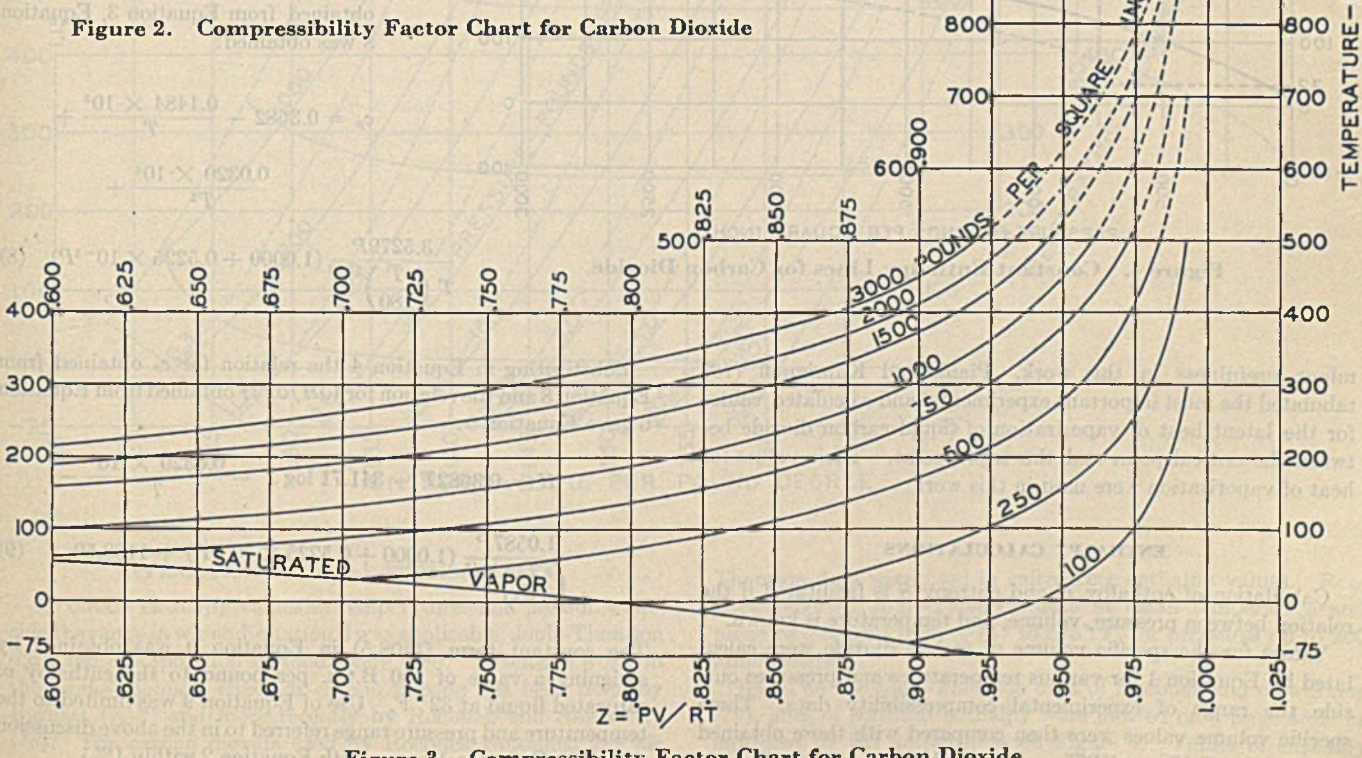

Figure 3. Compressibility Factor Chart for Carbon Dioxide

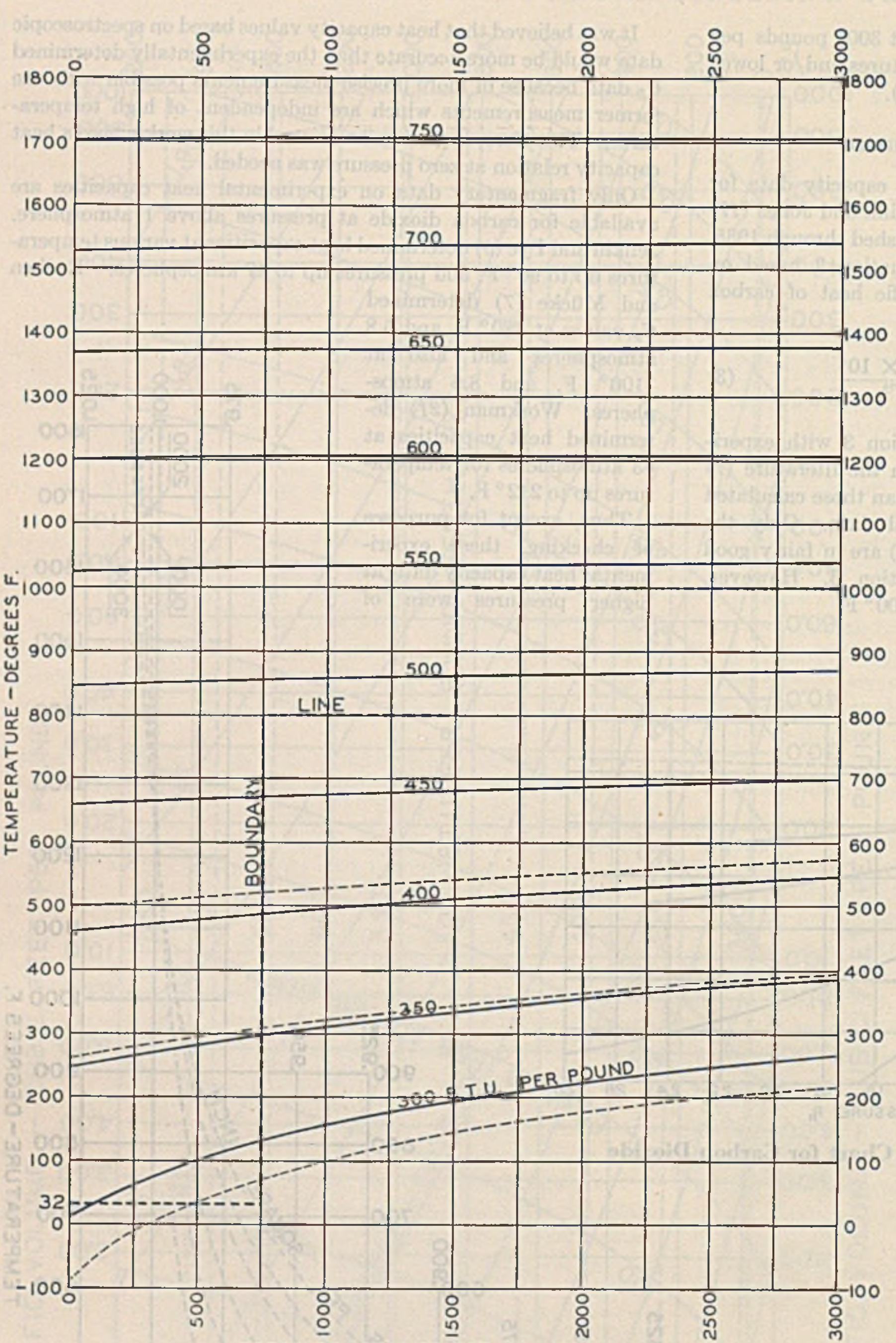

Figure 4. Constant Enthalpy Lines for Carbon Dioxide

minor usefulness in this work. Plank and Kuprianoff (*16*) tabulated the most important experimental and calculated values for the latent heat of vaporization of liquid carbon dioxide between the critical point and the triple point. Their values for heat of vaporization were used in this work.

ENTHALPY CALCULATIONS

Calculation of enthalpy H and entropy S is facilitated if the relation between pressure, volume, and temperature is known.

Values for the specific volume of carbon dioxide were calculated by Equation 1 for various temperatures and pressures outside the range of experimental compressibility data. These specific volume values were then compared with those obtained by Equation 2 ($Pv = ZRT$), using Z values taken from Figures 2 and 3. Equation 1 was found to agree within 1% with Equation 2 over the following ranges in the superheated vapor region: from 32° to 1800° F. at all pressures up to 750 pounds per square inch; from 800° at all pressures up to 1500 pounds; from 1000° to 1800° at all pressures up to 3000 pounds.

For calculation of enthalpy H in the superheated region over the temperature and pressure ranges just mentioned, Equation 9, developed from Equation 4, was used:

$$dH = c_p dT - A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dP \quad (4)$$

$$\text{where } c_p = \left(\frac{\partial H}{\partial T}\right)_p \quad (5)$$

$$-A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = \left(\frac{\partial H}{\partial P}\right)_T \quad (6)$$

Equation 7 was used to calculate heat capacities in these same temperature and pressure ranges:

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad (7)$$

Solving Equation 7 and substituting values for c_{p_0} for carbon dioxide obtained from Equation 3, Equation 8 was obtained:

$$c_p = 0.3682 - \frac{0.1484 \times 10^3}{T} + \frac{0.0320 \times 10^6}{T^2} + \frac{3.5279P}{T\left(\frac{T}{180}\right)^{10/3}}(1.0000 + 0.5225 \times 10^{-3}P) \quad (8)$$

Substituting in Equation 4 the relation for c_p obtained from Equation 8 and the relation for $(\partial H/\partial P)_T$ obtained from Equation 6 gave Equation 9:

$$H = 0.3682T - 341.71 \log T - \frac{0.0320 \times 10^6}{T} - \frac{1.0587P}{\left(\frac{T}{180}\right)^{10/3}}(1.0000 + 0.5225 \times 10^{-3}P) + 1108.50 \quad (9)$$

The constant term (1108.5) in Equation 9 was obtained by assigning a value of 180 B.t.u. per pound to the enthalpy of saturated liquid at 32° F. Use of Equation 9 was limited to the temperature and pressure range referred to in the above discussion (in which Equation 1 agrees with Equation 2 within 1%).

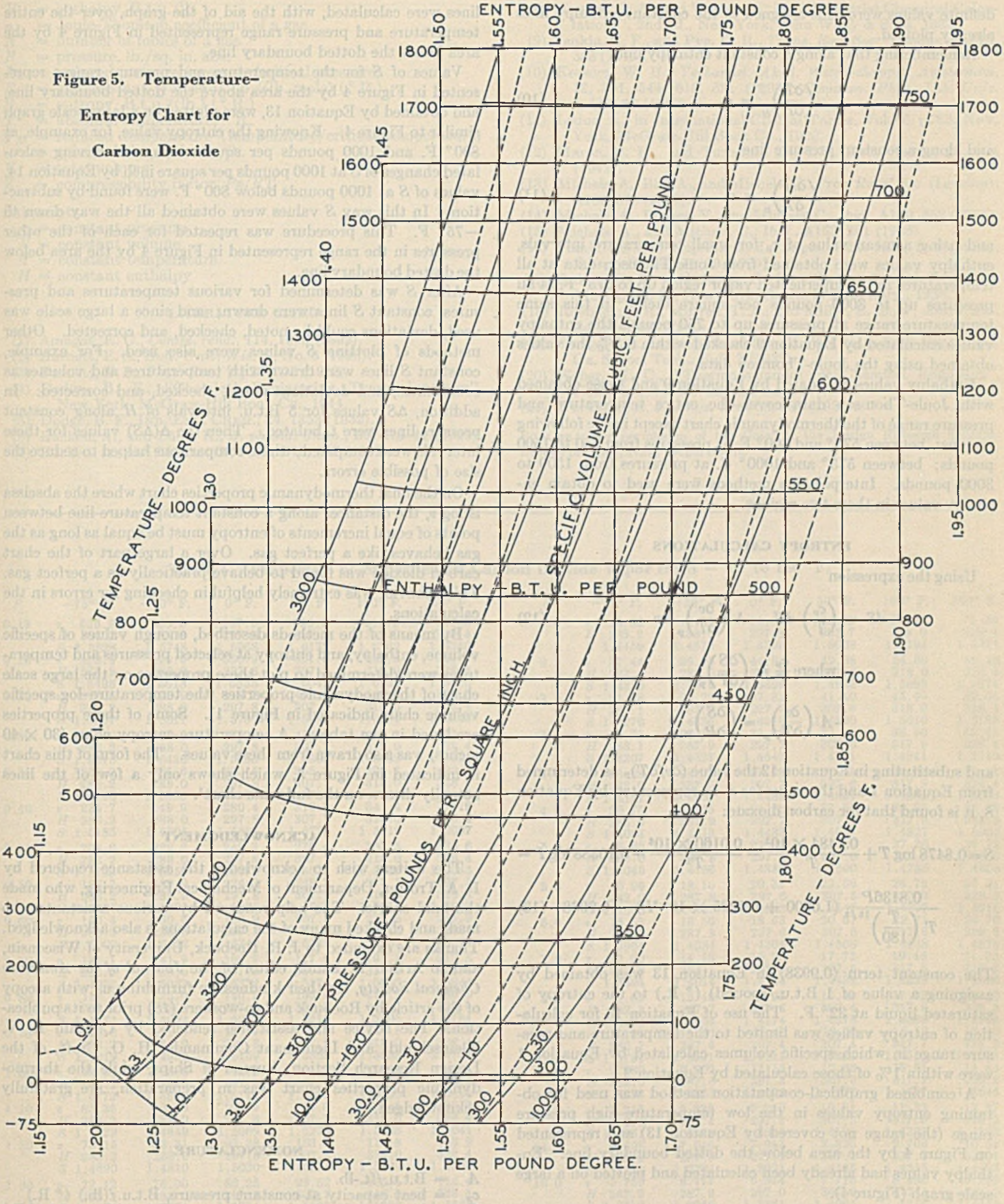

Figure 5. Temperature-Entropy Chart for Carbon Dioxide

APPLICATION OF JOULE-THOMSON DATA

To obtain enthalpy values at temperatures and pressures outside the range in which Equation 9 was applicable, Joule-Thomson data and extrapolation methods were used. Extensive work on the Joule-Thomson effect in carbon dioxide has been done by Burnett (*2, 3*) and more recently by Roebuck and co-workers (*18*). The carbon dioxide used by Roebuck contained less air impurity than that by Burnett; therefore the Roebuck Joule-Thomson data were used in calculating enthalpy values. Roebuck reported Joule-Thomson data at small temperature and pressure intervals from −75° to 575° F. for pressures up to 200 atmospheres.

Based on the Joule-Thomson data of Roebuck and co-workers (*19*), lines of constant enthalpy were plotted on a large scale as indicated by the dotted lines on Figure 4. Values of enthalpy along the zero pressure line were then calculated by Equation 9;

definite values were thus assigned to the constant enthalpy lines already plotted.

Remembering that along a constant enthalpy line

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu \tag{10}$$

and along a constant pressure line

$$\left(\frac{\partial H}{\partial T}\right)_p = c_p \tag{11}$$

and using a mean value of c_p for small temperature intervals, enthalpy values were obtained from Joule-Thomson data at all temperatures in the superheated vapor region up to 575° F. at all pressures up to 3000 pounds per square inch. In this same temperature range at pressures up to 750 pounds the enthalpy values calculated by Equation 9 checked within 0.5% the values obtained using the Joule-Thomson data.

Enthalpy values calculated by Equation 9 and those obtained with Joule-Thomson data cover the entire temperature and pressure range of the thermodynamic chart except in the following regions: between 575° and 800° F. at pressures from 750 to 1500 pounds; between 575° and 1000° F. at pressures from 1500 to 3000 pounds. Interpolation methods were used to obtain enthalpy values in these two regions.

ENTROPY CALCULATIONS

Using the expression

$$dS = \left(\frac{c_p}{T}\right) dT - A \left(\frac{\partial v}{\partial T}\right)_p dp \tag{12}$$

$$\text{where } \frac{c_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p$$

$$-A \left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial S}{\partial P}\right)_T$$

and substituting in Equation 12 the value $(\partial v/\partial T)_p$ as determined from Equation 1 and the value for c_p as represented by Equation 8, it is found that for carbon dioxide:

$$S = 0.8478 \log T + \frac{0.1484 \times 10^3}{T} - \frac{0.0160 \times 10^6}{T^2} - 0.10388 \log P - \frac{0.8136P}{T\left(\frac{T}{180}\right)^{10/3}} (1.0000 + 0.5225 \times 10^{-3}P) - 0.9938 \tag{13}$$

The constant term (0.9938) in Equation 13 was obtained by assigning a value of 1 B.t.u./(pound) (° R.) to the entropy of saturated liquid at 32° F. The use of Equation 13 for calculation of entropy values was limited to the temperature and pressure range in which specific volumes calculated by Equation 1 were within 1% of those calculated by Equation 2.

A combined graphical-computation method was used for obtaining entropy values in the low temperature–high pressure range (the range not covered by Equation 13) and represented on Figure 4 by the area below the dotted boundary line. Enthalpy values had already been calculated and plotted on a large scale graph (Figure 4).

Along a constant pressure path,

$$dS = dH/T \tag{14}$$

Small increments (0.1 B.t.u./pound) for dH were marked off along constant pressure ordinates in Figure 4 and the corresponding average temperatures for these small increments were read. Substitution in Equation 14 provided corresponding values for dS. In this way small increments of dS along constant pressure lines were calculated, with the aid of the graph, over the entire temperature and pressure range represented in Figure 4 by the area below the dotted boundary line.

Values of S for the temperature and pressure ranges represented in Figure 4 by the area above the dotted boundary line, and obtained by Equation 13, were plotted on a large scale graph similar to Figure 4. Knowing the entropy value, for example, at 800° F. and 1000 pounds per square inch, and having calculated changes of S at 1000 pounds per square inch by Equation 14, values of S at 1000 pounds below 800° F. were found by subtraction. In this way S values were obtained all the way down to −75° F. This procedure was repeated for each of the other pressures in the range represented in Figure 4 by the area below the dotted boundary line.

After S was determined for various temperatures and pressures, constant S lines were drawn; and since a large scale was used, deviations could be noted, checked, and corrected. Other methods of plotting S values were also used. For example, constant S lines were drawn with temperatures and volumes as coordinates, and deviations noted, checked, and corrected. In addition, ΔS values for 5 B.t.u. intervals of H along constant pressure lines were tabulated. Then the $\Delta(\Delta S)$ values for these intervals were compared; these comparisons helped to reduce the size of possible errors.

On the final thermodynamic properties chart where the abscissa is log v, the distances along a constant temperature line between points of equal increments of entropy must be equal as long as the gas behaves like a perfect gas. Over a large part of the chart carbon dioxide was found to behave practically as a perfect gas. This behavior was extremely helpful in checking for errors in the calculations.

By means of the methods described, enough values of specific volume, enthalpy, and entropy at selected pressures and temperatures were determined to plot these properties on the large scale chart of thermodynamic properties (the temperature–log specific volume chart indicated in Figure 1). Some of these properties are listed in the tables. A temperature-entropy chart (30 × 40 inches) was also drawn from these values. The form of this chart is indicated in Figure 5, which shows only a few of the lines actually drawn on the full scale chart[1].

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NOMENCLATURE

A = B.t.u./ft.-lb.
c_p = heat capacity at constant pressure, B.t.u./(lb.) (° R.)
C_p = heat capacity at constant pressure, B.t.u./(lb. mole) (° R.)

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[1] A limited number of full scale blue-line prints of the thermodynamic properties chart (Figure 1) and of the temperature-entropy chart (Figure 5) are available and can be obtained at $2.50 each and $1.50 each, respectively, by addressing the State Engineering Experiment Station, Georgia School of Technology, Atlanta, Ga. The quality of the prints of the thermodynamic properties chart is not quite so good as that of the smaller temperature-entropy chart prints because the original tracing was damaged slightly. However, the prints of the temperature-entropy chart are excellent.

H = enthalpy, B.t.u./lb.
μ = Joule-Thomson coefficient of a gas
N = number of moles of a gas
P = pressure, lb./sq. in. abs.
P_R = reduced pressure (pressure/critical pressure)
R = gas constant = 1544 ft.-lb./(lb. mole) (° R.)
S = entropy, B.t.u./(lb.) (° R.)
T = absolute temperature, ° R.
T_R = reduced temperature (temperature/critical temperature)
v = specific volume, cu. ft./lb.
V = total volume
Z = compressibility factor, Pv/RT

Subscripts
p = constant pressure
V = constant volume
T = constant temperature
H = constant enthalpy

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Table I. Properties of Superheated Carbon Dioxide Vapor from − 75° to 150° F.

P		−75° F.	−50° F.	0° F.	50° F.	100° F.	150° F.
0.15	v	625.9	666.6	747.9	829.2	910.5	991.8
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5628	1.5748	1.5968	1.6172	1.6362	1.6540
0.20	v	469.4	499.9	560.9	621.9	682.8	743.8
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5498	1.5618	1.5838	1.6042	1.6232	1.6410
0.25	v	375.5	399.9	448.7	497.5	546.3	595.0
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5397	1.5517	1.5737	1.5941	1.6131	1.6309
0.30	v	312.9	333.3	373.9	414.6	455.2	495.9
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5315	1.5435	1.5655	1.5859	1.6049	1.6227
0.35	v	268.2	285.6	320.5	355.3	300.2	425.0
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5246	1.5366	1.5586	1.5790	1.5980	1.6158
0.40	v	234.7	249.9	280.4	310.9	341.4	371.9
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5185	1.5305	1.5525	1.5729	1.5919	1.6097
0.45	v	208.6	222.2	249.3	276.4	303.5	330.6
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5133	1.5253	1.5473	1.5677	1.5867	1.6045
0.50	v	187.7	199.9	224.3	248.7	273.1	297.5
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5085	1.5205	1.5425	1.5629	1.5819	1.5997
0.60	v	156.4	166.6	186.9	207.3	227.6	247.9
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.5002	1.5122	1.5342	1.5546	1.5736	1.5914
0.70	v	134.1	141.9	160.2	177.6	195.1	212.5
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4932	1.5052	1.5272	1.5476	1.5666	1.5844
0.80	v	117.4	125.0	140.2	155.5	170.7	186.0
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4872	1.4992	1.5212	1.5416	1.5606	1.5784
0.90	v	104.3	111.1	124.7	138.2	151.8	165.3
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4819	1.4939	1.5159	1.5363	1.5553	1.5731
1.00	v	93.90	100.0	112.2	124.4	136.6	148.8
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4772	1.4892	1.5112	1.5316	1.5506	1.5684
1.10	v	85.36	90.90	101.9	113.0	124.1	135.2
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4729	1.4849	1.5069	1.5273	1.5463	1.5641
1.20	v	78.15	83.31	93.38	103.5	113.8	123.9
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4690	1.4810	1.5030	1.5234	1.5424	1.5602
1.30	v	72.12	76.90	86.25	95.62	105.1	114.4
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4654	1.4774	1.4994	1.5198	1.5388	1.5566
1.40	v	66.97	71.41	80.18	88.79	97.56	106.2
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4620	1.4740	1.4960	1.5164	1.5354	1.5532
1.50	v	62.49	66.65	74.73	82.85	90.39	99.18
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4589	1.4709	1.4929	1.5133	1.5323	1.5401
1.60	v	58.58	62.48	70.04	77.65	85.36	92.98
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4560	1.4680	1.4900	1.5104	1.5294	1.5472
1.80	v	52.09	55.53	62.26	69.02	75.88	82.65
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4507	1.4627	1.4847	1.5051	1.5241	1.5419
2.0	v	46.82	49.96	56.03	62.12	68.29	74.39
	H	283.2	288.0	297.8	307.7	318.0	328.4
	S	1.4459	1.4579	1.4799	1.5003	1.5193	1.5371
2.5	v	37.44	39.95	44.81	49.68	54.58	59.46
	H	283.1	288.0	297.8	307.7	318.0	328.4
	S	1.4359	1.4479	1.4699	1.4903	1.5093	1.5271
3.0	v	31.18	33.28	37.32	41.40	45.49	49.55
	H	283.1	287.9	297.7	307.6	318.0	328.4
	S	1.4276	1.4396	1.4616	1.4820	1.5010	1.5188
3.5	v	26.71	28.50	31.98	35.48	38.96	42.43
	H	283.1	287.9	297.7	307.6	317.9	328.4
	S	1.4207	1.4327	1.4547	1.4751	1.4941	1.5119
4.0	v	23.38	24.93	27.98	31.03	34.09	37.13
	H	283.0	287.9	297.7	307.6	317.9	328.4
	S	1.4147	1.4267	1.4487	1.4691	1.4881	1.5059
4.5	v	20.75	22.15	24.86	27.58	30.29	33.02
	H	283.0	287.9	297.7	307.6	317.9	328.4
	S	1.4093	1.4213	1.4433	1.4637	1.4827	1.5005
5.0	v	18.66	19.91	22.37	24.82	27.26	29.72
	H	283.0	287.8	297.6	307.6	317.9	328.3
	S	1.4046	1.4166	1.4386	1.4590	1.4780	1.4958
5.5	v	16.96	18.10	20.33	22.56	24.76	27.01
	H	282.9	287.8	297.6	307.5	317.9	328.3
	S	1.4003	1.4123	1.4343	1.4547	1.4737	1.4915
6.0	v	15.53	16.56	18.63	20.67	22.71	24.76
	H	282.9	287.8	297.6	307.5	317.8	328.3
	S	1.3964	1.4084	1.4304	1.4508	1.4698	1.4876
7.0	v	13.30	14.18	15.96	17.71	19.46	21.22
	H	282.8	287.7	297.5	307.5	317.8	328.3
	S	1.3894	1.4014	1.4234	1.4438	1.4628	1.4806
8.0	v	11.62	12.40	13.96	15.49	17.02	18.56
	H	282.8	287.7	297.5	307.4	317.8	328.3
	S	1.3834	1.3954	1.4174	1.4378	1.4568	1.4746
9.0	v	10.32	11.01	12.40	13.76	15.12	16.49
	H	282.7	287.6	297.4	307.4	317.7	328.2
	S	1.3781	1.3901	1.4121	1.4325	1.4515	1.4693
10.0	v	9.280	9.902	11.15	12.38	13.61	14.84
	H	282.6	287.5	297.3	307.3	317.7	328.2
	S	1.3733	1.3853	1.4073	1.4277	1.4467	1.4645
12.0	v	7.715	8.236	9.280	10.31	11.33	12.37
	H	282.5	287.4	297.2	307.2	317.6	328.2
	S	1.3651	1.3771	1.3991	1.4195	1.4385	1.4563
14.0	v	6.598	7.046	7.945	8.826	9.703	10.59
	H	282.3	287.3	297.1	307.1	317.5	328.1
	S	1.3580	1.3701	1.3921	1.4125	1.4315	1.4493
16.0	v	5.759	6.177	6.944	7.716	8.485	9.266
	H	282.2	287.2	297.0	307.0	317.4	328.0
	S	1.3519	1.3640	1.3861	1.4065	1.4255	1.4433
20.0	v	4.586	4.904	5.542	6.119	6.778	7.407
	H	281.9	287.0	296.8	306.8	317.3	327.9
	S	1.3417	1.3538	1.3759	1.3964	1.4154	1.4332
24.0	v	3.803	4.070	4.607	5.125	5.640	6.167
	H	281.7	286.8	296.6	306.6	317.1	327.8
	S	1.3331	1.3452	1.3674	1.3879	1.4070	1.4249
28.0	v	3.246	3.471	3.939	4.385	4.826	5.282
	H	281.4	286.6	296.4	306.4	317.0	327.7
	S	1.3260	1.3381	1.3603	1.3809	1.4000	1.4179

Continued on page 192

Table I (*Continued*)

P		−75° F.	−50° F.	0° F.	50° F.	100° F.	150° F.
32.0	v	2.825	3.028	3.439	3.829	4.217	4.617
	H	281.1	286.4	296.2	306.3	316.8	327.6
	S	1.3196	1.3318	1.3540	1.3746	1.3938	1.4117
36.0	v	2.499	2.681	3.050	3.398	3.743	4.101
	H	280.9	286.1	296.0	306.1	316.7	327.5
	S	1.3140	1.3262	1.3485	1.3691	1.3883	1.4063
40.0	v	2.239	2.404	2.738	3.053	3.363	3.688
	H	280.6	285.9	295.8	305.9	316.5	327.4
	S	1.3088	1.3211	1.3435	1.3642	1.3834	1.4014
44.0	v	2.025	2.177	2.483	2.771	3.054	3.349
	H	280.4	285.7	295.6	305.7	316.4	327.3
	S	1.3040	1.3163	1.3388	1.3596	1.3789	1.3969
48.0	v	1.847	1.987	2.270	2.535	2.795	3.068
	H	280.1	285.5	295.4	305.5	316.2	327.2
	S	1.2993	1.3118	1.3344	1.3553	1.3747	1.3928
52.0	v	1.696	1.827	2.091	2.335	2.576	2.829
	H	279.8	285.3	295.2	305.4	316.1	327.1
	S	1.2944	1.3072	1.3301	1.3511	1.3706	1.3888
56.0	v	1.568	1.690	1.936	2.164	2.388	2.625
	H	279.6	285.1	295.0	305.2	316.0	327.0
	S	1.2888	1.3024	1.3259	1.3472	1.3668	1.3851
60.0	v	1.456	1.571	1.803	2.016	2.225	2.448
	H	279.3	284.9	294.8	305.0	315.8	326.9
	S	1.2801	1.2961	1.3213	1.3432	1.3631	1.3815
70.0	v	....	1.329	1.536	1.720	1.901	2.094
	H	....	284.4	294.3	304.5	315.4	326.7
	S	....	1.2860	1.3120	1.3354	1.3557	1.3743
80.0	v	....	1.154	1.335	1.498	1.657	1.828
	H	....	283.8	293.8	304.1	315.1	326.4
	S	....	1.2778	1.3044	1.3284	1.3490	1.3679
90.0	v	....	1.015	1.179	1.325	1.476	1.621
	H	....	283.3	293.3	303.6	314.7	326.2
	S	....	1.2709	1.2981	1.3224	1.3433	1.3623
100	v	....	0.905	1.055	1.187	1.316	1.456
	H	....	282.8	292.7	303.2	314.3	325.9
	S	....	1.2649	1.2924	1.3171	1.3382	1.3573
120	v	....	....	0.8665	0.9799	1.088	1.208
	H	....	....	291.7	302.2	313.6	325.4
	S	....	....	1.2833	1.3086	1.3297	1.3488
140	v	....	....	0.7315	0.8317	0.9252	1.032
	H	....	....	290.7	301.3	312.8	324.9
	S	....	....	1.2747	1.3005	1.3220	1.3413
160	v	....	....	0.6305	0.7207	0.8033	0.8986
	H	....	....	289.7	300.4	312.1	324.4
	S	....	....	1.2666	1.2928	1.3154	1.3350
180	v	....	....	0.5519	0.6344	0.7110	0.7952
	H	....	....	288.7	299.5	311.3	323.9
	S	....	....	1.2590	1.2865	1.3093	1.3291
200	v	....	....	0.4891	0.5652	0.6376	0.7125
	H	....	....	287.7	298.6	310.6	323.4
	S	....	....	1.2519	1.2805	1.3038	1.3239
220	v	....	....	0.4376	0.5087	0.5755	0.6450
	H	....	....	286.6	297.7	309.8	322.9
	S	....	....	1.2454	1.2748	1.2987	1.3191
240	v	....	....	0.3948	0.4614	0.5237	0.5886
	H	....	....	285.6	296.7	309.1	322.4
	S	....	....	1.2395	1.2694	1.2940	1.3145
260	v	....	....	0.3584	0.4215	0.4799	0.5406
	H	....	....	284.6	295.8	308.4	321.9
	S	....	....	1.2344	1.2643	1.2896	1.3105
280	v	....	....	0.3286	0.3865	0.4425	0.4994
	H	....	....	283.6	294.9	307.6	321.4
	S	....	....	1.2299	1.2596	1.2853	1.3064
300	v	....	....	....	0.3563	0.4100	0.4636
	H	....	....	....	294.0	306.9	320.9
	S	....	....	....	1.2562	1.2813	1.3029
320	v	....	....	....	0.3298	0.3815	0.4322
	H	....	....	....	293.1	306.1	320.4
	S	....	....	....	1.2518	1.2774	1.2993
340	v	....	....	....	0.3065	0.3564	0.4045
	H	....	....	....	292.2	305.4	319.9
	S	....	....	....	1.2477	1.2736	1.2958
360	v	....	....	....	0.2858	0.3341	0.3780
	H	....	....	....	291.2	304.6	319.4
	S	....	....	....	1.2436	1.2699	1.2925
380	v	....	....	....	0.2672	0.3141	0.3581
	H	....	....	....	290.3	303.9	318.9
	S	....	....	....	1.2395	1.2661	1.2890
400	v	....	....	....	0.2505	0.2961	0.3383
	H	....	....	....	289.4	303.1	318.4
	S	....	....	....	1.2357	1.2627	1.2859
420	v	....	....	....	0.2354	0.2799	0.3203
	H	....	....	....	288.5	302.4	317.9
	S	....	....	....	1.2320	1.2593	1.2828
440	v	....	....	....	0.2216	0.2652	0.3040
	H	....	....	....	287.6	301.6	317.4
	S	....	....	....	1.2282	1.2559	1.2797
480	v	....	....	....	0.1975	0.2393	0.2657
	H	....	....	....	285.7	300.1	316.4
	S	....	....	....	1.2215	1.2498	1.2741
520	v	....	....	....	0.1772	0.2174	0.2513
	H	....	....	....	283.9	298.7	315.4
	S	....	....	....	1.2148	1.2438	1.2687
560	v	....	....	....	0.1598	0.1986	0.2304
	H	....	....	....	282.1	297.2	314.4
	S	....	....	....	1.2086	1.2381	1.2635
600	v	....	....	....	0.1452	0.1823	0.2123
	H	....	....	....	280.3	295.7	313.4
	S	....	....	....	1.2020	1.2323	1.2583
650	v	....	....	....	....	0.1648	0.1928
	H	....	....	....	....	293.8	312.2
	S	....	....	....	....	1.2269	1.2534
700	v	....	....	....	....	0.1453	0.1760
	H	....	....	....	....	292.0	310.9
	S	....	....	....	....	1.2216	1.2486
750	v	....	....	....	....	0.1320	0.1615
	H	....	....	....	....	290.1	309.7
	S	....	....	....	....	1.2161	1.2436
800	v	....	....	....	....	0.1196	0.1483
	H	....	....	....	....	288.2	308.4
	S	....	....	....	....	1.2111	1.2391
850	v	....	....	....	....	0.1089	0.1373
	H	....	....	....	....	286.4	307.2
	S	....	....	....	....	1.2061	1.2346
900	v	....	....	....	....	0.1000	0.1273
	H	....	....	....	....	284.5	305.9
	S	....	....	....	....	1.2010	1.2301
950	v	....	....	....	....	....	0.1183
	H	....	....	....	....	....	304.7
	S	....	....	....	....	....	1.2260
1000	v	....	....	....	....	....	0.1101
	H	....	....	....	....	....	303.4
	S	....	....	....	....	....	1.2218

Table II. Properties of Superheated Carbon Dioxide from 200° to 450° F.

P		200° F.	250° F.	300° F.	350° F.	400° F.	450° F.
0.20	v	804.8	865.8	926.7	987.7	....	....
	H	339.1	350.1	361.4	372.9	....	....
	S	1.6578	1.6738	1.6891	1.7037	....	....
0.25	v	643.8	692.6	741.4	790.1	838.9	887.7
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6477	1.6637	1.6790	1.6936	1.7076	1.7213
0.30	v	536.5	577.2	617.8	658.5	699.1	739.7
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6395	1.6555	1.6708	1.6854	1.6994	1.7131
0.35	v	459.9	494.7	529.5	564.4	599.2	634.1
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6326	1.6486	1.6639	1.6785	1.6925	1.7062
0.40	v	402.4	432.9	463.3	493.8	524.3	554.8
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6265	1.6425	1.6578	1.6724	1.6864	1.7001
0.45	v	357.7	384.8	411.9	438.9	466.0	493.1
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6213	1.6373	1.6526	1.6672	1.6812	1.6949
0.50	v	321.9	346.3	370.7	395.0	419.4	443.8
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6165	1.6325	1.6478	1.6624	1.6764	1.6901
0.60	v	268.2	288.6	308.9	329.2	349.5	369.8
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6082	1.6242	1.6395	1.6541	1.6681	1.6818
0.70	v	229.9	247.3	264.7	282.2	299.6	317.0
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.6012	1.6172	1.6325	1.6471	1.6611	1.6748
0.80	v	201.2	216.5	231.7	246.9	262.2	277.4
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5952	1.6112	1.6265	1.6411	1.6551	1.6688
0.90	v	178.9	192.4	206.0	219.5	233.0	246.5
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5899	1.6059	1.6212	1.6358	1.6498	1.6635
1.00	v	161.0	173.2	185.4	197.5	209.7	221.9
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5852	1.6012	1.6165	1.6311	1.6451	1.6588
1.10	v	146.3	157.4	168.5	179.5	190.6	201.7
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5809	1.5969	1.6120	1.6268	1.6408	1.6545
1.20	v	134.1	144.3	154.4	164.6	174.7	184.9
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5770	1.5930	1.6083	1.6229	1.6369	1.6506
1.30	v	123.8	133.2	142.5	151.9	161.3	170.7
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5734	1.5894	1.6047	1.6193	1.6333	1.6470
1.40	v	114.9	123.6	132.3	141.1	149.8	158.5
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5700	1.5860	1.6013	1.6159	1.6299	1.6436
1.50	v	107.3	115.4	123.5	131.7	138.9	147.9
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5669	1.5829	1.5982	1.6128	1.6268	1.6405
1.60	v	100.6	108.2	115.8	123.4	131.0	138.7
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5640	1.5800	1.5953	1.6099	1.6239	1.6376
1.80	v	89.42	96.20	102.9	109.7	116.5	123.2
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5587	1.5747	1.5900	1.6046	1.6186	1.6323
2.0	v	80.48	86.58	92.67	98.77	104.8	110.9
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5539	1.5699	1.5852	1.5998	1.6138	1.6275

Continued on page 193

Table II (*Continued*)

P		200° F.	250° F.	300° F.	350° F.	400° F.	450° F.
2.5	*v*	64.37	69.26	74.14	79.01	83.89	88.77
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5439	1.5599	1.5752	1.5898	1.6038	1.6175
3.0	*v*	53.64	57.72	61.78	65.85	69.91	73.97
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5356	1.5516	1.5669	1.5815	1.5955	1.6092
3.5	*v*	45.98	49.47	52.95	56.44	59.92	63.41
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5287	1.5447	1.5600	1.5746	1.5886	1.6023
4.0	*v*	40.22	43.29	46.33	49.38	52.43	55.48
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5227	1.5387	1.5540	1.5686	1.5826	1.5963
4.5	*v*	35.75	38.48	41.19	43.89	46.60	49.31
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5173	1.5333	1.5486	1.5632	1.5772	1.5909
5.0	*v*	32.17	34.61	39.06	39.51	41.93	44.38
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5126	1.5286	1.5439	1.5585	1.5725	1.5862
5.5	*v*	29.25	31.47	33.69	35.91	38.12	40.35
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5083	1.5243	1.5396	1.5542	1.5682	1.5819
6.0	*v*	26.80	28.84	30.87	32.92	34.94	36.98
	H	339.1	350.1	361.4	372.9	384.7	396.8
	S	1.5044	1.5204	1.5357	1.5503	1.5643	1.5780
7.0	*v*	22.97	24.71	26.46	28.21	29.94	31.70
	H	339.0	350.0	361.4	372.9	384.7	396.8
	S	1.4974	1.5134	1.5287	1.5433	1.5573	1.5710
8.0	*v*	20.09	21.62	23.14	24.60	26.20	27.74
	H	339.0	350.0	361.3	372.8	384.7	396.8
	S	1.4914	1.5074	1.5227	1.5373	1.5513	1.5650
9.0	*v*	17.85	19.21	20.57	21.93	23.28	24.66
	H	339.0	350.0	361.3	372.8	384.7	396.8
	S	1.4861	1.5021	1.5174	1.5320	1.5460	1.5597
10.0	*v*	16.06	17.29	18.51	19.74	20.96	22.19
	H	339.0	350.0	361.3	372.8	384.6	396.8
	S	1.4813	1.4973	1.5126	1.5272	1.5412	1.5549
12.0	*v*	13.38	14.41	15.42	16.44	17.46	18.49
	H	338.9	349.9	361.3	372.8	384.6	396.7
	S	1.4731	1.4891	1.5044	1.5190	1.5330	1.5467
14.0	*v*	11.46	12.34	13.22	14.09	14.96	15.84
	H	338.9	349.9	361.2	372.8	384.6	396.7
	S	1.4661	1.4821	1.4974	1.5120	1.5260	1.5397
16.0	*v*	10.03	10.80	11.56	12.33	13.09	13.86
	H	338.9	349.9	361.2	372.7	384.6	396.7
	S	1.4601	1.4761	1.4914	1.5060	1.5200	1.5337
20.0	*v*	8.016	8.633	9.247	9.861	10.47	11.09
	H	338.8	349.8	361.1	372.7	384.5	396.7
	S	1.4500	1.4660	1.4813	1.4959	1.5099	1.5236
24.0	*v*	6.674	7.190	7.701	8.215	8.724	9.236
	H	338.7	349.7	361.1	372.6	384.5	396.6
	S	1.4418	1.4578	1.4731	1.4877	1.5017	1.5154
28.0	*v*	5.718	6.160	6.599	7.039	7.475	7.918
	H	338.6	349.7	361.0	372.6	384.5	396.6
	S	1.4348	1.4509	1.4662	1.4808	1.4948	1.5085
32.0	*v*	4.999	5.387	5.773	6.157	6.541	6.925
	H	338.6	349.6	361.0	372.5	384.4	396.6
	S	1.4286	1.4447	1.4601	1.4747	1.4887	1.5024
36.0	*v*	4.441	4.785	5.130	5.470	5.812	6.156
	H	338.5	349.5	360.9	372.5	384.4	396.5
	S	1.4232	1.4393	1.4547	1.4694	1.4834	1.4971
40.0	*v*	3.993	4.304	4.615	4.922	5.230	5.538
	H	338.4	349.5	360.9	372.4	384.3	396.5
	S	1.4184	1.4345	1.4499	1.4646	1.4787	1.4924
44.0	*v*	3.628	3.972	4.193	4.473	4.753	5.034
	H	338.4	349.4	360.8	372.4	384.3	396.5
	S	1.4139	1.4301	1.4455	1.4602	1.4743	1.4881
48.0	*v*	3.323	3.587	3.843	4.099	4.355	4.614
	H	338.3	349.3	360.7	372.3	384.2	396.4
	S	1.4098	1.4260	1.4415	1.4562	1.4703	1.4841
52.0	*v*	3.065	3.306	3.545	3.783	4.019	4.258
	H	338.2	349.3	360.7	372.3	384.2	396.4
	S	1.4059	1.4221	1.4376	1.4524	1.4665	1.4803
56.0	*v*	2.844	3.068	3.291	3.511	3.731	3.954
	H	338.2	349.2	360.6	372.3	384.2	396.4
	S	1.4023	1.4186	1.4341	1.4489	1.4631	1.4769
60.0	*v*	2.652	2.862	3.070	3.276	3.481	3.689
	H	338.1	349.1	360.5	372.1	384.1	396.3
	S	1.3988	1.4152	1.4308	1.4456	1.4598	1.4737
70.0	*v*	2.269	2.450	2.628	2.806	2.982	3.071
	H	337.9	348.9	360.4	372.0	384.0	396.2
	S	1.3917	1.4082	1.4238	1.4386	1.4528	1.4667
80.0	*v*	1.982	2.141	2.298	2.453	2.608	2.764
	H	337.7	348.8	360.2	371.9	383.9	396.1
	S	1.3855	1.4020	1.4177	1.4326	1.4468	1.4607
90.0	*v*	1.758	1.900	2.040	2.178	2.317	2.457
	H	337.5	348.6	360.1	371.8	383.8	396.0
	S	1.3800	1.3966	1.4123	1.4272	1.4415	1.4554
100	*v*	1.579	1.708	1.834	1.960	2.083	2.210
	H	337.3	348.4	360.0	371.7	383.7	395.9
	S	1.3751	1.3917	1.4075	1.4224	1.4367	1.4506
120	*v*	1.311	1.420	1.525	1.630	1.734	1.840
	H	337.0	348.1	359.7	371.5	383.5	395.8
	S	1.3666	1.3835	1.3993	1.4142	1.4285	1.4424
140	*v*	1.118	1.214	1.305	1.395	1.485	1.576
	H	336.7	347.8	359.4	371.2	383.3	395.6
	S	1.3592	1.3759	1.3918	1.4068	1.4212	1.4352
160	*v*	0.9760	1.059	1.139	1.219	1.297	1.378
	H	336.3	347.4	359.1	371.0	383.1	395.4
	S	1.3529	1.3697	1.3857	1.4000	1.4151	1.4290
180	*v*	0.8642	0.9387	1.011	1.082	1.152	1.224
	H	836.0	347.1	358.8	370.7	382.9	395.3
	S	1.3472	1.3641	1.3802	1.3952	1.4097	1.4236
200	*v*	0.7748	0.8424	0.9075	0.9720	1.035	1.100
	H	335.6	346.7	358.5	370.5	382.7	395.2
	S	1.3421	1.3592	1.3753	1.3903	1.4049	1.4188
220	*v*	0.7017	0.7638	0.8233	0.8823	0.9400	0.9993
	H	335.3	346.4	358.2	370.2	382.5	395.0
	S	1.3374	1.3546	1.3707	1.3859	1.4004	1.4144
240	*v*	0.6407	0.6981	0.7532	0.8074	0.8604	0.9152
	H	334.9	346.1	358.0	370.0	382.3	394.8
	S	1.3330	1.3511	1.3671	1.3817	1.3963	1.4103
260	*v*	0.5890	0.6427	0.6938	0.7440	0.7933	0.8441
	H	334.6	345.7	357.7	369.8	382.1	394.7
	S	1.3297	1.3466	1.3629	1.3781	1.3928	1.4068
280	*v*	0.5448	0.5950	0.6428	0.6896	0.7358	0.7833
	H	334.2	345.4	357.4	369.5	381.8	394.5
	S	1.3253	1.3428	1.3592	1.3745	1.3891	1.4032
300	*v*	0.5065	0.5539	0.5985	0.6427	0.6868	0.7303
	H	333.9	345.1	357.1	369.3	381.6	394.3
	S	1.3219	1.3395	1.3560	1.3715	1.3862	1.4002
320	*v*	0.4729	0.5177	0.5601	0.6015	0.6422	0.6840
	H	333.5	344.7	356.8	369.0	381.4	394.2
	S	1.3185	1.3364	1.3530	1.3685	1.3832	1.3972
340	*v*	0.4434	0.4857	0.5261	0.5653	0.6037	0.6434
	H	333.2	344.4	356.5	368.8	381.2	394.0
	S	1.3154	1.3334	1.3501	1.3657	1.3804	1.3944
360	*v*	0.4171	0.4576	0.4958	0.5329	0.5693	0.6071
	H	332.8	344.0	356.3	368.6	381.0	393.7
	S	1.3124	1.3306	1.3475	1.3631	1.3779	1.3919
380	*v*	0.3936	0.4323	0.4687	0.5041	0.5387	0.5747
	H	332.5	343.7	356.0	368.3	380.8	393.5
	S	1.3092	1.3276	1.3446	1.3603	1.3751	1.3892
400	*v*	0.3724	0.4095	0.4443	0.4781	0.5110	0.5455
	H	332.1	343.4	355.7	368.1	380.6	393.4
	S	1.3064	1.3250	1.3421	1.3579	1.3728	1.3869
420	*v*	0.3532	0.3887	0.4222	0.4546	0.4861	0.5190
	H	331.8	343.0	355.4	367.8	308.4	393.2
	S	1.3035	1.3223	1.3395	1.3554	1.3704	1.3846
440	*v*	0.3358	0.3701	0.4022	0.4332	0.4633	0.4950
	H	331.4	342.7	355.1	367.6	380.2	393.0
	S	1.3006	1.3196	1.3370	1.3530	1.3681	1.3823
480	*v*	0.3054	0.3373	0.3670	0.3958	0.4236	0.4530
	H	330.7	342.0	354.5	367.1	379.8	392.7
	S	1.2954	1.3147	1.3324	1.3486	1.3637	1.3781
520	*v*	0.2795	0.3096	0.3374	0.3641	0.3901	0.4174
	H	330.0	341.4	354.0	366.6	379.4	392.3
	S	1.2905	1.3102	1.3281	1.3446	1.3599	1.3744
560	*v*	0.2574	0.2858	0.3119	0.3369	0.3613	0.3869
	H	329.3	340.7	353.4	366.2	379.0	392.0
	S	1.2857	1.3057	1.3239	1.3406	1.3561	1.3708
600	*v*	0.2383	0.2652	0.2898	0.3135	0.3363	0.3605
	H	328.6	340.0	352.8	365.7	378.6	391.7
	S	1.2809	1.3013	1.3198	1.3368	1.3525	1.3677
650	*v*	0.2176	0.2430	0.2661	0.2881	0.3094	0.3323
	H	327.7	339.2	352.1	365.1	378.1	391.1
	S	1.2763	1.2969	1.3156	1.3328	1.3486	1.3632
700	*v*	0.2000	0.2239	0.2457	0.2664	0.2864	0.3075
	H	326.9	338.3	351.4	364.5	377.6	390.8
	S	1.2718	1.2927	1.3117	1.3291	1.3450	1.3600
750	*v*	0.1846	0.2074	0.2281	0.2476	0.2664	0.2865
	H	326.0	337.5	350.7	363.9	377.0	390.3
	S	1.2672	1.2884	1.3076	1.3252	1.3412	1.3563
800	*v*	0.1712	0.1930	0.2126	0.2311	0.2489	0.2681
	H	325.1	336.6	350.0	363.3	376.5	389.9
	S	1.2631	1.2846	1.3041	1.3219	1.3380	1.3532
850	*v*	0.1594	0.1803	0.1990	0.2166	0.2335	0.2518
	H	324.2	335.8	349.2	362.7	376.0	389.5
	S	1.2590	1.2808	1.3005	1.3185	1.3348	1.3501
900	*v*	0.1489	0.1690	0.1869	0.2037	0.2198	0.2372
	H	323.4	334.9	348.5	362.1	375.5	389.1
	S	1.2549	1.2770	1.2970	1.3152	1.3317	1.3471
950	*v*	0.1394	0.1588	0.1761	0.1921	0.2075	0.2243
	H	322.5	344.1	347.8	361.5	375.0	388.6
	S	1.2511	1.2734	1.2937	1.3121	1.3288	1.3443
1000	*v*	0.1310	0.1497	0.1663	0.1819	0.1966	0.2126
	H	321.6	333.3	347.1	360.9	374.5	388.2
	S	1.2472	1.2697	1.2903	1.3089	1.3258	1.3415
1100	*v*	0.1164	0.1339	0.1495	0.1646	0.1778	0.1925
	H	320.7	331.6	345.7	359.7	373.5	387.3
	S	1.2405	1.2635	1.2844	1.3033	1.3205	1.3364
1200	*v*	0.1042	0.1208	0.1356	0.1493	0.1621	0.1756
	H	318.4	329.9	344.2	358.5	372.5	386.5
	S	1.2343	1.2579	1.2791	1.2983	1.3158	1.3319
1300	*v*	....	0.1100	0.1237	0.1368	0.1488	0.1614
	H	....	328.2	342.8	357.3	371.4	385.6
	S	....	1.2530	1.2746	1.2941	1.3117	1.3279
1400	*v*	....	....	0.1136	0.1260	0.1375	0.1492
	H	....	....	341.4	356.1	370.4	384.8
	S	....	....	1.2703	1.2901	1.3078	1.3242
1500	*v*	....	....	0.1049	0.1167	0.1277	0.1386
	H	....	....	339.9	354.9	369.1	383.9
	S	....	....	1.2659	1.2861	1.3039	1.3205
1600	*v*	....	....	....	0.1086	0.1191	0.1294
	H	....	....	....	353.7	367.6	383.0
	S	....	....	....	1.2822	1.3002	1.3170
1700	*v*	....	....	....	0.1014	0.1115	0.1213
	H	....	....	....	352.2	366.0	383.2
	S	....	....	....	1.2783	1.2966	1.3135
1800	*v*	....	....	....	....	0.1047	0.1140
	H	....	....	....	....	364.0	382.3
	S	....	....	....	....	1.2930	1.3101
1900	*v*	....	....	....	....	....	0.1075
	H	....	....	....	....	....	381.5
	S	....	....	....	....	....	1.3063
2000	*v*	....	....	....	....	....	0.1017
	H	....	....	....	....	....	379.4
	S	....	....	....	....	....	1.3029

Table III. Properties of Superheated Carbon Dioxide Vapor from 500° to 750° F.

P		500° F.	550° F.	600° F.	650° F.	700° F.	750° F.
0.25	v	936.5	985.3	....	....	....	....
	H	409.1	421.6	....	....	....	....
	S	1.7344	1.7471	....	....	....	....
0.30	v	780.4	821.0	861.7	902.3	943.0	983.6
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.7262	1.7389	1.7512	1.7630	1.7745	1.7857
0.35	v	668.9	703.7	738.6	773.4	808.3	843.1
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.7193	1.7320	1.7443	1.7561	1.7676	1.7788
0.40	v	585.3	615.8	646.3	676.7	707.2	737.7
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.7132	1.7259	1.7382	1.7500	1.7615	1.7727
0.45	v	520.2	547.3	574.4	601.5	628.6	655.7
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.7080	1.7207	1.7330	1.7448	1.7563	1.7675
0.50	v	468.2	492.6	517.0	541.4	565.8	590.2
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.7032	1.7159	1.7282	1.7400	1.7515	1.7627
0.60	v	390.2	410.5	430.8	451.1	471.5	491.8
	H	309.1	421.6	434.4	447.3	460.4	473.7
	S	1.6949	1.7076	1.7199	1.7317	1.7432	1.7544
0.70	v	334.4	351.8	369.3	386.7	404.1	421.5
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6879	1.7006	1.7129	1.7247	1.7362	1.7474
0.80	v	292.6	307.9	323.1	338.3	353.6	368.8
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6819	1.6946	1.7069	1.7187	1.7302	1.7414
.90	v	260.1	273.6	287.2	300.7	314.3	327.8
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6766	1.6893	1.7016	1.7134	1.7249	1.7361
.00	v	234.1	246.3	258.5	270.7	282.9	295.1
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6719	1.6846	1.6969	1.7087	1.7202	1.7314
1.10	v	212.8	223.9	235.0	246.1	257.1	268.2
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6676	1.6803	1.6926	1.7044	1.7159	1.7271
1.20	v	195.1	205.2	215.4	225.5	235.7	245.9
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6637	1.6764	1.6887	1.7005	1.7120	1.7232
1.30	v	180.1	189.4	198.8	208.2	217.6	227.0
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6601	1.6728	1.6851	1.6969	1.7084	1.7196
1.40	v	167.2	175.9	184.6	193.3	202.0	210.7
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6567	1.6694	1.6817	1.6935	1.7050	1.7162
1.50	v	156.0	164.2	172.3	180.4	188.6	196.7
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6536	1.6663	1.6786	1.6904	1.7019	1.7131
1.60	v	146.3	153.9	161.5	169.1	176.8	184.4
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6507	1.6634	1.6757	1.6875	1.6990	1.7102
1.80	v	130.0	136.8	143.6	150.3	157.1	163.9
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6454	1.6581	1.6704	1.6822	1.6937	1.7049
2.0	v	117.0	123.1	129.2	135.3	141.4	147.5
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6406	1.6533	1.6656	1.6774	1.6889	1.7001
2.5	v	93.65	98.53	103.4	108.2	113.1	118.0
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6306	1.6433	1.6556	1.6674	1.6789	1.6901
3.0	v	78.04	82.10	86.17	90.23	94.30	98.36
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6223	1.6350	1.6473	1.6591	1.6706	1.6818
3.5	v	66.89	70.37	73.86	77.34	80.83	84.31
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6154	1.6281	1.6404	1.6522	1.6637	1.6749
4.0	v	58.53	61.58	64.63	67.67	70.72	73.77
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6094	1.6221	1.6344	1.6462	1.6577	1.6689
4.5	v	52.02	54.73	57.44	60.15	62.86	65.57
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.6040	1.6167	1.6290	1.6408	1.6523	1.6635
5.0	v	46.82	49.26	51.70	54.14	56.58	59.02
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5993	1.6120	1.6243	1.6361	1.6476	1.6588
5.5	v	42.56	44.78	47.00	49.22	51.43	53.65
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5950	1.6077	1.6200	1.6318	1.6433	1.6545
6.0	v	39.02	41.05	43.08	45.11	47.15	49.18
	H	409.1	421.6	434.4	447.3	460.4	437.7
	S	1.5911	1.6038	1.6161	1.6279	1.6394	1.6506
7.0	v	33.44	35.18	36.93	38.67	40.41	42.15
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5841	1.5968	1.6091	1.6209	1.6324	1.6436
8.0	v	29.27	30.79	32.32	33.84	35.36	36.89
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5781	1.5908	1.6031	1.6149	1.6264	1.6376
9.0	v	26.01	27.37	28.72	30.08	31.43	32.80
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5728	1.5855	1.5978	1.6096	1.6211	1.6323
10.0	v	23.41	24.63	25.85	27.07	28.29	29.51
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5680	1.5807	1.5930	1.6048	1.6163	1.6275
12.0	v	19.51	20.53	21.54	22.55	23.57	24.59
	H	409.1	421.6	434.4	447.3	460.4	473.7
	S	1.5598	1.5725	1.5848	1.5066	1.6081	1.6193
14.0	v	16.72	17.59	18.46	19.33	20.20	21.07
	H	409.0	421.6	434.4	447.3	460.4	473.7
	S	1.5528	1.5655	1.5778	1.5896	1.6011	1.6123
16.0	v	14.62	15.39	16.15	16.91	17.68	18.44
	H	409.0	421.5	434.4	447.3	460.4	473.7
	S	1.5468	1.5595	1.5718	1.5836	1.5951	1.6063
20.0	v	11.70	12.31	12.92	13.53	14.14	14.75
	H	409.0	421.5	434.3	447.3	460.4	473.7
	S	1.5367	1.5494	1.5617	1.5735	1.5850	1.5962
24.0	v	9.750	10.26	10.77	11.27	11.78	12.29
	H	409.0	421.5	434.3	447.3	460.4	473.7
	S	1.5285	1.5412	1.5535	1.5653	1.5768	1.5880
28.0	v	8.355	8.790	9.232	9.668	10.10	10.53
	H	408.9	421.5	434.3	447.2	460.4	473.7
	S	1.5216	1.5343	1.5466	1.5584	1.5699	1.5811
32.0	v	7.380	7.691	8.078	8.459	8.840	9.222
	H	408.9	421.4	434.3	447.2	460.3	473.7
	S	1.5155	1.5282	1.5405	1.5523	1.5638	1.5750
36.0	v	6.496	6.835	7.181	7.519	7.858	8.197
	H	408.9	421.4	434.3	447.2	460.3	473.6
	S	1.5102	1.5229	1.5352	1.5470	1.5585	1.5697
40.0	v	5.845	6.151	6.458	6.764	7.069	7.377
	H	408.8	421.4	434.2	447.2	460.3	473.6
	S	1.5055	1.5182	1.5305	1.5423	1.5538	1.5650
44.0	v	5.314	5.592	5.870	6.149	6.426	6.706
	H	408.8	421.4	434.2	447.1	460.3	473.6
	S	1.5012	1.5139	1.5262	1.5380	1.5495	1.5607
48.0	v	4.871	5.124	5.380	5.636	5.891	6.148
	H	408.8	421.3	434.2	447.1	460.2	473.6
	S	1.4973	1.5100	1.5223	1.5341	1.5456	1.5568
52.0	v	4.495	4.730	4.964	5.201	5.436	5.672
	H	408.7	421.3	434.2	447.1	460.2	473.6
	S	1.4935	1.5063	1.5186	1.5304	1.5419	1.5531
56.0	v	4.173	4.391	4.610	4.830	5.048	5.267
	H	408.7	421.3	434.1	447.1	460.2	473.6
	S	1.4901	1.5029	1.5153	1.5271	1.5386	1.5498
60.0	v	3.893	4.098	4.303	4.507	4.710	4.917
	H	408.7	421.2	434.1	447.0	460.2	473.6
	S	1.4869	1.4997	1.5121	1.5240	1.5355	1.5466
70.0	v	3.336	3.512	3.687	3.863	4.037	4.212
	H	408.6	421.2	434.1	447.0	460.1	473.5
	S	1.4799	1.4927	1.5051	1.5170	1.5285	1.5397
80.0	v	2.918	3.072	3.226	3.379	3.531	3.686
	H	408.5	421.1	434.0	447.0	460.1	473.5
	S	1.4739	1.4867	1.4991	1.5110	1.5225	1.5337
90.0	v	2.593	2.729	2.867	3.003	3.138	3.275
	H	408.4	421.1	434.0	447.0	460.1	473.5
	S	1.4686	1.4814	1.4938	1.5057	1.5172	1.5284
100	v	2.333	2.456	2.579	2.702	2.824	2.948
	H	408.3	421.0	433.9	446.9	460.0	473.5
	S	1.4638	1.4766	1.4890	1.5009	1.5124	1.5236
120	v	1.943	2.045	2.148	2.251	2.353	2.456
	H	408.2	420.9	433.8	446.8	459.9	473.4
	S	1.4556	1.4684	1.4808	1.4927	1.5042	1.5154
140	v	1.664	1.752	1.841	1.928	2.016	2.105
	H	408.0	420.7	433.7	446.7	459.8	473.3
	S	1.4485	1.4614	1.4739	1.4858	1.4973	1.5085
160	v	1.455	1.533	1.610	1.687	1.764	1.841
	H	407.9	420.6	433.6	446.6	459.8	473.3
	S	1.4422	1.4551	1.4675	1.4796	1.4912	1.5024
180	v	1.293	1.361	1.431	1.499	1.567	1.636
	H	407.7	420.5	433.5	446.5	459.7	473.2
	S	1.4369	1.4497	1.4622	1.4741	1.4856	1.4971
200	v	1.163	1.225	1.287	1.349	1.410	1.472
	H	407.6	420.4	433.4	446.4	459.6	473.1
	S	1.4321	1.4449	1.4574	1.4693	1.4809	1.4922
220	v	1.056	1.113	1.169	1.225	1.282	1.338
	H	407.4	420.2	433.2	446.4	459.5	473.0
	S	1.4277	1.4406	1.4531	1.4658	1.4766	1.4879
240	v	0.9675	1.019	1.071	1.123	1.174	1.226
	H	407.3	420.1	433.1	446.3	459.4	473.0
	S	1.4238	1.4365	1.4490	1.4609	1.4725	1.4839
260	v	0.8926	0.9405	0.9887	1.036	1.084	1.131
	H	407.1	420.0	433.0	446.2	459.4	472.9
	S	1.4202	1.4330	1.4456	1.4575	1.4691	1.4805
280	v	0.8283	0.8730	0.9172	0.9616	1.006	1.050
	H	407.0	419.8	432.9	446.1	459.3	472.8
	S	1.4166	1.4295	1.4420	1.4540	1.4655	1.4769
300	v	0.7727	0.8143	0.8556	0.8972	0.9387	0.9800
	H	406.9	419.7	432.8	446.0	459.2	472.7
	S	1.4136	1.4265	1.4389	1.4508	1.4624	1.4738
320	v	0.7237	0.7629	0.8017	0.8409	0.8798	0.9187
	H	406.8	419.6	432.7	445.9	459.1	472.6
	S	1.4106	1.4235	1.4360	1.4479	1.4595	1.4709
340	v	0.6808	0.7176	0.7543	0.7924	0.8278	0.8645
	H	406.6	419.5	432.6	445.9	459.0	472.6
	S	1.4078	1.4207	1.4332	1.4451	1.4567	1.4681
360	v	0.6424	0.6774	0.7122	0.7468	0.7816	0.8162
	H	406.5	419.3	432.5	445.8	459.0	472.6
	S	1.4053	1.4182	1.4307	1.4426	1.4542	1.4656
380	v	0.6082	0.6413	0.6745	0.7073	0.7403	0.7730
	H	406.3	419.2	432.4	445.7	458.9	472.5
	S	1.4027	1.4157	1.4282	1.4401	1.4517	1.4631
400	v	0.5775	0.6089	0.6404	0.6718	0.7030	0.7342
	H	406.1	419.1	432.3	445.6	458.8	472.4
	S	1.4004	1.4134	1.4259	1.4378	1.4494	1.4608
420	v	0.5497	0.5796	0.6096	0.6395	0.6694	0.6991
	H	405.9	419.0	432.2	445.5	458.7	472.3
	S	1.3981	1.4111	1.4235	1.4356	1.4472	1.4586
440	v	0.5242	0.5530	0.5817	0.6102	0.6388	0.6673
	H	405.8	418.8	432.1	445.4	458.6	472.2
	S	1.3959	1.4090	1.4215	1.4335	1.4451	1.4565
480	v	0.4799	0.5063	0.5326	0.5589	0.5852	0.6113
	H	405.5	418.6	431.9	445.2	458.5	472.0
	S	1.3918	1.4049	1.4074	1.4294	1.4411	1.4525
520	v	0.4424	0.4669	0.4912	0.5156	0.5397	0.5640
	H	405.2	418.3	431.7	445.1	458.3	471.8
	S	1.3882	1.4013	1.4138	1.4258	1.4375	1.4489

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Table III (*Continued*)

P		500° F.	550° F.	600° F.	650° F.	700° F.	750° F.
560	v	0.4102	0.4331	0.4557	0.4783	0.5009	0.5235
	H	404.9	418.1	431.5	444.9	458.2	471.7
	S	1.3847	1.3978	1.4103	1.4223	1.4340	1.4455
600	v	0.3823	0.4038	0.4250	0.4462	0.4682	0.4883
	H	404.6	417.8	430.1	444.7	458.0	471.5
	S	1.3813	1.3945	1.4071	1.4192	1.4309	1.4424
650	v	0.3523	0.3721	0.3918	0.4114	0.4310	0.4505
	H	404.2	417.5	429.9	444.5	457.8	471.3
	S	1.3776	1.3908	1.4034	1.4155	1.4272	1.4387
700	v	0.3267	0.3450	0.3634	0.3817	0.3999	0.4181
	H	403.8	417.2	429.6	444.3	457.6	471.2
	S	1.3742	1.3874	1.4000	1.4121	1.4239	1.4354
750	v	0.3044	0.3217	0.3388	0.3558	0.3730	0.3899
	H	403.4	416.9	429.4	444.1	457.4	471.0
	S	1.3705	1.3838	1.3965	1.4087	1.4206	1.4322
800	v	0.2848	0.3011	0.3173	0.3333	0.3494	0.3653
	H	403.1	416.6	429.1	443.9	457.2	470.8
	S	1.3675	1.3808	1.3935	1.4057	1.4176	1.4292
850	v	0.2676	0.2830	0.2983	0.3134	0.3286	0.3436
	H	402.7	416.3	428.8	443.6	457.0	470.7
	S	1.3644	1.3778	1.3906	1.4029	1.4149	1.4265
900	v	0.2523	0.2669	0.2814	0.2957	0.3101	0.3243
	H	402.3	416.0	428.6	443.4	456.8	470.5
	S	1.3615	1.3749	1.3877	1.4000	1.4121	1.4238
950	v	0.2386	0.2524	0.2662	0.2799	0.2936	0.3070
	H	401.9	415.6	428.4	443.2	456.6	470.3
	S	1.3588	1.3723	1.3852	1.3976	1.4097	1.4214
1000	v	0.2263	0.2396	0.2526	0.2657	0.2787	0.2916
	H	401.6	415.3	428.1	443.0	456.4	470.2
	S	1.3562	1.3698	1.3828	1.3952	1.4073	1.4190
1100	v	0.2050	0.2172	0.2291	0.2411	0.2529	0.2647
	H	400.8	414.7	428.6	442.6	456.0	469.9
	S	1.3513	1.3650	1.3781	1.3906	1.4027	1.4144
1200	v	0.1873	0.1985	0.2096	0.2206	0.2315	0.2424
	H	400.0	414.1	428.1	442.1	455.7	469.5
	S	1.3470	1.3608	1.3740	1.3865	1.3986	1.4103
1300	v	0.1723	0.1827	0.1930	0.2032	0.2134	0.2234
	H	399.3	413.5	427.6	441.7	455.3	469.2
	S	1.3431	1.3570	1.3703	1.3828	1.3949	1.4066
1400	v	0.1594	0.1692	0.1788	0.1884	0.1979	0.2072
	H	398.5	412.8	427.0	441.3	455.0	468.9
	S	1.3395	1.3535	1.3668	1.3794	1.3915	1.4032
1500	v	0.1483	0.1575	0.1665	0.1754	0.1844	0.1932
	H	397.7	412.2	426.5	440.8	454.6	468.5
	S	1.3359	1.3500	1.3634	1.3760	1.3881	1.3999
1600	v	0.1385	0.1472	0.1557	0.1642	0.1726	0.1809
	H	397.0	411.6	426.0	440.4	454.3	468.2
	S	1.3325	1.3468	1.3602	1.3729	1.3851	1.3969
1700	v	0.1299	0.1381	0.1462	0.1542	0.1622	0.1700
	H	396.3	411.0	425.5	440.0	453.9	467.9
	S	1.3291	1.3436	1.3571	1.3699	1.3821	1.3939
1800	v	0.1223	0.1301	0.1377	0.1454	0.1530	0.1604
	H	395.5	410.3	424.9	439.5	453.4	467.6
	S	1.3258	1.3403	1.3539	1.3668	1.3790	1.3909
1900	v	0.1154	0.1229	0.1302	0.1375	0.1447	0.1518
	H	394.8	409.6	424.4	439.1	453.1	467.2
	S	1.3223	1.3372	1.3511	1.3641	1.3764	1.3883
2000	v	0.1093	0.1164	0.1234	0.1303	0.1373	0.1440
	H	394.0	409.0	423.9	438.8	452.8	466.9
	S	1.3192	1.3345	1.3486	1.3616	1.3740	1.3860
2100	v	0.1039	0.1108	0.1174	0.1240	0.1307	0.1371
	H	392.2	408.1	423.3	438.2	452.3	466.6
	S	1.3155	1.3311	1.3455	1.3587	1.3713	1.3834
2200	v	....	0.1056	0.1120	0.1183	0.1246	0.1308
	H	....	407.0	421.7	437.8	451.9	466.2
	S	....	1.3279	1.3426	1.3561	1.3688	1.3809
2300	v	....	0.1009	0.1070	0.1131	0.1192	0.1250
	H	....	406.2	420.7	437.4	451.4	465.9
	S	....	1.3246	1.3396	1.3534	1.3663	1.3785
2400	v	....	....	0.1024	0.1083	0.1141	0.1197
	H	....	....	419.5	436.9	450.9	465.6
	S	....	....	1.3370	1.3510	1.3640	1.3763
2500	v	....	....	....	0.1039	0.1095	0.1149
	H	....	....	....	436.5	450.4	465.2
	S	....	....	....	1.3483	1.3615	1.3739
2600	v	....	....	....	....	0.1052	0.1104
	H	....	....	....	....	450.0	464.9
	S	....	....	....	....	1.3588	1.3715
2700	v	....	....	....	....	0.1013	0.1063
	H	....	....	....	....	449.5	464.6
	S	....	....	....	....	1.3565	1.3695
2800	v	....	....	....	....	....	0.1025
	H	....	....	....	....	....	464.3
	S	....	....	....	....	....	1.3673

Table IV. Properties of Superheated Carbon Dioxide Vapor from 800° to 1050° F.

P		800° F.	850° F.	900° F.	950° F.	1000° F.	1050° F.
0.35	v	877.9	912.8	947.6	982.5	....	....
	H	487.1	500.7	514.5	528.4	....	....
	S	1.7897	1.8003	1.8105	1.8205	....	....
0.40	v	768.2	798.7	829.2	859.7	890.1	920.6
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7836	1.7942	1.8044	1.8144	1.8242	1.8337
0.45	v	682.8	709.9	737.0	764.1	791.2	818.3
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7784	1.7890	1.7992	1.8092	1.8190	1.8285
0.50	v	614.5	638.9	663.3	687.7	712.1	736.5
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7736	1.7842	1.7944	1.8044	1.8142	1.8237
0.60	v	512.1	532.4	552.8	573.1	593.4	613.7
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7653	1.7759	1.7861	1.7961	1.8059	1.8154
0.70	v	438.9	456.4	473.8	491.2	508.6	526.1
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7583	1.7689	1.7791	1.7891	1.7989	1.8084
0.80	v	384.1	399.3	414.6	429.8	445.0	460.3
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7523	1.7629	1.7731	1.7831	1.7929	1.8024
0.90	v	341.4	354.9	368.5	382.0	395.6	409.1
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7470	1.7576	1.7678	1.7778	1.7876	1.7971
1.00	v	307.2	319.4	331.6	343.8	356.0	368.2
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7423	1.7529	1.7631	1.7731	1.7829	1.7924
1.10	v	279.3	290.4	301.5	312.6	323.7	334.7
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7380	1.7486	1.7588	1.7688	1.7786	1.7881
1.20	v	256.0	266.2	276.4	286.5	296.7	306.8
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7341	1.7447	1.7549	1.7649	1.7747	1.7842
1.30	v	236.3	245.7	255.1	264.5	273.9	283.2
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7305	1.7411	1.7513	1.7613	1.7711	1.7806
1.40	v	219.4	228.2	236.9	245.6	254.3	263.0
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7271	1.7377	1.7479	1.7579	1.7677	1.7772
1.50	v	204.8	212.9	221.1	229.2	237.3	245.5
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7240	1.7346	1.7448	1.7548	1.7646	1.7741
1.60	v	192.0	199.6	207.3	214.9	222.5	230.1
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7211	1.7317	1.7419	1.7519	1.7617	1.7712
1.80	v	170.7	177.4	184.2	191.0	197.8	204.5
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7158	1.7264	1.7366	1.7466	1.7564	1.7659
2.0	v	153.6	159.7	165.8	171.9	178.0	184.1
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7110	1.7216	1.7318	1.7418	1.7516	1.7611
2.5	v	122.9	127.7	132.6	137.5	142.4	147.3
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.7010	1.7116	1.7218	1.7318	1.7416	1.7511
3.0	v	102.4	106.4	110.5	114.6	118.6	122.7
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6927	1.7033	1.7135	1.7235	1.7333	1.7428
3.5	v	87.79	91.28	94.76	98.25	101.7	105.2
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6858	1.6964	1.7066	1.7166	1.7264	1.7359
4.0	v	76.82	79.87	82.92	85.97	89.01	92.06
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6798	1.6904	1.7006	1.7106	1.7204	1.7299
4.5	v	68.28	70.99	73.70	76.41	79.12	81.83
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6744	1.6850	1.6952	1.7052	1.7150	1.7245
5.0	v	61.45	63.89	66.33	68.77	71.21	73.65
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6697	1.6803	1.6905	1.7005	1.7103	1.7198
5.5	v	55.87	58.08	60.30	62.52	64.74	66.95
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6654	1.6760	1.6862	1.6962	1.7060	1.7155
6.0	v	51.21	53.24	55.28	57.31	59.34	61.37
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6615	1.6721	1.6823	1.6923	1.7021	1.7116
7.0	v	43.89	45.64	47.38	49.12	50.86	52.61
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6545	1.6651	1.6753	1.6853	1.6951	1.7046
8.0	v	38.41	39.94	41.46	42.99	44.51	46.03
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6485	1.6591	1.6693	1.6793	1.6891	1.6986
9.0	v	34.14	35.50	36.85	38.21	39.56	40.92
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6432	1.6538	1.6640	1.6740	1.6838	1.6933
10.0	v	30.73	31.95	33.17	34.39	35.61	36.83
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6384	1.6490	1.6592	1.6692	1.6790	1.6835
12.0	v	25.60	26.62	27.64	28.65	29.67	30.68
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6302	1.6408	1.6510	1.6610	1.6708	1.6803
14.0	v	21.94	22.82	23.69	24.56	25.43	26.30
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6232	1.6338	1.6440	1.6540	1.6638	1.6733
16.0	v	19.20	19.96	20.73	21.49	22.25	23.01
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6172	1.6278	1.6380	1.6480	1.6578	1.6673

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Table IV (*Continued*)

P		800° F.	850° F.	900° F.	950° F.	1000° F.	1050° F.
20.0	*v*	15.36	15.97	16.58	17.19	17.80	18.41
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.6071	1.6177	1.6279	1.6379	1.6477	1.6572
24.0	*v*	12.80	13.31	13.82	14.32	14.83	15.34
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.5989	1.6095	1.6197	1.6297	1.6395	1.6490
28.0	*v*	10.97	11.41	11.84	12.28	12.71	13.15
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.5920	1.6026	1.6128	1.6228	1.6326	1.6421
32.0	*v*	9.603	9.984	10.36	10.74	11.12	11.50
	H	487.1	500.7	514.5	528.4	542.4	556.6
	S	1.5859	1.5965	1.6067	1.6167	1.6265	1.6360
36.0	*v*	8.536	8.874	9.213	9.552	9.891	10.22
	H	487.0	500.7	514.5	528.4	542.4	556.6
	S	1.5806	1.5912	1.6014	1.6114	1.6212	1.6307
40.0	*v*	7.688	7.987	8.292	8.597	8.091	9.206
	H	487.0	500.6	514.4	528.4	542.4	556.6
	S	1.5759	1.5865	1.5967	1.6067	1.6165	1.6260
44.0	*v*	6.984	7.261	7.538	7.815	8.092	8.369
	H	487.0	500.6	514.4	528.3	542.4	556.6
	S	1.5716	1.5822	1.5924	1.6024	1.6122	1.6217
48.0	*v*	6.402	6.656	6.910	7.164	7.418	7.672
	H	487.0	500.6	514.4	528.3	542.3	556.6
	S	1.5677	1.5783	1.5885	1.5985	1.6083	1.6178
52.0	*v*	5.908	6.142	6.376	6.613	6.847	7.082
	H	487.0	500.6	514.4	528.3	542.3	556.5
	S	1.5640	1.5746	1.5848	1.5948	1.6046	1.6141
56.0	*v*	5.486	5.703	5.921	6.140	6.358	6.576
	H	487.0	500.6	514.4	528.3	542.3	556.5
	S	1.5607	1.5713	1.5815	1.5915	1.6013	1.6108
60.0	*v*	5.126	5.323	5.526	5.731	5.934	6.137
	H	487.0	500.6	514.4	528.3	542.3	556.5
	S	1.5576	1.5682	1.5784	1.5884	1.5982	1.6077
70.0	*v*	4.388	4.561	4.735	4.911	5.084	5.259
	H	487.0	500.6	514.4	528.3	542.3	556.5
	S	1.5506	1.5612	1.5714	1.5814	1.5912	1.6007
80.0	*v*	3.839	3.991	4.143	4.297	4.448	4.602
	H	486.9	500.5	514.3	528.3	542.3	556.5
	S	1.5446	1.5552	1.5654	1.5754	1.5852	1.5947
90.0	*v*	3.412	3.546	3.683	3.818	3.954	4.090
	H	486.9	500.5	514.3	528.2	542.3	556.5
	S	1.5393	1.5499	1.5601	1.5701	1.5799	1.5894
100	*v*	3.070	3.192	3.315	3.436	3.559	3.682
	H	486.9	500.5	514.3	528.2	542.3	556.5
	S	1.5345	1.5451	1.5553	1.5653	1.5751	1.5846
120	*v*	2.559	2.659	2.762	2.864	2.966	3.067
	H	486.8	500.4	514.2	528.2	542.3	556.5
	S	1.5263	1.5369	1.5471	1.5571	1.5669	1.5764
140	*v*	2.193	2.279	2.367	2.455	2.541	2.629
	H	486.7	500.4	514.2	528.1	542.3	556.5
	S	1.5194	1.5300	1.5402	1.5502	1.5600	1.5695
160	*v*	1.918	1.995	2.071	2.148	2.224	2.300
	H	486.6	500.3	514.1	528.1	542.2	556.5
	S	1.5133	1.5239	1.5341	1.5441	1.5539	1.5634
180	*v*	1.705	1.772	1.841	1.909	1.977	2.045
	H	486.6	500.3	514.1	528.0	542.2	556.4
	S	1.5080	1.5186	1.5288	1.5388	1.5486	1.5581
200	*v*	1.534	1.595	1.656	1.718	1.779	1.840
	H	486.5	500.2	514.1	528.0	542.2	556.4
	S	1.5033	1.5139	1.5241	1.5341	1.5439	1.5534
220	*v*	1.395	1.450	1.506	1.561	1.617	1.673
	H	486.5	500.1	514.0	528.0	542.1	556.4
	S	1.4989	1.5096	1.5198	1.5298	1.5396	1.5491
240	*v*	1.273	1.329	1.380	1.431	1.482	1.533
	H	486.4	500.1	514.0	527.9	542.1	556.3
	S	1.4948	1.5056	1.5158	1.5259	1.5356	1.5451
260	*v*	1.180	1.226	1.274	1.321	1.368	1.415
	H	486.3	500.0	513.9	527.9	542.0	556.3
	S	1.4914	1.5022	1.5124	1.5224	1.5322	1.5417
280	*v*	1.095	1.138	1.183	1.227	1.271	1.314
	H	486.3	500.0	513.9	527.8	542.0	556.3
	S	1.4879	1.4987	1.5089	1.5189	1.5287	1.5382
300	*v*	1.021	1.063	1.104	1.145	1.186	1.227
	H	486.2	499.9	513.8	527.8	542.0	556.2
	S	1.4848	1.4956	1.5058	1.5158	1.5256	1.5351
320	*v*	0.9560	0.9958	1.034	1.073	1.111	1.149
	H	486.2	499.9	513.8	527.8	542.0	556.2
	S	1.4819	1.4927	1.5029	1.5129	1.5227	1.5322
340	*v*	0.9002	0.9372	0.9736	1.009	1.046	1.082
	H	486.1	499.8	513.7	527.7	541.9	556.2
	S	1.4791	1.4899	1.5001	1.5101	1.5199	1.5294
360	*v*	0.8502	0.8852	0.9195	0.9533	0.9874	1.022
	H	486.0	499.8	513.7	527.7	541.9	556.1
	S	1.4766	1.4874	1.4976	1.5076	1.5174	1.5269
380	*v*	0.8055	0.8381	0.8708	0.9031	0.9354	0.9677
	H	486.0	499.7	513.6	527.6	541.8	556.1
	S	1.4741	1.4849	1.4951	1.5051	1.5149	1.5244
400	*v*	0.7642	0.7962	0.8273	0.8577	0.8887	0.9193
	H	485.9	499.7	513.6	527.6	541.8	556.0
	S	1.4718	1.4826	1.4928	1.5028	1.5126	1.5221
420	*v*	0.7281	0.7581	0.7877	0.8168	0.8464	0.8753
	H	485.9	499.6	513.5	527.5	541.7	556.0
	S	1.4696	1.4804	1.4906	1.5006	1.5104	1.5199
440	*v*	0.6950	0.7236	0.7521	0.7797	0.8079	0.8355
	H	485.8	499.5	513.5	527.5	541.7	556.0
	S	1.4675	1.4783	1.4885	1.4985	1.5083	1.5178
480	*v*	0.6371	0.6633	0.6894	0.7147	0.7406	0.7659
	H	485.7	499.4	513.4	527.4	541.6	555.9
	S	1.4635	1.4743	1.4845	1.4945	1.5043	1.5138
520	*v*	0.5881	0.6123	0.6360	0.6596	0.6832	0.7067
	H	485.5	499.3	513.3	527.3	541.5	555.8
	S	1.4599	1.4707	1.4809	1.4909	1.5007	1.5102
560	*v*	0.5461	0.5684	0.5902	0.6124	0.6344	0.6563
	H	485.4	499.2	513.2	527.2	541.5	555.7
	S	1.4565	1.4673	1.4775	1.4875	1.4973	1.5068
600	*v*	0.5093	0.5300	0.5507	0.5714	0.5921	0.6125
	H	485.3	499.1	513.1	527.1	541.4	555.7
	S	1.4534	1.4642	1.4744	1.4844	1.4942	1.5037
650	*v*	0.4698	0.4891	0.5082	0.5273	0.5463	0.5652
	H	485.2	499.0	513.0	527.0	541.3	555.6
	S	1.4498	1.4606	1.4708	1.4808	1.4906	1.5001
700	*v*	0.4360	0.4539	0.4718	0.4895	0.5072	0.5248
	H	485.0	498.9	512.9	526.9	541.2	555.5
	S	1.4465	1.4573	1.4675	1.4775	1.4873	1.4968
750	*v*	0.4068	0.4234	0.4402	0.4568	0.4731	0.4897
	H	484.9	498.7	512.8	526.8	541.1	555.4
	S	1.4433	1.4541	1.4643	1.4743	1.4841	1.4936
800	*v*	0.3812	0.3968	0.4126	0.4281	0.4436	0.4592
	H	484.7	498.6	512.7	526.7	541.0	555.3
	S	1.4404	1.4512	1.4614	1.4714	1.4812	1.4907
850	*v*	0.3585	0.3734	0.3882	0.4029	0.4175	0.4320
	H	484.6	498.5	512.5	526.6	540.9	555.2
	S	1.4377	1.4485	1.4587	1.4687	1.4785	1.4880
900	*v*	0.3384	0.3525	0.3665	0.3804	0.3943	0.4080
	H	484.4	498.3	512.4	526.5	540.8	555.2
	S	1.4350	1.4458	1.4561	1.4661	1.4759	1.4854
950	*v*	0.3207	0.3338	0.3471	0.3603	0.3733	0.3861
	H	484.3	498.2	512.3	526.4	540.7	555.1
	S	1.4326	1.4434	1.4537	1.4637	1.4735	1.4830
1000	*v*	0.3048	0.3170	0.3297	0.3422	0.3547	0.3671
	H	484.0	498.1	512.2	526.3	540.6	555.0
	S	1.4302	1.4410	1.4513	1.4614	1.4712	1.4807
1100	*v*	0.2764	0.2880	0.2996	0.3109	0.3222	0.3335
	H	483.8	497.8	511.9	526.1	540.4	554.8
	S	1.4257	1.4366	1.4470	1.4571	1.4669	1.4764
1200	*v*	0.2531	0.2638	0.2744	0.2849	0.2953	0.3057
	H	483.5	497.5	511.7	525.9	540.2	554.7
	S	1.4216	1.4325	1.4429	1.4530	1.4628	1.4723
1300	*v*	0.2334	0.2433	0.2532	0.2629	0.2724	0.2820
	H	483.2	497.3	511.5	525.7	540.0	554.5
	S	1.4179	1.4288	1.4392	1.4493	1.4592	1.4687
1400	*v*	0.2160	0.2257	0.2350	0.2440	0.2529	0.2619
	H	482.9	497.0	511.2	525.5	539.8	554.3
	S	1.4145	1.4254	1.4358	1.4459	1.4558	1.4654
1500	*v*	0.2014	0.2106	0.2192	0.2276	0.2359	0.2443
	H	482.6	496.7	511.0	525.3	539.7	554.1
	S	1.4112	1.4221	1.4326	1.4427	1.4526	1.4622
1600	*v*	0.1898	0.1972	0.2053	0.2133	0.2211	0.2290
	H	482.3	496.5	510.8	525.1	539.5	554.0
	S	1.4083	1.4192	1.4297	1.4398	1.4497	1.4593
1700	*v*	0.1775	0.1855	0.1931	0.2006	0.2080	0.2154
	H	482.0	496.2	510.5	524.9	539.3	553.8
	S	1.4053	1.4163	1.4268	1.4369	1.4468	1.4564
1800	*v*	0.1675	0.1750	0.1823	0.1894	0.1964	0.2034
	H	481.7	496.0	510.3	524.7	539.1	553.6
	S	1.4023	1.4133	1.4238	1.4340	1.4440	1.4537
1900	*v*	0.1587	0.1657	0.1726	0.1793	0.1859	0.1926
	H	481.4	495.7	510.1	524.5	538.9	553.4
	S	1.3998	1.4108	1.4214	1.4316	1.4416	1.4513
2000	*v*	0.1508	0.1573	0.1639	0.1703	0.1766	0.1829
	H	481.1	495.4	509.8	524.3	538.7	553.3
	S	1.3975	1.4085	1.4191	1.4293	1.4393	1.4490
2100	*v*	0.1424	0.1497	0.1560	0.1621	0.1681	0.1742
	H	480.8	495.2	509.6	524.0	538.6	553.1
	S	1.3950	1.4061	1.4167	1.4269	1.4369	1.4466
2200	*v*	0.1368	0.1429	0.1489	0.1547	0.1605	0.1663
	H	480.5	494.9	509.4	523.8	538.4	552.9
	S	1.3925	1.4036	1.4142	1.4244	1.4344	1.4442
2300	*v*	0.1308	0.1366	0.1424	0.1479	0.1535	0.1591
	H	480.2	494.6	509.1	523.6	538.2	552.8
	S	1.3902	1.4014	1.4121	1.4224	1.4324	1.4422
2400	*v*	0.1258	0.1309	0.1364	0.1417	0.1471	0.1524
	H	479.9	494.4	508.9	523.4	538.0	552.6
	S	1.3880	1.3992	1.4099	1.4202	1.4303	1.4401
2500	*v*	0.1203	0.1256	0.1308	0.1359	0.1412	0.1463
	H	479.6	494.1	508.7	523.2	537.8	552.4
	S	1.3857	1.3970	1.4077	1.4181	1.4282	1.4380
2600	*v*	0.1156	0.1207	0.1258	0.1306	0.1357	0.1407
	H	479.3	493.8	508.4	523.0	537.6	552.2
	S	1.3834	1.3947	1.4055	1.4159	1.4260	1.4359
2700	*v*	0.1113	0.1162	0.1211	0.1259	0.1307	0.1355
	H	479.0	493.6	508.2	522.8	537.4	552.1
	S	1.3815	1.3928	1.4036	1.4140	1.4241	1.4340
2800	*v*	0.1073	0.1121	0.1168	0.1214	0.1260	0.1303
	H	478.7	493.3	508.0	522.6	537.2	551.9
	S	1.3797	1.3911	1.4019	1.4123	1.4224	1.4323
2900	*v*	0.1036	0.1082	0.1127	0.1172	0.1217	0.1262
	H	478.4	493.1	507.7	522.4	537.0	551.7
	S	1.3770	1.3884	1.3993	1.4098	1.4200	1.4300
3000	*v*	0.1001	0.1045	0.1089	0.1133	0.1176	0.1219
	H	478.1	492.8	507.5	522.1	536.8	551.5
	S	1.3752	1.3867	1.3976	1.4081	1.4183	1.4283

Table V. Properties of Superheated Carbon Dioxide Vapor from 1100° to 1350° F.

P		1100° F.	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
0.40	*v*	951.1	981.6	....	....	....	....
	H	570.8	585.2	....	....	....	....
	S	1.8430	1.8521	....	....	....	....
0.45	*v*	845.4	872.5	899.6	926.7	953.8	980.9
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8378	1.8469	1.8558	1.8645	1.8730	1.8813
0.50	*v*	760.9	785.3	809.7	834.0	858.4	882.8
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8330	1.8421	1.8510	1.8597	1.8682	1.8765
0.60	*v*	634.1	654.4	674.7	695.0	715.4	735.7
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8247	1.8338	1.8427	1.8514	1.8599	1.8682
0.70	*v*	543.5	560.9	578.3	595.7	613.2	630.6
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8177	1.8268	1.8357	1.8444	1.8529	1.8612
0.80	*v*	475.5	490.8	506.0	521.3	536.5	551.7
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8117	1.8208	1.8297	1.8384	1.8469	1.8552
0.90	*v*	422.7	436.2	449.8	463.3	476.9	490.4
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8064	1.8155	1.8244	1.8331	1.8416	1.8499
1.00	*v*	380.4	392.6	404.8	417.0	429.2	441.4
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.8017	1.8108	1.8197	1.8284	1.8369	1.8452
1.10	*v*	345.8	356.9	368.0	379.1	390.2	401.3
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7974	1.8065	1.8154	1.8241	1.8326	1.8409
1.20	*v*	317.0	327.2	337.3	347.5	357.7	367.8
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7935	1.8026	1.8115	1.8202	1.8287	1.8370
1.30	*v*	292.6	302.0	311.4	320.8	330.1	339.5
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7899	1.7990	1.8079	1.8166	1.8251	1.8334
1.40	*v*	271.7	280.4	289.1	297.8	306.6	315.3
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7865	1.7956	1.8045	1.8132	1.8217	1.8300
1.50	*v*	253.6	261.7	269.9	278.0	286.1	294.2
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7834	1.7925	1.8014	1.8101	1.8186	1.8269
1.60	*v*	237.7	245.4	253.0	260.6	268.2	275.8
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7805	1.7896	1.7985	1.8072	1.8157	1.8240
1.80	*v*	211.3	218.1	224.9	231.6	238.4	245.2
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7752	1.7843	1.7932	1.8019	1.8104	1.8187
2.00	*v*	190.2	196.3	202.4	208.5	214.6	220.7
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7704	1.7795	1.7884	1.7971	1.8056	1.8139
2.50	*v*	152.1	157.0	161.9	166.8	171.6	176.5
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7604	1.7695	1.7784	1.7871	1.7956	1.8039
3.00	*v*	126.8	130.8	134.9	139.0	143.0	147.1
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7521	1.7612	1.7701	1.7788	1.7873	1.7956
3.50	*v*	108.7	112.1	115.6	119.1	122.6	126.1
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7452	1.7543	1.7632	1.7719	1.7804	1.7887
4.00	*v*	95.11	98.16	101.2	104.2	107.3	110.3
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7392	1.7483	1.7572	1.7659	1.7744	1.7827
4.50	*v*	84.54	87.25	89.96	92.67	95.38	98.09
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7338	1.7429	1.7518	1.7605	1.7690	1.7773
5.00	*v*	76.09	78.53	80.97	83.40	85.84	88.28
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7291	1.7382	1.7471	1.7558	1.7643	1.7726
5.50	*v*	69.17	71.39	73.61	75.82	78.04	80.26
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7248	1.7339	1.7428	1.7515	1.7600	1.7683
6.0	*v*	63.41	65.44	67.47	69.50	71.54	73.57
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7209	1.7300	1.7389	1.7476	1.7561	1.7644
7.0	*v*	54.35	56.09	57.83	59.57	61.32	63.06
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7139	1.7230	1.7319	1.7406	1.7491	1.7574
8.0	*v*	47.56	49.08	50.61	52.13	53.66	55.18
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7079	1.7170	1.7259	1.7346	1.7431	1.7514
9.0	*v*	42.27	43.63	44.98	46.34	47.69	49.05
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.7026	1.7117	1.7206	1.7293	1.7378	1.7461
10.0	*v*	38.05	39.37	40.49	41.70	42.92	44.14
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6978	1.7069	1.7158	1.7245	1.7330	1.7413
12.0	*v*	31.70	32.72	33.73	34.75	35.77	36.78
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6896	1.6987	1.7076	1.7163	1.7248	1.7331
14.0	*v*	27.17	28.04	28.91	29.78	30.66	31.53
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6826	1.6917	1.7006	1.7093	1.7178	1.7261
16.0	*v*	23.77	24.54	25.30	26.06	26.82	27.58
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6766	1.6857	1.6946	1.7033	1.7118	1.7201
20.0	*v*	19.02	19.63	20.24	20.85	21.46	22.07
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6665	1.6756	1.6845	1.6932	1.7017	1.7100
24.0	*v*	15.85	16.36	16.86	17.37	17.88	18.39
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6583	1.6674	1.6763	1.6850	1.6935	1.7018
28.0	*v*	13.58	14.02	14.45	14.89	15.33	15.76
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6514	1.6605	1.6694	1.6781	1.6866	1.6949
32.0	*v*	11.88	12.27	12.65	13.03	13.41	13.79
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6453	1.6544	1.6633	1.6720	1.6805	1.6888
36.0	*v*	10.56	10.90	11.24	11.58	11.92	12.26
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6400	1.6491	1.6580	1.6667	1.6752	1.6835
40.0	*v*	9.511	9.816	10.12	10.42	10.73	11.03
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6353	1.6444	1.6533	1.6620	1.6705	1.6788
44.0	*v*	8.646	8.924	9.201	9.478	9.755	10.03
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6310	1.6401	1.6490	1.6577	1.6662	1.6745
48.0	*v*	7.926	8.180	8.434	8.688	8.942	9.196
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6271	1.6362	1.6451	1.6538	1.6623	1.6706
52.0	*v*	7.316	7.551	7.785	8.020	8.254	8.489
	H	570.8	585.2	599.6	614.2	629.0	643.8
	S	1.6234	1.6325	1.6414	1.6501	1.6586	1.6669
56.0	*v*	6.794	7.011	7.229	7.447	7.665	7.882
	H	570.7	585.2	599.6	614.2	629.0	643.8
	S	1.6201	1.6292	1.6381	1.6468	1.6553	1.6636
60.0	*v*	6.341	6.544	6.747	6.950	7.154	7.357
	H	570.7	585.1	599.6	614.2	629.0	643.8
	S	1.6170	1.6261	1.6350	1.6437	1.6522	1.6605
70.0	*v*	5.435	5.609	5.783	5.957	6.132	6.306
	H	570.7	585.1	599.6	614.2	629.0	643.8
	S	1.6100	1.6191	1.6280	1.6367	1.6452	1.0535
80.0	*v*	4.755	4.908	5.060	5.213	5.365	5.517
	H	570.7	585.1	599.5	614.2	629.0	643.8
	S	1.6042	1.6131	1.6220	1.6307	1.6392	1.6475
90.0	*v*	4.227	4.362	4.498	4.633	4.769	4.904
	H	570.7	585.1	599.5	614.2	629.0	643.8
	S	1.5987	1.6078	1.6167	1.6254	1.6339	1.6422
100	*v*	3.805	3.927	4.048	4.170	4.292	4.414
	H	570.7	585.1	599.5	614.1	629.0	643.8
	S	1.5939	1.6030	1.6119	1.6206	1.6291	1.6374
120	*v*	3.169	3.271	3.373	3.475	3.577	3.679
	H	570.7	585.1	599.5	614.1	629.0	643.8
	S	1.5857	1.5948	1.6037	1.6124	1.6209	1.6292
140	*v*	2.717	2.804	2.892	2.978	3.066	3.153
	H	570.7	585.1	599.5	614.1	628.9	643.8
	S	1.5788	1.5879	1.5968	1.6055	1.6140	1.6223
160	*v*	2.377	2.453	2.530	2.607	2.683	2.759
	H	570.7	585.1	599.5	614.1	628.9	643.8
	S	1.5727	1.5818	1.5907	1.5994	1.6079	1.6162
180	*v*	2.113	2.181	2.249	2.317	2.385	2.452
	H	570.7	585.1	599.5	614.1	628.9	643.7
	S	1.5674	1.5765	1.5854	1.5941	1.6026	1.6109
200	*v*	1.902	1.963	2.024	2.085	2.146	2.208
	H	570.7	585.1	599.5	614.1	628.9	643.7
	S	1.5627	1.5718	1.5807	1.5894	1.5979	1.6062
220	*v*	1.728	1.784	1.840	1.895	1.951	2.007
	H	570.6	585.1	599.5	614.1	628.9	643.7
	S	1.5584	1.5675	1.5764	1.5851	1.5936	1.6019
240	*v*	1.584	1.635	1.687	1.738	1.789	1.839
	H	570.6	585.1	599.5	614.1	628.9	643.7
	S	1.5544	1.5635	1.5724	1.5811	1.5896	1.5979
260	*v*	1.462	1.509	1.557	1.604	1.651	1.698
	H	570.6	585.0	599.5	614.1	628.9	643.7
	S	1.5510	1.5601	1.5690	1.5777	1.5862	1.5945
280	*v*	1.358	1.402	1.446	1.489	1.533	1.577
	H	570.6	585.0	599.5	614.1	628.9	643.7
	S	1.5475	1.5566	1.5655	1.5742	1.5827	1.5910
300	*v*	1.267	1.308	1.349	1.390	1.431	1.471
	H	570.6	585.0	599.4	614.1	628.9	643.7
	S	1.5444	1.5535	1.5624	1.5711	1.5796	1.5879
320	*v*	1.187	1.226	1.265	1.303	1.342	1.379
	H	570.5	584.9	599.4	614.0	628.9	643.7
	S	1.5415	1.5506	1.5595	1.5682	1.5767	1.5850
340	*v*	1.118	1.154	1.191	1.227	1.263	1.299
	H	570.5	584.9	599.4	614.0	628.8	643.7
	S	1.5387	1.5478	1.5567	1.5654	1.5739	1.5822
360	*v*	1.056	1.089	1.125	1.158	1.192	1.227
	H	570.4	584.9	599.4	614.0	628.8	643.6
	S	1.5362	1.5453	1.5542	1.5629	1.5714	1.5797
380	*v*	1.000	1.032	1.065	1.097	1.129	1.162
	H	570.4	584.8	599.4	614.0	628.8	643.6
	S	1.5337	1.5428	1.5517	1.5604	1.5689	1.5772
400	*v*	0.9500	0.9805	1.012	1.043	1.073	1.104
	H	570.4	584.8	599.3	614.0	628.8	643.6
	S	1.5314	1.5405	1.5494	1.5581	1.5666	1.5749
420	*v*	0.9048	0.9338	0.9639	0.9929	1.022	1.051
	H	570.3	584.8	599.3	613.9	628.8	643.6
	S	1.5292	1.5383	1.5472	1.5559	1.5644	1.5727
440	*v*	0.8637	0.8913	0.9201	0.9478	0.9980	1.004
	H	570.3	584.7	599.3	613.9	628.7	643.5
	S	1.5271	1.5362	1.5451	1.5538	1.5023	1.5706
480	*v*	0.7917	0.8171	0.8434	0.8689	0.8945	0.9199
	H	570.2	584.7	599.2	613.8	628.7	643.5
	S	1.5231	1.5322	1.5411	1.5498	1.5583	1.5666
520	*v*	0.7308	0.7544	0.7785	0.8022	0.8257	0.8444
	H	570.2	584.6	599.2	613.8	628.6	643.5
	S	1.5195	1.5286	1.5375	1.5462	1.5547	1.5630
560	*v*	0.6786	0.7003	0.7229	0.7449	0.7667	0.7887
	H	570.1	584.5	599.1	613.7	628.6	643.4
	S	1.5161	1.5252	1.5341	1.5428	1.5513	1.5596

Continued on page 198

Table V (*Continued*)

P		1100° F.	1150° F.	1200° F.	1250° F.	1300° F.	1350° F.
600	*v*	0.6333	0.6536	0.6747	0.6952	0.7158	0.7361
	H	570.0	584.5	599.0	613.7	628.5	643.4
	S	1.5130	1.5221	1.5310	1.5397	1.5482	1.5565
650	*v*	0.5844	0.6032	0.6228	0.6417	0.6606	0.6795
	H	569.9	584.4	599.0	613.6	628.5	643.3
	S	1.5094	1.5185	1.5274	1.5361	1.5446	1.5529
700	*v*	0.5427	0.5601	0.5783	0.5959	0.6135	0.6309
	H	569.9	584.3	598.9	613.6	628.4	643.3
	S	1.5061	1.5152	1.5241	1.5328	1.5413	1.5496
750	*v*	0.5065	0.5228	0.5398	0.5562	0.5727	0.5890
	H	569.8	584.2	598.8	613.5	628.4	643.2
	S	1.5029	1.5120	1.5209	1.5296	1.5381	1.5464
800	*v*	0.4747	0.4901	0.5060	0.5214	0.5368	0.5522
	H	569.7	584.2	598.8	613.4	628.3	643.2
	S	1.5000	1.5091	1.5180	1.5267	1.5352	1.5435
850	*v*	0.4467	0.4611	0.4762	0.4907	0.5052	0.5197
	H	569.6	584.1	598.7	613.4	628.2	643.1
	S	1.4973	1.5064	1.5153	1.5240	1.5325	1.5408
900	*v*	0.4218	0.4355	0.4498	0.4635	0.4772	0.4909
	H	569.6	584.0	598.6	613.3	628.2	643.1
	S	1.4947	1.5038	1.5127	1.5214	1.5299	1.5382
950	*v*	0.3996	0.4127	0.4261	0.4391	0.4522	0.4650
	H	569.5	583.9	598.6	613.3	628.1	643.0
	S	1.4923	1.5014	1.5103	1.5190	1.5275	1.5358
1000	*v*	0.3797	0.3919	0.4049	0.4172	0.4296	0.4418
	H	569.4	583.8	598.5	613.2	628.1	642.9
	S	1.4900	1.4991	1.5080	1.5167	1.5252	1.5335
1100	*v*	0.3450	0.3563	0.3680	0.3792	0.3905	0.4017
	H	569.3	583.7	598.4	613.1	628.0	642.8
	S	1.4857	1.4948	1.5037	1.5124	1.5209	1.5292
1200	*v*	0.3162	0.3265	0.3374	0.3476	0.3580	0.3683
	H	569.1	583.5	598.2	612.9	627.8	642.7
	S	1.4816	1.4907	1.4996	1.5083	1.5168	1.5251
1300	*v*	0.2918	0.3014	0.3114	0.3209	0.3304	0.3399
	H	568.9	583.4	598.1	612.8	627.7	642.6
	S	1.4780	1.4871	1.4960	1.5047	1.5132	1.5215
1400	*v*	0.2709	0.2798	0.2892	0.2979	0.3070	0.3158
	H	568.8	583.2	598.0	612.7	627.6	642.5
	S	1.4747	1.4838	1.4927	1.5014	1.5099	1.5182
1500	*v*	0.2528	0.2611	0.2699	0.2782	0.2865	0.2947
	H	568.6	583.1	597.8	612.6	627.5	642.4
	S	1.4715	1.4800	1.4895	1.4982	1.5067	1.5150
1600	*v*	0.2370	0.2447	0.2530	0.2608	0.2686	0.2763
	H	568.5	582.9	597.7	612.4	627.4	642.3
	S	1.4687	1.4778	1.4867	1.4954	1.5039	1.5122
1700	*v*	0.2229	0.2303	0.2381	0.2455	0.2529	0.2601
	H	568.3	582.8	597.6	612.3	627.3	642.2
	S	1.4658	1.4749	1.4838	1.4925	1.5010	1.5093
1800	*v*	0.2106	0.2175	0.2249	0.2318	0.2388	0.2457
	H	568.1	582.6	597.4	612.2	627.2	642.1
	S	1.4631	1.4723	1.4812	1.4899	1.4984	1.5067
1900	*v*	0.1994	0.2060	0.2131	0.2196	0.2262	0.2327
	H	568.0	582.4	597.3	612.1	627.0	642.0
	S	1.4607	1.4699	1.4788	1.4875	1.4960	1.5043
2000	*v*	0.1894	0.1957	0.2024	0.2086	0.2149	0.2211
	H	567.8	582.3	597.2	612.0	626.9	641.9
	S	1.4585	1.4677	1.4767	1.4854	1.4939	1.5022
2100	*v*	0.1804	0.1863	0.1928	0.1987	0.2047	0.2106
	H	567.7	582.1	597.0	611.8	626.8	641.8
	S	1.4561	1.4653	1.4743	1.4830	1.4915	1.4998
2200	*v*	0.1722	0.1779	0.1840	0.1896	0.1954	0.2011
	H	567.5	582.0	596.9	611.7	626.8	641.7
	S	1.4537	1.4630	1.4720	1.4808	1.4893	1.4976
2300	*v*	0.1647	0.1701	0.1760	0.1814	0.1869	0.1924
	H	567.3	581.1	596.8	611.6	626.7	641.6
	S	1.4517	1.4610	1.4700	1.4788	1.4873	1.4956
2400	*v*	0.1578	0.1630	0.1687	0.1739	0.1792	0.1844
	H	567.2	581.7	596.6	611.5	626.7	641.5
	S	1.4496	1.4589	1.4680	1.4768	1.4854	1.4937
2500	*v*	0.1515	0.1565	0.1619	0.1670	0.1720	0.1770
	H	567.0	581.5	596.5	611.2	626.6	641.4
	S	1.4476	1.4569	1.4660	1.4748	1.4834	1.4917
2600	*v*	0.1457	0.1505	0.1557	0.1605	0.1654	0.1702
	H	566.9	581.3	596.4	611.1	626.5	641.3
	S	1.4455	1.4549	1.4640	1.4729	1.4816	1.4900
2700	*v*	0.1403	0.1449	0.1499	0.1546	0.1593	0.1639
	H	566.7	581.2	596.2	611.0	626.3	641.2
	S	1.4436	1.4530	1.4622	1.4711	1.4798	1.4882
2800	*v*	0.1353	0.1398	0.1446	0.1491	0.1536	0.1581
	H	566.5	581.1	596.1	610.9	626.2	641.1
	S	1.4420	1.4514	1.4606	1.4695	1.4782	1.4866
2900	*v*	0.1306	0.1349	0.1396	0.1439	0.1483	0.1527
	H	566.4	581.0	596.0	610.8	626.0	641.0
	S	1.4397	1.4492	1.4585	1.4675	1.4763	1.4848
3000	*v*	0.1262	0.1304	0.1349	0.1391	0.1434	0.1476
	H	566.2	580.9	595.8	610.7	625.9	640.9
	S	1.4381	1.4476	1.4569	1.4659	1.4747	1.4832

Table VI. Properties of Superheated Carbon Dioxide Vapor from 1400° to 1650° F.

P		1400° F.	1450° F.	1500° F.	1550° F.	1600° F.	1650° F.
0.50	*v*	907.2	931.6	956.0	980.2	....	....
	H	658.6	673.5	688.5	703.6	....	....
	S	1.8846	1.8925	1.9002	1.9077	....	....
0.60	*v*	756.0	776.3	797.0	817.5	837.6	857.9
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8763	1.8842	1.8919	1.8994	1.9068	1.9141
0.70	*v*	648.0	665.4	683.2	700.5	718.0	735.6
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8693	1.8772	1.8849	1.8924	1.8998	1.9071
0.80	*v*	567.0	582.2	598.0	613.0	628.1	643.8
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8633	1.8721	1.8789	1.8864	1.8938	1.9011
0.90	*v*	504.0	517.5	531.6	544.7	558.2	572.0
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8580	1.8659	1.8736	1.8811	1.8850	1.8958
1.00	*v*	453.6	465.8	478.2	490.1	502.3	514.6
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8533	1.8612	1.8689	1.8764	1.8838	1.8911
1.10	*v*	412.3	423.4	434.5	445.5	456.8	467.7
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8490	1.8569	1.8646	1.8721	1.8795	1.8868
1.20	*v*	378.0	388.1	398.5	408.5	418.5	428.7
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8451	1.8530	1.8607	1.8682	1.8756	1.8829
1.30	*v*	348.9	358.3	367.7	377.0	386.4	395.8
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8415	1.8494	1.8571	1.8646	1.8720	1.8793
1.40	*v*	324.0	332.7	341.5	350.0	358.8	367.5
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8381	1.8460	1.8537	1.8612	1.8686	1.8759
1.50	*v*	302.4	310.5	318.8	326.8	334.9	343.0
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8350	1.8429	1.8506	1.8581	1.8655	1.8728
1.60	*v*	283.5	291.1	298.8	306.3	314.0	321.6
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8321	1.8400	1.8477	1.8552	1.8626	1.8799
1.80	*v*	252.0	258.7	265.6	272.2	278.9	285.8
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8268	1.8347	1.8424	1.8499	1.8573	1.8646
2.00	*v*	226.8	232.9	239.0	245.0	251.1	257.2
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8220	1.8299	1.8376	1.8451	1.8525	1.8598
2.50	*v*	181.4	186.3	191.2	195.8	200.8	205.6
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8120	1.8199	1.8276	1.8351	1.8425	1.8498
3.00	*v*	151.2	155.2	159.2	163.3	167.4	171.5
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.8037	1.8116	1.8193	1.8268	1.8342	1.8415
3.50	*v*	129.6	133.0	135.5	140.1	143.6	147.0
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7968	1.8047	1.8124	1.8199	1.8273	1.8346
4.00	*v*	113.4	116.4	119.5	122.5	125.6	128.6
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7908	1.7987	1.8064	1.8139	1.8213	1.8286
4.50	*v*	100.8	103.5	106.2	108.9	111.7	114.4
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7854	1.7933	1.8010	1.8085	1.8159	1.8232
5.00	*v*	90.72	93.16	95.63	98.00	100.4	102.8
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7807	1.7886	1.7963	1.8038	1.8112	1.8185
5.50	*v*	82.47	84.69	86.85	89.10	91.38	93.54
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7764	1.7843	1.7920	1.7995	1.8069	1.8142
6.0	*v*	75.60	77.63	79.70	81.75	83.76	85.80
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7725	1.7804	1.7881	1.7956	1.8030	1.8103
7.0	*v*	64.80	66.54	68.32	70.05	71.80	73.56
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7655	1.7734	1.7811	1.7886	1.7960	1.8033
8.0	*v*	56.70	58.22	59.75	61.28	62.80	64.33
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7595	1.7674	1.7751	1.7826	1.7900	1.7973
9.0	*v*	50.40	51.76	53.11	54.47	55.82	57.18
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7542	1.7621	1.7698	1.7773	1.7847	1.7920
10.0	*v*	45.36	46.58	47.80	49.02	50.24	51.46
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7494	1.7573	1.7650	1.7725	1.7799	1.7872
12.0	*v*	37.80	38.81	39.85	40.85	41.85	42 87
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7412	1.7491	1.7568	1.7643	1.7717	1.7790
14.0	*v*	32.40	33.27	34.15	35.00	35.88	36.75
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7342	1.7421	1.7498	1.7573	1.7647	1.7720
16.0	*v*	28.35	29.11	29.88	30.63	31.40	32.16
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7282	1.7361	1.7438	1.7513	1.7587	1.7660
20.0	*v*	22.68	23.29	23.90	24.50	25.11	25.72
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7181	1.7260	1.7337	1.7412	1.7486	1.7559

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Table VI (*Continued*)

P		1400° F.	1450° F.	1500° F.	1550° F.	1600° F.	1650° F.
24.0	*v*	18.90	19.40	19.92	20.42	20.93	21.44
	H	685.6	673.5	688.5	703.6	718.8	734.0
	S	1.7099	1.7178	1.7255	1.7330	1.7404	1.7477
28.0	*v*	16.20	16.63	17.07	17.50	17.94	18.37
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.7030	1.7109	1.7186	1.7261	1.7335	1.7408
32.0	*v*	14.17	14.55	14.93	15.31	15.70	16.08
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6969	1.7048	1.7125	1.7200	1.7274	1.7347
36.0	*v*	12.60	12.93	13.27	13.62	13.95	14.29
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6916	1.6995	1.7072	1.7147	1.7221	1.7294
40.0	*v*	11.37	11.64	11.95	12.25	12.56	12.86
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6869	1.6948	1.7025	1.7100	1.7174	1.7247
44.0	*v*	10.30	10.58	10.86	11.14	11.42	11.69
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6826	1.6905	1.6982	1.7057	1.7131	1.7204
48.0	*v*	9.450	9.704	9.958	10.21	10.46	10.72
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6787	1.6866	1.6943	1.7018	1.7092	1.7165
52.0	*v*	8.723	8.958	9.192	9.430	9.662	9.898
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6750	1.6829	1.6906	1.6981	1.7055	1.7128
56.0	*v*	8.100	8.318	8.535	8.756	8.975	9.193
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6717	1.6796	1.6873	1.6948	1.7022	1.7095
60.0	*v*	7.500	7.763	7.970	8.175	8.376	8.580
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6686	1.6765	1.6842	1.6917	1.6991	1.7064
70.0	*v*	6.480	6.654	6.832	7.005	7.180	7.356
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6616	1.6695	1.6772	1.6847	1.6921	1.6994
80.0	*v*	5.670	5.822	5.980	6.130	6.281	6.438
	H	658.6	673.5	688.5	703.7	718.8	734.0
	S	1.6556	1.6635	1.6712	1.6787	1.6861	1.6934
90.0	*v*	5.040	5.176	5.316	5.447	5.582	5.720
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6503	1.6582	1.6659	1.6734	1.6808	1.6881
100	*v*	4.536	4.658	4.782	4.901	5.023	5.146
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6455	1.6534	1.6611	1.6686	1.6760	1.6833
120	*v*	3.781	3.883	3.985	4.086	4.188	4.289
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6373	1.6452	1.6529	1.6604	1.6678	1.6751
140	*v*	3.241	3.328	3.415	3.502	3.590	3.677
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6304	1.6383	1.6460	1.6535	1.6609	1.6682
160	*v*	2.836	2.912	2.988	3.065	3.141	3.217
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6243	1.6322	1.6399	1.6474	1.6548	1.6621
180	*v*	2.521	2.589	2.656	2.724	2.792	2.860
	H	658.6	673.5	688.5	703.6	718.8	734.0
	S	1.6190	1.6269	1.6346	1.6421	1.6495	1.6568
200	*v*	2.269	2.330	2.390	2.452	2.513	2.574
	H	658.5	673.5	688.5	703.6	718.8	734.0
	S	1.6143	1.6222	1.6299	1.6374	1.6448	1.6521
220	*v*	2.063	2.119	2.173	2.228	2.285	2.340
	H	658.5	673.4	688.5	703.6	718.8	734.0
	S	1.6100	1.6179	1.6256	1.6331	1.6405	1.6478
240	*v*	1.891	1.942	1.992	2.043	2.095	2.145
	H	658.5	673.4	688.4	703.6	718.8	734.0
	S	1.6060	1.6139	1.6216	1.6291	1.6365	1.6438
260	*v*	1.746	1.793	1.839	1.886	1.933	1.980
	H	658.5	673.4	688.4	703.5	718.8	734.0
	S	1.6026	1.6105	1.6182	1.6257	1.6331	1.6404
280	*v*	1.621	1.665	1.707	1.751	1.795	1.839
	H	658.5	673.4	688.4	703.5	718.7	734.0
	S	1.5991	1.6070	1.6147	1.6223	1.6296	1.6369
300	*v*	1.513	1.553	1.594	1.635	1.676	1.717
	H	658.5	673.4	688.4	703.5	718.7	734.0
	S	1.5960	1.6039	1.6116	1.6191	1.6265	1.6338
320	*v*	1.418	1.457	1.494	1.533	1.571	1.609
	H	658.5	673.4	688.4	703.5	718.7	733.9
	S	1.5931	1.6010	1.6087	1.6162	1.6236	1.6309
340	*v*	1.335	1.371	1.406	1.443	1.479	1.515
	H	658.5	673.4	688.4	703.5	718.7	733.9
	S	1.5903	1.5982	1.6059	1.6134	1.6208	1.6281
360	*v*	1.261	1.295	1.328	1.362	1.397	1.431
	H	658.5	673.4	688.4	703.5	718.7	733.9
	S	1.5878	1.5957	1.6034	1.6109	1.6183	1.6256
380	*v*	1.194	1.227	1.258	1.291	1.323	1.355
	H	658.4	673.4	688.4	703.5	718.7	733.9
	S	1.5853	1.5932	1.6009	1.6084	1.6159	1.6231
400	*v*	1.135	1.166	1.196	1.227	1.257	1.288
	H	658.4	673.3	688.3	703.4	718.7	733.9
	S	1.5830	1.5909	1.5986	1.6061	1.6135	1.6208
420	*v*	1.081	1.110	1.139	1.168	1.197	1.227
	H	658.4	673.3	688.3	703.4	718.6	733.9
	S	1.5808	1.5887	1.5964	1.6039	1.6113	1.6186
440	*v*	1.032	1.059	1.087	1.115	1.142	1.171
	H	658.4	673.3	688.3	703.4	718.6	733.8
	S	1.5787	1.5866	1.5943	1.6018	1.6092	1.6165
480	*v*	0.9461	0.9713	0.9967	1.022	1.048	1.073
	H	658.3	673.2	688.3	703.4	718.6	733.8
	S	1.5747	1.5826	1.5903	1.5978	1.6052	1.6125
520	*v*	0.8733	0.8965	0.9201	0.9437	0.9672	0.9910
	H	658.3	673.2	688.3	703.4	718.6	733.8
	S	1.5711	1.5790	1.5867	1.5942	1.6016	1.6089
560	*v*	0.8109	0.8325	0.8543	0.8763	0.8981	0.9202
	H	658.3	673.2	688.2	703.4	718.6	733.8
	S	1.5677	1.5756	1.5833	1.5908	1.5982	1.6055
600	*v*	0.7571	0.7772	0.7976	0.8179	0.8385	0.8591
	H	658.2	673.2	688.2	703.3	718.6	733.8
	S	1.5646	1.5725	1.5802	1.5877	1.5951	1.6024
650	*v*	0.6988	0.7174	0.7362	0.7550	0.7742	0.7930
	H	658.2	673.1	688.2	703.3	718.5	733.7
	S	1.5610	1.5689	1.5766	1.5841	1.5915	1.5988
700	*v*	0.6489	0.6662	0.6838	0.7013	0.7189	0.7366
	H	658.1	673.1	688.1	703.3	718.5	733.7
	S	1.5577	1.5656	1.5733	1.5808	1.5882	1.5955
750	*v*	0.6058	0.6219	0.6382	0.6547	0.6712	0.6877
	H	658.1	673.0	688.1	703.2	718.5	733.7
	S	1.5545	1.5624	1.5701	1.5776	1.5850	1.5923
800	*v*	0.5680	0.5831	0.5984	0.6138	0.6292	0.6447
	H	658.0	673.0	688.1	703.2	718.4	733.7
	S	1.5516	1.5595	1.5672	1.5747	1.5821	1.5894
850	*v*	0.5345	0.5488	0.5632	0.5777	0.5924	0.6067
	H	658.0	673.0	688.0	703.2	718.4	733.6
	S	1.5489	1.5568	1.5645	1.5720	1.5794	1.5867
900	*v*	0.5048	0.5184	0.5320	0.5456	0.5595	0.5732
	H	657.9	672.9	688.0	703.1	718.4	733.6
	S	1.5463	1.5542	1.5619	1.5694	1.5768	1.5841
950	*v*	0.4784	0.4911	0.5040	0.5170	0.5302	0.5430
	H	657.9	672.9	687.9	703.1	718.3	733.5
	S	1.5439	1.5518	1.5595	1.5670	1.5744	1.5817
1000	*v*	0.4545	0.4666	0.4789	0.4912	0.5037	0.5161
	H	657.8	672.8	687.9	703.0	718.3	733.5
	S	1.5416	1.5495	1.5572	1.5647	1.5721	1.5794
1100	*v*	0.4132	0.4243	0.4354	0.4466	0.4580	0.4693
	H	657.7	672.7	687.8	703.0	718.2	733.4
	S	1.5373	1.5452	1.5529	1.5604	1.5678	1.5751
1200	*v*	0.3789	0.3889	0.3992	0.4094	0.4199	0.4303
	H	657.7	672.6	687.7	702.9	718.2	733.4
	S	1.5332	1.5411	1.5488	1.5563	1.5637	1.5710
1300	*v*	0.3497	0.3591	0.3687	0.3780	0.3876	0.3973
	H	657.6	672.6	687.6	702.8	718.1	733.3
	S	1.5296	1.5375	1.5452	1.5527	1.5601	1.5674
1400	*v*	0.3249	0.3334	0.3423	0.3511	0.3601	0.3690
	H	657.5	672.5	687.6	702.8	718.0	733.3
	S	1.5263	1.5342	1.5419	1.5494	1.5568	1.5641
1500	*v*	0.3032	0.3113	0.3196	0.3278	0.3362	0.3444
	H	657.3	672.4	687.5	702.7	718.0	733.2
	S	1.5231	1.5310	1.5387	1.5462	1.5536	1.5609
1600	*v*	0.2843	0.2919	0.2997	0.3073	0.3153	0.3230
	H	657.2	672.3	687.4	702.6	717.9	733.2
	S	1.5203	1.5282	1.5359	1.5434	1.5508	1.5581
1700	*v*	0.2676	0.2748	0.2820	0.2893	0.2968	0.3041
	H	657.1	672.2	687.3	702.5	717.8	733.1
	S	1.5174	1.5253	1.5330	1.5405	1.5479	1.5552
1800	*v*	0.2528	0.2596	0.2664	0.2733	0.2804	0.2873
	H	657.0	672.1	687.2	702.5	717.8	733.1
	S	1.5148	1.5227	1.5304	1.5379	1.5453	1.5526
1900	*v*	0.2395	0.2460	0.2525	0.2589	0.2656	0.2722
	H	656.9	672.0	687.2	702.4	717.7	733.0
	S	1.5124	1.5203	1.5280	1.5355	1.5429	1.5502
2000	*v*	0.2276	0.2337	0.2399	0.2460	0.2524	0.2587
	H	656.8	672.0	687.1	702.3	717.6	733.0
	S	1.5103	1.5182	1.5259	1.5334	1.5408	1.5481
2100	*v*	0.2168	0.2226	0.2285	0.2344	0.2404	0.2464
	H	656.7	671.9	687.0	702.2	717.6	732.9
	S	1.5079	1.5158	1.5235	1.5310	1.5384	1.5457
2200	*v*	0.2070	0.2125	0.2182	0.2237	0.2296	0.2353
	H	656.6	671.8	686.9	702.2	717.5	732.9
	S	1.5057	1.5136	1.5213	1.5288	1.5362	1.5435
2300	*v*	0.1980	0.2033	0.2087	0.2141	0.2196	0.2251
	H	656.5	671.7	686.9	702.1	717.4	732.8
	S	1.5037	1.5116	1.5193	1.5268	1.5342	1.5415
2400	*v*	0.1898	0.1949	0.2001	0.2052	0.2105	0.2154
	H	656.5	671.6	686.8	702.0	717.4	732.8
	S	1.5018	1.5097	1.5174	1.5249	1.5323	1.5396
2500	*v*	0.1822	0.1871	0.1921	0.1970	0.2022	0.2073
	H	656.4	671.5	686.7	702.0	717.3	732.7
	S	1.4998	1.5077	1.5154	1.5229	1.5303	1.5376
2600	*v*	0.1752	0.1799	0.1847	0.1895	0.1945	0.1994
	H	656.3	671.4	686.6	701.9	717.2	732.7
	S	1.4981	1.5060	1.5137	1.5212	1.5286	1.5359
2700	*v*	0.1687	0.1733	0.1779	0.1825	0.1872	0.1920
	H	656.2	671.4	686.5	701.8	717.2	732.6
	S	1.4963	1.5042	1.5119	1.5194	1.5268	1.5341
2800	*v*	0.1627	0.1671	0.1716	0.1760	0.1807	0.1896
	H	656.1	671.3	686.5	701.7	717.1	732.6
	S	1.4947	1.5026	1.5103	1.5178	1.5252	1.5325
2900	*v*	0.1571	0.1614	0.1657	0.1700	0.1745	0.1789
	H	656.1	671.2	686.4	701.7	717.1	732.5
	S	1.4930	1.5009	1.5086	1.5161	1.5235	1.5308
3000	*v*	0.1519	0.1560	0.1602	0.1643	0.1687	0.1730
	H	656.0	671.1	686.3	701.6	717.0	732.4
	S	1.4915	1.4994	1.5071	1.5146	1.5220	1.5293

Table VII. Properties of Superheated Carbon Dioxide Vapor from 1700° to 1800° F.

P		1700° F.	1750° F.	1800° F.
0.60	v	878.1	898.6	918.4
	H	749.3	764.6	780.0
	S	1.9213	1.9284	1.9353
0.70	v	753.0	769.9	787.5
	H	749.3	764.6	780.0
	S	1.9143	1.9214	1.9283
0.80	v	658.8	673.6	689.0
	H	749.3	764.6	780.0
	S	1.9083	1.9154	1.9223
0.90	v	585.4	598.7	612.1
	H	749.3	764.6	780.0
	S	1.9030	1.9101	1.9170
1.00	v	526.8	538.6	551.0
	H	749.3	764.6	780.0
	S	1.8983	1.9054	1.9123
1.10	v	478.8	489.9	501.0
	H	749.3	764.6	780.0
	S	1.8940	1.9011	1.9080
1.20	v	438.7	449.0	459.0
	H	749.3	764.6	780.0
	S	1.8901	1.8972	1.9041
1.30	v	405.2	414.6	423.9
	H	749.3	764.6	780.0
	S	1.8865	1.8936	1.9005
1.40	v	376.1	384.9	393.5
	H	749.3	764.6	780.0
	S	1.8831	1.8902	1.8971
1.50	v	351.1	359.3	367.3
	H	749.3	764.6	780.0
	S	1.8800	1.8871	1.8940
1.60	v	329.1	336.8	344.3
	H	749.3	764.6	780.0
	S	1.8771	1.8842	1.8911
1.80	v	292.5	299.4	306.0
	H	749.3	764.6	780.0
	S	1.8718	1.8789	1.8858
2.00	v	263.4	269.4	275.5
	H	749.3	764.6	780.0
	S	1.8670	1.8741	1.8810
2.50	v	210.5	215.7	220.2
	H	749.3	764.6	780.0
	S	1.8570	1.8641	1.8710
3.00	v	175.5	179.7	183.7
	H	749.3	764.6	780.0
	S	1.8487	1.8558	1.8627
3.50	v	150.5	154.0	157.5
	H	749.3	764.6	780.0
	S	1.8418	1.8489	1.8558
4.00	v	131.7	134.8	137.8
	H	749.3	764.6	780.0
	S	1.8358	1.8429	1.8498
4.50	v	117.1	119.8	122.5
	H	749.3	764.6	780.0
	S	1.8304	1.8375	1.8444
5.00	v	105.3	107.8	110.2
	H	749.3	764.6	780.0
	S	1.8257	1.8328	1.8397
5.50	v	95.78	98.02	100.2
	H	749.3	764.6	780.0
	S	1.8214	1.8285	1.8354
6.00	v	87.80	89.86	91.83
	H	749.3	764.6	780.0
	S	1.8175	1.8246	1.8315
7.00	v	75.30	76.99	78.75
	H	749.3	764.6	780.0
	S	1.8105	1.8176	1.8245
8.00	v	65.85	67.37	68.89
	H	749.3	764.6	780.0
	S	1.8045	1.8116	1.8185
9.00	v	58.53	59.89	61.24
	H	749.3	764.6	780.0
	S	1.7992	1.8063	1.8132
10.00	v	52.68	53.90	55.11
	H	749.3	764.6	780.0
	S	1.7944	1.8015	1.8084
12.00	v	43.88	44.90	45.90
	H	749.3	764.6	780.0
	S	1.7862	1.7933	1.8002
14.00	v	37.61	38.49	39.35
	H	749.3	764.6	780.0
	S	1.7792	1.7863	1.7932
16.00	v	32.91	33.68	34.43
	H	749.3	764.6	780.0
	S	1.7732	1.7803	1.7872
20.00	v	26.34	26.94	27.55
	H	749.3	764.6	780.0
	S	1.7631	1.7702	1.7771
24.00	v	21.95	22.46	22.97
	H	749.3	764.6	780.0
	S	1.7549	1.7620	1.7689
28.00	v	18.81	19.25	19.68
	H	749.3	764.6	780.0
	S	1.7480	1.7551	1.7620
32.00	v	16.45	16.85	17.22
	H	749.3	764.6	780.0
	S	1.7419	1.7490	1.7559
36.00	v	14.63	14.98	15.31
	H	749.3	764.6	780.0
	S	1.7366	1.7437	1.7506
40.00	v	13.17	13.48	13.78
	H	749.3	764.6	780.0
	S	1.7319	1.7390	1.7459
44.00	v	11.97	12.25	12.53
	H	749.3	764.6	780.0
	S	1.7276	1.7347	1.7416
48.00	v	10.97	11.23	11.48
	H	749.3	764.6	780.0
	S	1.7237	1.7308	1.7377
52.00	v	10.13	10.37	10.60
	H	749.3	764.6	780.0
	S	1.7200	1.7271	1.7340
56.00	v	9.402	9.630	9.840
	H	749.3	764.6	780.0
	S	1.7167	1.7238	1.7307
60.00	v	8.780	8.986	9.183
	H	749.3	764.6	780.0
	S	1.7136	1.7207	1.7276
70.00	v	7.530	7.699	7.873
	H	749.3	764.6	780.0
	S	1.7066	1.7137	1.7206
80.00	v	6.588	6.736	6.887
	H	749.3	764.6	780.0
	S	1.7006	1.7077	1.7146
90.00	v	5.855	5.987	6.122
	H	749.3	764.6	780.0
	S	1.6953	1.7024	1.7093
100	v	5.269	5.386	5.510
	H	749.3	764.6	780.0
	S	1.6905	1.6976	1.7045
120	v	4.391	4.493	4.592
	H	749.3	764.6	780.0
	S	1.6823	1.6894	1.6963
140	v	3.763	3.851	3.935
	H	749.3	764.6	780.0
	S	1.6754	1.6825	1.6894
160	v	3.293	3.369	3.445
	H	749.3	764.6	780.0
	S	1.6693	1.6764	1.6833
180	v	2.928	2.996	3.062
	H	749.3	764.6	780.0
	S	1.6640	1.6711	1.6780
200	v	2.636	2.697	2.757
	H	749.3	764.6	780.0
	S	1.6593	1.6664	1.6733
220	v	2.396	2.452	2.506
	H	749.3	764.6	780.0
	S	1.6550	1.6621	1.6690
240	v	2.196	2.247	2.297
	H	749.3	764.6	780.0
	S	1.6510	1.6581	1.6650
260	v	2.027	2.074	2.121
	H	749.3	764.6	780.0
	S	1.6476	1.6547	1.6616
280	v	1.883	1.927	1.970
	H	749.3	764.6	780.0
	S	1.6441	1.6512	1.6581
300	v	1.758	1.798	1.838
	H	749.3	764.6	780.0
	S	1.6410	1.6481	1.6550
320	v	1.648	1.686	1.724
	H	749.3	764.6	780.0
	S	1.6381	1.6452	1.6521
340	v	1.551	1.586	1.622
	H	749.2	764.6	780.0
	S	1.6353	1.6424	1.6493
360	v	1.465	1.498	1.533
	H	749.2	764.5	779.9
	S	1.6328	1.6399	1.6468
380	v	1.388	1.420	1.452
	H	749.2	764.5	779.9
	S	1.6303	1.6374	1.6443
400	v	1.319	1.349	1.380
	H	749.2	764.5	779.9
	S	1.6280	1.6351	1.6420
420	v	1.256	1.284	1.314
	H	749.2	764.5	779.9
	S	1.6258	1.6329	1.6398
440	v	1.199	1.226	1.255
	H	749.1	764.4	779.9
	S	1.6237	1.6308	1.6377
480	v	1.099	1.124	1.150
	H	749.1	764.4	779.9
	S	1.6197	1.6268	1.6337
520	v	1.014	1.038	1.062
	H	749.1	764.4	779.9
	S	1.6161	1.6232	1.6301
560	v	0.9420	0.9639	0.9860
	H	749.1	764.4	779.8
	S	1.6127	1.6198	1.6267
600	v	0.8795	0.8999	0.9202
	H	749.1	764.4	779.8
	S	1.6096	1.6167	1.6236
650	v	0.8118	0.8306	0.8500
	H	749.0	764.3	779.8
	S	1.6060	1.6131	1.6200
700	v	0.7540	0.7715	0.7900
	H	749.0	764.3	779.8
	S	1.6027	1.6098	1.6167
750	v	0.7040	0.7203	0.7370
	H	749.0	764.3	779.7
	S	1.5995	1.6066	1.6135
800	v	0.6600	0.6755	0.6906
	H	749.0	764.3	779.7
	S	1.5966	1.6037	1.6106
850	v	0.6213	0.6357	0.6500
	H	749.0	764.3	779.7
	S	1.5939	1.6010	1.6079
900	v	0.5868	0.6006	0.6138
	H	748.9	764.2	779.7
	S	1.5913	1.5984	1.6053
950	v	0.5561	0.5689	0.5816
	H	748.9	764.2	779.6
	S	1.5889	1.5960	1.6029
1000	v	0.5283	0.5407	0.5526
	H	748.9	764.2	779.6
	S	1.5866	1.5937	1.6006
1100	v	0.4804	0.4916	0.5024
	H	748.8	764.1	779.6
	S	1.5823	1.5894	1.5963
1200	v	0.4405	0.4508	0.4609
	H	748.8	764.1	779.5
	S	1.5782	1.5853	1.5922
1300	v	0.4067	0.4164	0.4254
	H	748.7	764.1	779.5
	S	1.5746	1.5817	1.5886
1400	v	0.3777	0.3866	0.3551
	H	748.7	764.0	779.5
	S	1.5713	1.5784	1.5853
1500	v	0.3527	0.3609	0.3690
	H	748.6	764.0	779.4
	S	1.5681	1.5752	1.5821
1600	v	0.3307	0.3385	0.3461
	H	748.6	764.0	779.4
	S	1.5653	1.5724	1.5793
1700	v	0.3113	0.3186	0.3259
	H	748.5	763.9	779.4
	S	1.5624	1.5695	1.5764
1800	v	0.2941	0.3010	0.3079
	H	748.5	763.9	779.3
	S	1.5598	1.5669	1.5738
1900	v	0.2787	0.2852	0.2917
	H	748.4	763.9	779.3
	S	1.5574	1.5645	1.5714
2000	v	0.2649	0.2711	0.2770
	H	748.4	763.8	779.3
	S	1.5553	1.5624	1.5693
2100	v	0.2523	0.2582	0.2640
	H	748.3	763.8	779.2
	S	1.5529	1.5600	1.5669
2200	v	0.2409	0.2466	0.2522
	H	748.3	763.7	779.2
	S	1.5507	1.5578	1.5647
2300	v	0.2305	0.2360	0.2413
	H	748.2	763.7	779.2
	S	1.5487	1.5558	1.5627
2400	v	0.2210	0.2262	0.2313
	H	748.2	763.6	779.1
	S	1.5468	1.5539	1.5608
2500	v	0.2122	0.2172	0.2223
	H	748.1	763.6	779.1
	S	1.5448	1.5519	1.5588
2600	v	0.2041	0.2089	0.2137
	H	748.1	763.5	779.1
	S	1.5431	1.5502	1.5571
2700	v	0.1966	0.2012	0.2059
	H	748.0	763.5	779.0
	S	1.5413	1.5484	1.5553
2800	v	0.1896	0.1941	0.1986
	H	748.0	763.4	779.0
	S	1.5397	1.5468	1.5537
2900	v	0.1831	0.1875	0.1918
	H	747.9	763.4	778.9
	S	1.5380	1.5451	1.5520
3000	v	0.1771	0.1813	0.1856
	H	747.8	763.3	778.8
	S	1.5365	1.5436	1.5505

END OF ARTICLE ON

THERMODYNAMIC PROPERTIES OF GASES

Extraction of Aconitic Acid from Sorgo

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Aconitic acid in the sorgo plant occurs both as free acid and combined with the cations of the juice. The aconitate precipitated from sorgo juice contains magnesium as well as calcium. Efficient precipitation of the aconitate requires concentration to a density of 50° to 60° Brix and heating to temperature above 75° C. Almost twice as much aconitate was precipitated by using lime and calcium chloride as by using lime alone.

ACONITIC acid (1,2,3-propenetricarboxylic acid) was discovered in 1820 in *Aconitum napellus* by Peschier (*2*), and since then numerous investigators have reported aconitic acid in sugar cane juices and its products. The early literature contains only two references to the occurrence of aconitic acid in sorgo. Parsons (*5*) reported the calcium salt of aconitic acid deposited on the heating surface of evaporating pans used to concentrate sorgo juices which had previously been limed to neutrality. Wiley and Maxwell (*10*) reported a qualitative determination of the acids occurring in the sorgo plant and considered aconitic acid to be first in order of the proportions of the acids determined. These early investigators did not report the aconitic acid content of the sorgo juices and there was no reason to expect that the sorgo plant could be a source of aconitic acid. Ventre (*7*) and Ventre and Paine (*9*) reported that the calcium salt of aconitic acid interfered with the extraction of sucrose from the sorgo plant, and devised a method for separation of calcium aconitate as a by-product in manufacture of sugar from sorgo.

Table I presents analyses of sorgo juices processed at the pilot plant located at the U. S. Department of Agriculture's Sugar Plant Field Station, Meridian, Miss., during the 1941 and 1942 seasons. Some runs consisted of only one variety, and other runs were of mixed varieties. 1941 was a normal growing season and all the runs were harvested in the dead-ripe stage of maturity. 1942 was a "late" season, and the sorgo was harvested in the ripe stage of maturity. Table I shows a lower average percentage of Brix solids, a lower titratable acidity, and a lower aconitic acid content in the ripe stage as compared with the more mature dead-ripe stage, an indication that all three of these characteristics of the juices increased with maturity. There was considerable variation in the aconitic acid content of individual lots of the same variety through each season. This also applies to the titratable acidity; while in general it may be said that the titratable acidity increased when the aconitic acid content increased, the data in Table I do not give a smooth correlation.

Titratable acidity measures the free acid content of the sorgo juice; it may consist entirely of aconitic acid or may consist of other acids that are known to occur in sorgo. If we calculate the average titratable acidity as aconitic acid and compare it with the average aconitic acid content of the juices, we find that aconitic acid cannot occur wholly as the free acid. This is evident if we take the free acidity of the 1941 season and calculate it as aconitic acid:

$$\frac{4.8 \text{ cc.} \times 0.0058}{10 \text{ cc.} \times 1.078 \times 0.1944} = 1.33\%$$

The total aconitic acid per cent solids for this season was 4.47% of which only (1.33 × 100)/4.47 or 29.53% could occur as free acid in the juices. Likewise, for the 1942 season the titratable acidity calculated as aconitic acid was:

$$\frac{3.6 \text{ cc.} \times 0.0058}{10 \text{ cc.} \times 1.072 \times 0.1807} = 1.07\%$$

However, the total aconitic acid solids content was 2.85%, of which only (1.07 × 100)/2.85, or 37.54%, could occur as free aconitic acid. The more mature cane of the 1941 season had a lower ratio of free acid to total aconitic acid than the less mature cane of the 1942 season.

The combined aconitic acid is easily liberated by mineral acids and is capable of reacting by double decomposition with other salts. Therefore, it would seem that the combined aconitic acid is present as soluble aconitates of the cations in the juice. Since

Table I. Aconitic Acid, Titratable Acidity, and Brix Solids in Sorgo Juices

Variety	Date	% Brix Solids	Titratable Acidity, Cc. of 0.1 *N* NaOH per 10 Cc. Juice	Aconitic Acid, % Brix Solids[a]
Dead-Ripe Stage of Maturity, 1941 Season				
Straight Neck & Early Folger	8-15-41	18.60	5.0	3.80
S.A. 287C	8-19-41	17.77	4.5	4.26
S.A. 287C	8-20-41	18.12	4.5	3.83
S.A. 287C	8-26-41	19.37	5.2	3.58
S.A. 287C	8-28-41	20.16	5.4	3.44
Straight Neck ABC	9-3-41	17.78	5.0	5.23
Colman Y1	9-5-41	19.43	5.0	4.17
S.A. 287C	9-9-41	20.17	4.8	4.96
Early Folger 16154 & Red X	9-11-41	20.78	5.9	4.81
Iceberg	9-16-41	18.96	3.2	3.96
S.A. 287C	9-18-41	21.48	6.3	5.24
Iceberg & Red X	9-22-41	18.58	3.6	5.38
Collier	9-24-41	20.82	4.1	4.56
Straight Neck	9-26-41	19.89	4.7	5.65
S.A. 287C	9-29-41	19.74	5.8	4.27
	Average	19.44	4.8	4.47
Ripe Stage of Maturity, 1942 Season				
Red X	8-25-42	15.30	3.0	2.72
S.A. 287C	9-4-42	16.44	2.7	3.55
S.A. 287C	9-1-42	17.16	2.9	2.60
S.A. 287C	9-8-42	17.01	3.0	2.55
S.A. 287C	9-2-42	17.28	2.6	2.70
Straight Neck	9-9-42	19.39	3.6	2.24
S.A. 287C	9-15-42	20.60	4.0	2.75
Ga. Blue Ribbon	9-10-42	17.17	2.1	2.62
S.A. 287C	9-16-42	19.28	4.0	2.53
Straight Neck	9-21-42	20.04	4.6	3.54
S.A. 287C	9-17-42	16.68	3.0	2.30
Straight Neck	9-22-42	19.69	5.7	2.54
S.A. 287C	9-23-42	17.65	3.7	3.31
S.A. 287C	9-24-42	15.61	3.9	3.73
Straight Neck	9-28-42	18.16	4.4	3.21
Straight Neck	9-29-42	20.09	4.5	2.74
Straight Neck	9-30-42	18.80	4.1	2.66
Straight Neck	10-1-42	19.00	4.4	3.12
	Average	18.07	3.6	2.85

[a] The determination of aconitic acid was the authors' adaptation of the color reaction of C. S. Taylor [*J. Chem. Soc.*, 115, 886 (1919)] as modified by O. Furth and H. Herrmann [*Biochem. Z.*, 280, 448–57 (1935)].

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Table II. Flow Sheet of Aconitic Acid in Sugar Manufacturing Process

(Juices treated with lime only; dead-ripe stage of maturity; average determinations of ten pilot-plant runs)

Material	% Brix Solids	Purity, %	pH	Aconitic Acid, % Brix Solids
Raw juice[a]	19.70	71.36	4.85	4.68
Centrifuged juice	19.36	73.02	...	4.92
Cold limed juice	...	...	10.07	..
Defecated juice	19.60	74.23	8.2	4.53
Sirup	60.70	75.99	7.5	4.59
Defecated sirup	59.54	77.35	6.67	2.67

[a] Raw juice average acidity, 4.9 cc. of 0.1 *N* NaOH per 10 cc.; average removal of aconitic acid by analysis, 42.95% of total acid; yield of washed and dried aconitate, equivalent to 40.77% of total acid.

the predominating cation in plant juices is potassium, it follows that the combined aconitic acid is probably present in the juice in large part as potassium aconitate.

METHOD OF EXTRACTION

For the most efficient utilization of the sorgo plant, the aconitic acid must be necessarily extracted as a by-product in the manufacture of the principal commercial constituent of the juice—namely, sucrose. Aconitic acid is removed from the evaporator sirup by heating the sirup above 75° C. and separating the aconitate precipitated, which is principally calcium aconitate. The principal influencing factor on aconitic acid removal from sorgo juice from which the starch has been previously removed is the quantity of lime that may be added to the juice. The use of lime for the neutralization and clarification of the sorgo juices from which sugar is to be extracted permits the introduction of a quantity of lime sufficient to neutralize the free acid of the juices; however, it has just been shown that this amount of lime would only be equivalent to 29.53 to 37.54% of the amount required to combine with the total amount of aconitic acid occurring in the juices. The addition of lime much in excess of the quantity required to neutralize the free acid results in such high alkalinities that the monosaccharides of the juices are decomposed with the formation in the juices of undesirable products. The liming of the juices should be controlled so that, when the sirup is heated, the pH drops to just below 7.0. It was found that sirups having a pH over 7.0 after being heated did not precipitate a granular aconitate but produced an amorphous precipitate that was water soluble and could not be recovered from the sirup.

Table II presents a flow sheet of aconitic acid in the sorgo juices and sirups at different stages of the sugar manufacturing process. The removal of aconitic acid was practically negligible previous to the heat treatment of the sirups. Theoretically, the calcium that could be introduced by neutralization of the free acid was equivalent, on the average, to

$$\frac{4.9 \text{ cc.} \times 0.0058}{10 \text{ cc.} \times 1.080 \times 0.1907} = 1.33\% \text{ aconitic acid}$$

which was $\dfrac{1.33 \times 100}{4.68} = 28.41\%$ of total aconitic acid in juice.

Therefore, in these runs this value represents the average removal of aconitic acid as calcium aconitate to be expected by neutralization with lime. However, the average removal actually obtained was 42.95%. This increased removal over that which would be expected is undoubtedly due to the occurrence in raw sorgo juice not only of calcium but also of magnesium, which plays a role in the precipitation of insoluble aconitate from the juice.

Table III gives some analyses of the insoluble aconitate obtained from sorgo and sugar cane products. The only recorded analysis of this material obtained from sorgo is by Parsons (*5*). Unfortunately he did not determine aconitic acid directly, but assumed that it was represented by the remainder left after all the mineral matter and "moisture" at 125° C. had been determined. It is now known (*1*) that drying at 125° removes only an indefinite portion of the water of crystallization from the aconitate. Consequently his "organic matter by difference" represents not only the aconitic acid present, but includes an uncertain amount of water, and his formulas for the aconitates are in error. However, there is no reason to suppose that his analyses of the mineral constituents are in error. He found a significant amount of magnesium oxide which, he believed, was probably present in the material as the oxide or hydrate, held in colloidal suspension in the juices after liming until occluded in the precipitate of calcium aconitate. Until recently it was generally accepted that the magnesium in the natural aconitates from both sorgo and sugar cane products is present as either the hydrate or the carbonate (*6*).

The only other recorded analyses of such aconitates are given by McCalip and Seibert (*4*), as Table III shows. They obtained their material from sugar cane products. These investigators reported much higher contents of magnesium oxide but stated that no carbon dioxide was evolved when the insoluble sediments were dissolved in hydrochloric acid. Therefore, neither the magnesium nor the calcium could have been present as carbonate. During recent studies on aconitic acid, many analyses of the insoluble aconitates obtained from sorgo and sugar cane products have been made; a few are given in Table III. All of these precipitates contained varying but significant percentages of magnesium but no detectable amounts of carbonates.

By calculating the percentages of the constituents of the aconitates as chemical equivalents and comparing the basic and the acidic equivalents (as in Table IV), it is evident that the calcium oxide does not furnish enough basic equivalents to equal (i.e., to neutralize) the acidic equivalents of the aconitic acid. Therefore, the combination of the calcium oxide present with the aconitic acid present would leave an excess of the latter, or would result in the formation of an acidic aconitate. But either an excess of aconitic acid or an acidic calcium aconitate would neutralize magnesium oxide or hydrate in suspension in the original solution (*1*) since none of these possible reactants is so insoluble that the basic ones would not neutralize the acidic ones in aqueous media such as juices and sirups. Therefore, Parsons' idea of the presence of free magnesium oxide in the insoluble aconitates is untenable. This is also shown by balancing the total major basic equivalents with the total major acidic equivalents[3], as in Table IV. If the equivalents of the calcium and magnesium oxides are added and the acidic equivalents of the sulfur trioxide are subtracted from this sum, it is found that the remain-

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[3] Equivalents for SiO_2 are ignored, since silicic acid is but slightly acidic and its salts are highly hydrolyzed in dilute solution.

Table III. Analyses of Insoluble Aconitates from Sorgo and Sugar Cane Products

Source	Aconitic Acid, %	CaO, %	MgO, %	M_2O_3[a], %	SiO_2, %	SO_3, %	P_2O_5, %	Alkalies, %	Moisture, %
Sorgo (*5*)	[b]	22.87	3.65	0.57	1.57	..	0.19	Trace	7.48 (125° C.)
Sorgo[c]	67.81	25.98	3.61	Trace	..	..	Trace	0.73	8.18 (105° C.)
Sorgo	59.3	23.9	3.3	0.14	0.16	0.0	...	...	...
Sorgo	59.2	23.4	3.8	0.37	0.07	0.03	...	...	...
Sugar cane[d]	56.98	23.96	5.76	...	..	6.61	...	...	...
Sugar cane (*4*)	56.21	15.66	9.78	0.78	2.35	4.08	0.13	...	...
Sugar cane (*4*)	57.44	13.58	11.98	0.66	3.58	1.25	Trace	...	...

[a] M_2O_3 = total Fe_2O_3, Al_2O_3, etc.
[b] Organic matter by difference, 63.67%.
[c] This analysis was made by the late E. K. Nelson, U. S. Department of Agriculture.
[d] Acknowledgment is made to C. A. Fort, U. S. Department of Agriculture, for this analysis.

ing basic equivalents are practically equal to the acidic equivalents of the aconitic acid, which indicates that the insoluble aconitates are neutral salts.

More recently Ventre and Paine (*9*) considered these materials as mixtures of calcium and magnesium aconitates. However, it has not been possible to remove the magnesium by leaching with water or with calcium chloride solutions. If the insoluble aconitates were physical mixtures, it should be possible to wash the very soluble magnesium aconitate (*3*) out and leave behind magnesium-free calcium aconitate.

The facts given above lead to the conclusion that the natural insoluble aconitates must be double salts of aconitic acid with calcium and magnesium, or mixed salts of a more complex nature. This was confirmed by Ambler, Turer, and Keenan (*1*) by means of chemical and microscopical studies of insoluble aconitates prepared under different conditions from solutions containing varying proportions of calcium and magnesium. Solutions which contained no magnesium and which were maintained at temperatures below 70° C. deposited crystals of the hexahydrate of tricalcium aconitate; but if kept at temperatures above 80° C., they deposited the trihydrate of tricalcium aconitate. Solutions which contained amounts of magnesium greater than 6% of the weight of the calcium present deposited, at temperatures up to 100° C., crystals which contained both calcium and magnesium and which were always hexahydrates. When these different crystalline preparations were examined under the microscope and compared with the natural insoluble aconitates, the crystals of the latter were different from those of the tri- and hexahydrates of tricalcium aconitate, but were identical in optical-crystallographic properties with the crystals containing both calcium and magnesium.

A few of the laboratory preparations of the calcium-magnesium aconitate contained sufficient magnesium oxide (7.6, 7.1, 7.68% MgO; average 7.4%) to correspond to the formula for dicalcium magnesium aconitate hexahydrate, $Ca_2MgAcon_2.6H_2O$ (theoretical MgO = 7.27%), but most of them contained less magnesium oxide than this formula would require. However, all of them showed the same crystalline characteristics, and no crystals of either the tri- or hexahydrate of tricalcium aconitate could be detected in them. Specimens were prepared whose magnesium oxide content varied between 1.9 and 7.6%. In each case, however, the sum of the equivalents of the calcium oxide and the magnesium oxide equaled the equivalents of the aconitic acid, as noted above in the cases of the natural materials. The results indicate that calcium and magnesium form a double salt with aconitic acid, and that this double salt can, and generally does, form homogeneous mixed crystals or solid solutions with tricalcium aconitate hexahydrate[4]. This explains the fact that it is impossible to separate the two salts by leaching or by any mechanical means. Solid solutions are more insoluble than either of the salts comprising them, and this accounts for the facts that dicalcium magnesium aconitate is so rarely formed and that tricalcium aconitates will not form if much magnesium is present in the solution.

When the dry salts are heated, the crystals of tricalcium aconitate hexahydrate lose water of crystallization more easily than the crystals of the calcium-magnesium aconitate hexahydrate. Whereas the former began to lose water at 70° to 75° C., and lost four of the six molecules of water at 120° C., the solid solutions did not begin to lose weight until heated to 80° C., and did not lose four molecules of water until the temperature reached 140° C. Temperatures above 250° C. are required to remove the water completely from either of them. Crystals of tricalcium aconitate trihydrate lost no water when heated to 140° C.

TABLE IV. EQUIVALENTS OF CONSTITUENTS OF INSOLUBLE ACONITATES

Source	*A* Aconitic Acid	*B* CaO	*C* MgO	*D* SO_3	*E* (*B* + *C* − *D*)	*F* Ratio *E*/*A*
Sorgo (*5*)	...	0.816	0.182	...	0.998	...
Sorgo[a]	1.169	0.927	0.179	...	1.106	0.947
Sorgo	1.022	0.852	0.163	...	1.015	0.993
Sorgo	1.020	0.835	0.187	0.001	1.021	1.001
Sugar cane[b]	0.982	0.854	0.285	0.165	0.974	0.992
Sugar cane (*4*)	0.969	0.559	0.483	0.102	0.940	0.970
Sugar cane (*4*)	0.990	0.484	0.594	0.031	1.047	1.057

[a] See Table III, footnote[c].
[b] See Table III, footnote[d].

TABLE V. FLOW SHEET OF ACONITIC ACID IN SUGAR MANUFACTURING PROCESS

(Juices treated with lime and calcium chloride from typical pilot-plant run)

Material[a]	% Brix Solids	Purity of Sucrose, % Brix	pH	Total Aconitic Acid, % Brix Solids
Raw juice	19.82	72.41	4.85	3.12
Limed juice	...	...	8.32	..
Defecated juice	19.08	76.59	8.10	3.0
Sirup	66.42	76.50	7.52	2.86
Defecated sirup	65.26	79.66	6.80	0.57

[a] Calcium chloride added equivalent to 60% of total aconitic acid; aconitic acid elimination in sirup by analysis, 81.73% total aconitic acid in juice; yield of washed and dried aconitate, 12.96 pounds per ton of juice.

Both of the insoluble tricalcium aconitates and the calcium-magnesium aconitate separate best, and in greatest yield, from solutions of pH 6.7 to 6.9. At pH 7.0 and higher they generally separate in a mass of very small amorphous spheres or droplets which are soluble in cold water (*1*). This is especially true when they precipitate from sugar solutions of high Brix. In this form it is impossible to wash them free from sugar before they dissolve. Sirups containing this amorphous form filter slowly because of the fineness of the particles. When a sirup containing such a precipitate of aconitates was maintained at high temperature, the amorphous spheres slowly crystallized from the center out, forming spherical aggregates of minute radiating crystals. Complete transformation from amorphous to crystalline condition required several days, and as it proceeded, filterability became less and less. This confirms the observation made above that, when precipitating aconitate from sorgo and sugar cane products, care must be taken that the insoluble material does not separate at a pH greater than 6.9.

IMPROVED METHODS OF EXTRACTION

It has been shown that the amount of calcium which may be added to the juices by neutralizing the free acidity and yet not attack the monosaccharides is sufficient to precipitate only an average of 42.9% of the total aconitic acid occurring in the juices, and that most of the aconitic acid in the juices must be in a combined form of the nature of a soluble aconitate. Therefore, the addition of more calcium in the form of a soluble salt should precipitate an increased amount of calcium aconitate. The combined use of calcium hydroxide for the neutralization of sorgo juices and of calcium chloride to furnish soluble calcium to precipitate aconitate in excess of that obtained from neutralization of the free acids of the juice was studied and is the subject of a patent by Ventre, Ambler, Byall, and Henry (*8*).

Table V presents data from a typical sorgo juice treated by this method. The percentage of aconitate precipitated was 81.7%, nearly double that obtained by the use of lime only. In applying this process, if the juices did not normally contain some calcium and magnesium, the amount of calcium chloride to be added should be the equivalent of the difference between the free acids calculated as aconitic acid and the total aconitic acid contained in the juices. However, as has been pointed out, some of the cal-

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[4] It may also be reasoned that trimagnesium aconitate crystallizes with tricalcium aconitate to form the series of salts being discussed. At present it is merely an academic question as to which is the correct way to interpret the results. Practically, it makes no material difference.

cium and magnesium naturally occurring in the juice is utilized in the formation of the insoluble aconitate with the result that the amount of aconitate precipitated is in excess of that to be expected from neutralization of the free acids of the juices. The average was almost 43% of the total aconitic acid present. Therefore, it is necessary to add only a maximum of calcium chloride equivalent to 60% of the total aconitic acid contained in the juices. The use of calcium chloride and lime might be expected to cut down materially the amount of magnesium in the precipitated aconitate; however, in duplicate runs made in 1942 for comparison of the lime alone with the lime and calcium chloride treatments, the magnesium was not eliminated from the aconitate by use of calcium chloride, but 13 to 14% of the aconitic acid in the precipitated aconitate was in combination with magnesium.

In the sugar manufacturing process when juices are treated by lime only or by lime and calcium chloride, the aconitic acid content is not significantly changed until the sirup is heated. The removal of the aconitate from the sirup removes solids by both methods. In the sirups made from juices treated with lime and calcium chloride, a slightly greater increase in purity is obtained than when lime only is used. This is attributed to the replacement of the aconitate radical, whose combining weight is 58, by the chloride radical, whose combining weight is 35.5. As an example, potassium aconitate in the juices would be changed to potassium chloride and calcium aconitate, the latter being removed by precipitation. The remaining potassium chloride has a lower equivalent weight than the potassium aconitate originally present.

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Yeasts from Wood Sugar Stillage

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Three strains of yeasts, *Torula utilis* No. 3, *Mycotorula lipolytica* (P-13), and *Hansenula suaveolens* Y-838, were grown on still waste liquor from the production of wood sugar alcohol. All three were found to utilize a large proportion of the unfermentable sugars and acids in the liquor, which indicates that these yeasts have possibilities for a practical utilization of such still waste liquors. The yield of dry Torula yeast may exceed 50% of the weight of sugar consumed, which indicates that components other than sugars are assimilated for yeast growth. Air diffusion was found to be an important factor in the rate of yeast growth and consumption of sugar. With proper aeration the assimilable sugar is consumed by Torula in 18 hours.

THE wood-sugar alcohol plant at Springfield, Oreg., will have approximately one-half million gallons of still waste liquors for disposal each day. This dark colored liquor contains the unfermentable sugars (pentoses), organic acids and salts, and miscellaneous other products resulting from the hydrolysis of Douglas fir wood. The primary hydrolysis products from wood are lignin, wood sugars, and acetic and formic acids. Secondary products, such as levulinic acid from the hexoses and furfural from the pentoses, are produced by further decomposition of the sugars during hydrolysis of the hemicelluloses and cellulose. Normally, softwoods give sugar mixtures that include glucose, galactose, mannose, arabinose, and xylose. The first three sugars are decomposed with brewer's yeast, *Saccharomyces cerevisae*, to alcohol and carbon dioxide, whereas the pentoses are unaffected and remain in the spent beers. Distillation of the alcohol from the beers gives a liquor which is still high in biochemical oxygen demand.

It is desirable to find a use for this still waste liquor and simultaneously decrease its stream pollution load. For this purpose the feasibility of manufacturing feeding yeast by growing species capable of utilizing the residual pentoses was investigated by the Oregon Forest Products Laboratory in cooperation with the U. S. Forest Products Laboratory and the Willamette Valley Wood Chemical Company. *Torula utilis* is of particular importance in Europe for the manufacture of fodder yeast and protein feeding stuffs. Its high nutritional value has been established (*1, 3, 6*). Yields of dry yeast of 35 to 50% on wood sugar have been reported (*4, 7, 10*), and Lechner (*5*) has obtained a yield of 46–49% on xylose. Its ability to utilize arabinose is reported to be negligible (*5*).

The feasibility of growing fodder yeast on the still waste liquor raises several important questions. Among them are the yield of yeast that may be expected, the extent to which the materials in the still waste liquor are assimilable, and the time required for their utilization by yeast. The fermentation of the fermentable sugars to alcohol is complete within 24 hours. Therefore, the utilization of the unfermentable sugars in a similar period is desirable from the standpoint of plant operation.

The still waste liquors used in this work were prepared from Douglas fir hydrolyzates fermented with brewer's yeast in the pilot plant of the U. S. Forest Products Laboratory. In the pilot plant, wood waste, including some bark, was first subjected to hydrolysis at 150° to 185° C. with concentrations of 0.5 to 1.0% of sulfuric acid. The hot wood sugar solutions were neutralized with lime to a pH of approximately 5.0 under 35 pounds steam pressure and passed through a filter press to remove the calcium sulfate sludge. After cooling and the addition of urea and NaH_2PO_4 as nutrients, the wood sugar wort was adjusted to a pH of approximately 5.8 and fermented with a strain of *Saccharomyces cerevisae*. Fermentation of roughly 5% wood sugar worts was complete within 24 hours with 80 to 83% utilization of the reducing sugar present. The yeast was recovered by centrifuging and re-used for the fermentation of the next batch of wood hydrolyzate.

TABLE I. ANALYSIS OF LIQUOR BEFORE AND AFTER TORULA GROWTH

	Still Waste Liquor	Torula Spent Liquors
Total solids, %	3.2	2.40
Reducing sugar (xylose), %	0.81	0.20
Reducing sugar after hydrolysis with H_2SO_4, %	0.97	0.34
Volatile acid (acetic), %	0.24	0.10
Volatile and nonvolatile acid (acetic), %	0.78	0.31 to 0.5
Ash, %		
Residue upon combustion	0.65	0.36 to 0.47
Residue converted to sulfate	1.03	0.58 to 0.68
Total carbon, %	1.42	0.94 to 1.04
5-Day B.O.D.	16,400	9600
pH	5.0	7.5 to 8.0

In the preliminary yeast work done at the Forest Products Laboratory, the alcohol was stripped from the beers by distilling off 20% of their volume in a 45-gallon batch copper still. This amount of water was then returned to the still residues to bring them to the same volume as the original beers. The reducing sugar content of these liquors varied from 0.6 to 1.5% with a normal reducing sugar content of 0.8%.

Other analytical data showed pH of 5.5 to 5.7, 2.3 to 2.5% dissolved solids, 0.5 to 0.7% ash, 0.2% volatile acid calculated as acetic, and 0.45% volatile and nonvolatile acid calculated as acetic. Boiling with 2.50% sulfuric acid for 1 hour gave a 20 to 27% increase in reducing sugar. Analysis of the sulfated ash residue showed calcium 26.0%, potassium 17.0%, iron 2.9%, magnesium 2.4%, and phosphorus 0.16%. Only traces of nitrogen were found in the liquor with a Kjeldahl determination.

Inasmuch as it was desirable to carry out the yeast studies on liquors representative of alcohol plant operating conditions, much of the quantitative work was performed on a still waste liquor produced in the pilot-plant distillation unit of The Vulcan Copper & Supply Company. The analytical data obtained are included in Table I. All of the still waste liquors were black and gave an amorphous deposit upon standing.

Torula utilis No. 3, *Mycotorula lipolytica* (P-13), and *Hansenula suaveolens* Y-838 have been reported as good consumers of pentose sugars (*7, 11*). Cultures of these yeasts were obtained and grown without difficulty on the still waste liquors. A phenomenon observed with all three is that they are able to remove acidic components in addition to approximately three fourths of the unfermentable sugar present. The unconsumed reducing material appears to be incompletely hydrolyzed substances that have reducing properties and are calculated as reducing sugar. The utilization of the acids in the liquor produces a change from an initial pH of 5.0 to a final pH of 7.5 to 8.0. The growth of the yeasts in the liquor is accompanied with deposition of mineral matter, chiefly calcium carbonate, and an amorphous ligninlike material. The comparative performance of these three yeasts, together with vitamin and amino acid assays, was continued as a separate study.

UTILIZATION OF ARABINOSE AND XYLOSE BY *Torula utilis* NO. 3

A yeast suitable for the complete utilization of the pentoses in still waste liquors obtained from wood hydrolyzates should consume arabinose and xylose. The capacity of *Torula utilis* No. 3 to utilize these sugars was tested on still waste liquors with added amounts of arabinose and xylose. The arabinose media were prepared by diluting 50 ml. of still waste liquor with 50 ml. of an approximately 1% solution of *d*-arabinose (levorotatory). Similarly, the xylose media were prepared with 50 ml. of still waste liquor and 50 ml. of an approximately 1.0% solution of *l*-xylose (dextrorotatory). Nutrients added were 0.1% of urea and 0.05% of KH_2PO_4. The initial pH of the media was 5.6. Transfer of the yeast was made from a stock slant culture to a sterile glucose–malt sprouts medium. After 48 hours the yeast was centrifuged from this medium and added to sterile shake flasks containing the prepared sugar solutions. Sufficient yeast was added to give a 1% suspension of yeast by volume (1 ml. yeast precipitate to 100 ml. of solution). The flasks, containing the yeast-inoculated and uninoculated arabinose and xylose solutions, were placed in a shaker in a room maintained at 30° C. The experimental data in Table II demonstrated that *Torula utilis* No. 3 is able to consume both arabinose and xylose.

ANALYTICAL METHODS

YEAST. The foreign matter deposited with the yeast made the standard centrifuge and turbidity procedures not applicable. For routine qualitative tests, cell counts were made under a microscope with a Bausch & Lomb hemacytometer cell. A determination of the relation between cell counts and dry weight of yeast showed that there may be a 33% variation from the average value of the tests. The procedure adopted for separating the foreign matter from the yeast to give a quantitative estimate of the dry weight of yeast present follows:

Pipet 10 ml. of the yeast suspension into a 15-ml. tared centrifuge tube. Centrifuge out the yeast and wash the precipitate in the tube with 10 ml. of 0.35% hydrochloric acid (1 ml. concentrated hydrochloric acid in 100 ml. of water). Disperse the yeast uniformly in the acid solution with a heavy platinum wire. Centrifuge out the yeast and repeat the washing immediately with a 1% solution of sodium carbonate. Dry the tube with the washed yeast in a vacuum oven at 65° C. for 3 hours. Cool in a desiccator, and weigh the tube and dried yeast on the analytical balance.

The washings produced no apparent harmful effects. Torula yeast washed with 0.35% hydrochloric acid and 1 to 2% sodium carbonate solutions (pH 10.7) showed no loss in the number of yeast cells through autolysis and, when added to aerated sugar solutions, resumed normal growth. The weight per hundred million Torula cells from glucose solutions averaged 1.67 mg.; from neutral still waste liquor clarified with lead acetate, 1.62 mg.; and from still waste liquor (acid- and alkali-washed yeast), 1.54 mg.

TABLE II. UTILIZATION OF ARABINOSE AND XYLOSE BY *Torula utilis* NO. 3

Medium	No. of Tests	Hours of Incubation	Reducing Sugar, %
Arabinose solution			
Yeast-inoculated	6	0	0.96
		24	0.63
		48	0.16
Uninoculated	1	48	0.96
Xylose solution			
Yeast-inoculated	3	0	0.97
		24	0.40
		48	0.18
Uninoculated	1	48	0.97
Still waste liquor diluted with equal vol. of water			
Yeast-inoculated	1	0	0.49
		24	0.25
		48	0.16
Uninoculated	1	48	0.49

REDUCING SUGAR. The micro sugar method of Schaffer and Somogyi (*9*) was found excellent for this purpose. The procedure was standardized against C.P. xylose, and all reducing sugar values are calculated for this sugar.

VOLATILE ACID. The volatile acid content was determined by distilling a 100-ml. sample of the liquor acidified with 2 ml. of concentrated sulfuric acid. Distillation was made until the volume in the distilling flask was reduced to 20 ml. when carbon-dioxide-free water was added from a separatory funnel. When 100 ml. of distillate were obtained, the distillation was stopped. Aliquots of the volatile acid distillate were titrated with standard 0.1 *N* sodium hydroxide to phenolphthalein.

NONVOLATILE ACID. The nonvolatile acid content was determined by extracting with ether, in a liquid-liquid continuous extractor for 24 hours, a 100-ml. sample acidified with 2 ml. of

Table III. Effect of Aeration

Aerator	Time, Hours	Final Reducing Sugar, %
C-porosity fritted-glass tubes	16	0.30
	19	0.20
Cloth or EC-porosity fritted-glass disks	24	0.20–0.22
4-mm. glass tubing	24	0.40–0.49
Shaker flasks	72	0.30

Table IV. Effect of Size of Inoculum

Temp., ° C.	Initial Concn., Million Cells/Cc.	Time, Hours	Yeast Increase, Million Cells/Cc.	Reducing Sugar Content, %	pH
28	26	24	76	0.65	7.1
		39	130	0.47	7.7
	51	24	139	0.61	7.4
		39	198	0.38	7.5
	106	24	184	0.39	7.0
		39	299	0.21	7.6
	124	24	205	0.40	7.8
		39	212	0.20	7.6
28	174	24	207	0.49	7.4
	217	24	291	0.49	7.5
	364	24	160	0.47	7.6
28	242	24	230	0.47	7.9
	331	24	200	0.49	7.9
32	100	22	219	0.20	7.9
	186	22	179	0.24	7.5
	211	22	191	0.32	7.2

concentrated sulfuric acid. The increase in extracted acid beyond the 24-hour period was negligible. The ether was evaporated, and aliquots of the acid solution were titrated with standard 0.1 *N* sodium hydroxide to phenolphthalein.

Total Solids. Samples (25 ml.) in glass beakers were evaporated to dryness in a vacuum oven at 65° C.

Ash. Samples (25 ml.) evaporated to dryness in a platinum dish were ashed over a Meeker burner. Weighings were made of the residue as such and when further ignited with sulfuric acid. Increase in ash weight, when converted to sulfates, was over 50%.

Total Carbon. The total carbon content was determined by wet combustion with iodic acid in concentrated sulfuric acid, using the micro procedure of Christensen, Wong, and Facer (*2*).

In the early part of the investigation several small and large scale runs with *Torula utilis* No. 3 were made on still waste liquors using continuous feed and batch processes. Minimum reducing sugar content of the spent Torula liquors was invariably about 0.2%. No increase in yeast growth was observed with reducing sugar content below 0.2%, and rapid autolysis of the yeast occurred when the runs were continued beyond this point. The consumption of the reducing sugar in the still waste liquors ranged from 75 to 90%, depending upon the initial sugar concentration; a liquor with a high initial sugar content, indicating unfermented hexoses present, showed a high percentage of sugar consumed, whereas a liquor with a low initial reducing sugar content showed lower percentages of sugar utilized. These trial tests left unanswered the effect of aeration, temperature, nutrients, hydrogen ion concentration, and size of yeast inoculum on the yield and rate of yeast growth. The effect of these factors was studied on the liquor prepared in the pilot-plant distillation unit of The Vulcan Copper & Supply Company under proposed alcohol plant distillation conditions.

Table I gives analytical data obtained on this liquor before and after yeast growth. This liquor had 3.2% dissolved solids, of which 25.3% is total reducing sugar, 24.5% total acids calculated as acetic, 7.5% volatile acid calculated as acetic, and 20.3% ash residue upon combustion. When the nonvolatile acid is calculated as levulinic (32.6%) the sum of the above constituents accounts for 85.7% of the solid matter. Acid hydrolysis of the liquor increased the reducing sugar content 20%, which indicates that 6.2% unhydrolyzed carbohydrate was present. The liquor could be decolorized with neutral lead acetate to a light yellow color with no loss in reducing sugar.

The growth of Torula yeast on the liquor removed roughly one fourth of the dissolved solid matter, three fourths of the reducing sugar, 60% of the volatile acid, 36 to 60% of the volatile and nonvolatile acids, 26 to 34% of the total carbon, and roughly 40% of the biochemical oxygen demand. The yield of oven-dry yeast grown under laboratory conditions was 0.30 to 0.33%. With a daily production of 500,000 gallons of still wastes, this would indicate about 12,500 pounds of dry yeast per day.

EFFECT OF VARIABLES

The effect of various factors on the time and yield of yeast growth were studied in a series of runs made, as far as practical, under the same conditions except for the factor under consideration. These runs were repeated until the results were consistent. The runs were generally made with 200 ml. of medium in 400-ml. glass bottles in a constant temperature chamber. The recorded temperature was that of the medium. The inoculum was obtained by centrifugation of an aliquot of the immediately preceding run. Aseptic technique was not followed after the first propagation on still waste liquor. No interfering contamination developed during several weeks of successive transfers for 103 runs. No growth of organisms or decrease in sugar content occurred in the liquor, stored in its wooden shipping barrel, during the course of the investigation.

Nutrients. Ammonium sulfate and urea were tried as sources of nitrogen. Monobasic potassium phosphate and diammonium hydrogen phosphate in concentrations of 0.05% were used as sources of phosphorus. No variation in yeast yield or rate of growth was observed between the two or with concentrations exceeding 0.05%. The final pH of the Torula liquor is independent of the nitrogen nutrient. Concentrations of urea in excess of 0.05% showed no beneficial results in respect to yeast yield or rate of sugar consumption, whereas concentrations of urea in excess of 0.2% retarded cell multiplication and rate of sugar consumption.

Aeration. This was found to be the most important factor affecting the rate of yeast growth and sugar consumption. The fineness of the air diffusion appears more important than the volume of air (Table III). In shake flasks, the consumption of sugar may be incomplete after 72 hours. Aeration through 4-mm. glass tubing may require 36 to 48 hours. With temperatures of 30° to 34° C. and air diffusion by means of cloth bags or gas dispersion disks made of extracoarse-porosity fritted glass, the sugar was reduced to the minimum 0.2% under 24 hours; whereas with gas dispersion tubes of coarse-porosity fritted glass (Corning No. 39533, C porosity) the time was reduced to approximately 18 hours. Aeration studies on small amounts of liquor in glass bottles tell little concerning the optimum conditions or the quantity of air required in yeast manufacture.

Aeration of the still waste liquor is accompanied by profuse foaming. Peterson, Snell, and Frazier found it was necessary to use liberal quantities of Vegifat as a foam breaker on whole wood sugar solutions (*7*). Among those tried in the present work were oleic acid, corn oil, cottonseed oil, soybean oil, castor oil, and sulfonated castor oil (Turkey-red oil). The latter appeared most satisfactory; no foam difficulties occurred with yeast concentrations up to 400,000,000 cells per cc. With higher yeast concentrations foaming was more noticeable.

Initial pH. Sansur (*8*) mentioned that for the optimum growth of *Torula utilis* the pH must be 7.0 to 8.0, whereas Peterson, Snell, and Frazier (*7*) found that the production of yeast from whole wood hydrolyzate occurred efficiently when the initial pH was adjusted between 4.5 and 5.5. Inasmuch as the still waste liquor had a pH of 5.0, runs were made with the pH adjusted between 5.0 and 6.5 with ammonia. The addition of ammonia to the liquor invariably formed an amorphous precipitate. No beneficial results were obtained by raising the initial pH of the liquor with ammonia. Good yeasts growth occurred at an initial pH of 4.5.

Table V. Effect of Temperature

Temp., ° C.	No. of Runs	Time, Hours	Yeast Yield, %	Final Reducing Sugar Content, %	Final pH
Cloth Aerators					
25	3	24	....	0.30–0.47	7.4
28	6	23	0.30–0.33	0.23–0.32	7.5
32	4	22	0.33	0.20	7.4
34	11	22	0.30–0.31	0.18–0.20	7.4–7.9
C-Porosity Fritted-Glass Tubes					
30	3	18	0.31	0.20–0.21	7.8

Size of Inoculum. Studies made of the optimum yeast inoculum (Table IV) indicated that initial yeast concentrations of approximately 100,000,000 yeast cells per cc. were desirable. The experimental data further indicate that yeast concentrations considerably in excess of 100,000,000 cells per cc. did not increase the rate of sugar consumption.

Dilution with Water. The dilution of the still waste liquor with water speeded the removal of the sugar but had no apparent effect on the yield of yeast. The unconsumed residual reducing sugar content of 0.2 per cent was decreased proportionately with the amount of dilution.

Temperature. Studies were made between 25° and 34° C. The rate of sugar consumption increased with increase in temperature (Table V).

ACKNOWLEDGMENT

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Benzyl Benzoate from Benzyl Chloride and Sodium Benzoate

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As a RESULT of wartime restrictions on the availability of toluene and, hence, benzaldehyde, production processes for the manufacture of the miticide benzyl benzoate other than by the Claisen condensation of benzaldehyde (*4*, *5*) had to be investigated. Simultaneously, improved processes for production of benzyl chloride by chloromethylation of benzene and of benzoic acid through the aluminum-chloride-catalyzed reaction between benzene and phosgene were also studied in this laboratory (*6*).

These developments led to two methods for carrying out the double decomposition between benzyl chloride and sodium benzoate to form benzyl benzoate. One of them depends upon the presence of water as reaction solvent for sodium benzoate, as first described by Gomberg and Buchler (*3*); the other relies on the catalytic activity of a small amount of tertiary amine in the absence of any reaction solvent other than that supplied by the reacting materials (*1*).

Although the results in Table I and Figures 1 and 2 on the aqueous double decomposition between benzyl chloride and sodium benzoate generally agree with those of Gomberg and Buchler (*3*), it should be noted that reaction times in excess of 6 hours tend to lower the yield of the ester. Also, Table I shows that 42% aqueous solutions of sodium benzoate may be employed in place of 22–27% solutions as used by Gomberg and Buchler without noticeably affecting the ester yield. Thus, much valuable reactor space is not surrendered to an inert solvent.

The amine-catalyzed reaction on a slurry of dry sodium benzoate in benzyl chloride is interesting. Despite the fact that practically quantitative yields of aromatic acid esters may be obtained easily, this method has strangely remained out of the chemical literature since its first appearance as a German patent in 1912 (*1*). Scelba (*7*) reports that dry sodium benzoate, heated with a slight excess of benzyl chloride at 170–175° C. for 24 hours, produces a 70–75% yield of benzyl benzoate. According to the German patent (*1*), a small quantity of triethylamine lowers the reaction temperature required for this same reaction to about 130–140° C., the reaction time to about one hour, and raises the ester yield to 95% or higher.

Volwiler and Vliet (*10*) found that diethylamine possesses definite catalytic activity in the synthesis of benzyl salicylate and benzyl *p*-nitrobenzoate. Their data, as well as that presented

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Table I. Formation of Benzyl Benzoate from Benzyl Chloride and Aqueous Sodium Benzoate

Expt. No.	Benzyl Chloride, Moles	Sodium Benzoate[a], Moles	Reflux Period at 100–110° C., Hours	Benzoic Acid Recovered, Grams	Distillation, Grams: Benzyl chloride	Distillation, Grams: Benzyl alcohol	Distillation, Grams: Benzyl benzoate residue	Analysis of Stripped Benzyl Benzoate: Cl, %	Analysis of Stripped Benzyl Benzoate: Free[b] acid, %	Analysis of Stripped Benzyl Benzoate: Ester, %	Analysis of Stripped Benzyl Benzoate: n_D^{20}	Analysis of Stripped Benzyl Benzoate: Color of product	Analysis of Stripped Benzyl Benzoate: M. P., ° C.	Yield[c], %
1	1.5	1.0	8	52.0	54.6	18.8	118.0	0.18	<0.1	94.9	1.569	Light amber	16.5	52.8
2	1.5	1.0	6	Not detd.	67.0	12.8	121.4	0.09	<0.01	97.1	1.569	Amber	17.9	55.5
3	1.5	1.0	4	55.8	73.7	11.7	119.7	0.33	<0.01	94.7	1.569	Light amber	15.5	53.4
4	1.5	1.0	2	65.6	89.0	About 8	103.3	0.28	<0.01	96.8	1.569	Dark amber	15.9	47.1
5	1.0	1.5	8	90.2	3.5	1.1	159.0	0.34	<0.01	94.0	1.5675	Light amber	15.3	70.4
6	1.0	1.5	6	104.5	5.0	5.6	157.0	0.11	0.01	96.9	1.569	Light amber	17.0	71.7
7	1.0	1.5	4	93.1	5.8	0.6	148.6	0.11	<0.01	99.1	1.569	Light amber	18.2	69.4
8	1.0	1.5	3.25	93.9	5.8	0.9	159.2	0.15	<0.01	95.1	1.5675	Light amber	15.4	71.3
9	1.0	1.5	2	96.0	5.4	3.6	147.0	0.28	<0.01	96.8	1.5685	Light amber	16.8	67.0
10	0.5	1.0	6	75.4	About 0.5	0	80.9	0.06	<0.01	97.7	1.569	Light amber	17.2	74.4
11	0.5	1.0	4	85.1	1.6	0.5	77.7	0.16	<0.01	98.6	1.569	Light amber	17.4	72.2
12	0.5	1.0	2	76.1	1.9	0	76.1	0.15	<0.01	97.7	1.569	Light amber	17.2	70.0
13	0.25	1.0	4	96.8	0	0	41.8	0.28	<0.01	96.9	1.568	Pale yellow	16.5	76.4
14	0.25	1.0	2	103.0	0	0	40.9	0.07	<0.01	97.3	1.568	Pale yellow	16.9	75.0
Gomberg & Buchler (*3*)	0.25	0.38[d]	4–5	20–22	.....	.....	37	..[e]	....	..	....	.....	..	70
Gomberg & Buchler (*3*)	0.51	1.53[d]	4–5	143	.....	.....	84	..[e]	....	..	....	.....	..	79

[a] Employed as a 42% solution by weight in water.
[b] Calculated as benzoic acid.
[c] Based on benzyl chloride.
[d] Employed as a 22–27% solution by weight in water.
[e] Stated for comparison; dots indicate lack of information.

A study was made to determine the optimum reaction conditions for two methods given in the literature for preparing benzyl benzoate from benzyl chloride and sodium benzoate. One of these methods consists in refluxing an aqueous solution of sodium benzoate with benzyl chloride, the other in the catalytic action of an amine on a slurry of dry sodium benzoate and excess benzyl chloride. The data indicate that in the aqueous method the yield of benzyl benzoate depends on the ratio of benzyl chloride to sodium benzoate and on the time of reflux. An excess of sodium benzoate, preferably 2 to 4 moles per mole of benzyl chloride, produces benzyl benzoate in yields above 70% in about 4–6 hours at about 110° C.; shorter or longer reaction times produce lower yields of ester. In the amine-catalyzed reaction between 1 mole of dry sodium benzoate and 1.4 moles of benzyl chloride, the results indicate that tertiary amines, such as triethylamine, will produce benzyl benzoate in yields of over 90% for a reaction period of about 1 hour at 110–140° C. The quantity of amine necessary ranges from 0.45 to 0.65% by weight based on the weight of the benzyl chloride–sodium benzoate reaction mixture. A probable reaction mechanism for the amine-catalyzed reaction is proposed.

in Table II, indicate that diethylamine does not exhibit the superior catalytic activity characteristic of some tertiary amines. The results of the present investigation (Table II) indicate that unsubstituted saturated *tert*-alkyl amines are the best catalysts in this type of double decomposition.

PROCEDURE

All materials were used as indicated without further purification.

Benzoic Acid. Mallinckrodt's reagent grade.

Benzyl Chloride. In the aqueous process a commercial grade was used throughout (chlorine: calculated for C_7H_7Cl, 28.01; found, 28.50; n_D^{20}, 1.5388). The amine-catalyzed nonaqueous procedures utilized a pure grade of benzyl chloride which had been prepared at Edgewood Arsenal by chloromethylation of benzene (*6*) (chlorine: calculated for C_7H_7Cl, 28.01; found, 27.98, 28.01; n_D^{20}, 1.5388).

Hexamethylene Tetramine. E. I. du Pont de Nemours and Company, Inc.

N-Methylmorpholine, Morpholine, and Triethanolamine. Carbide and Carbon Chemicals Corporation.

Pyridine. City Chemical Corporation, c.p. grade.

Sodium Benzoate. The Coleman and Bell Company, U.S.P. grade.

Triethyl- and Diethylamines. Eastman Kodak Company, White label grade.

Aqueous Double Decomposition. One mole of sodium hydroxide in the form of a 16.7% aqueous solution by weight (40 grams of NaOH pellets in 200 ml. H_2O) and one mole of benzoic acid are placed in a 1-liter, three-neck, round-bottom flask equipped with a mercury-seal stirrer, a thermometer, and a water-cooled reflux condenser. The reaction flask, immersed in an oil bath, is brought to reflux temperature (100–110° C.), and the desired amount of benzyl chloride (ranging from 0.25 to 1.5 mole of benzyl chloride per mole of sodium benzoate) is added through the condenser. The reaction mixture is stirred vigorously at reflux temperature for 2 to 8 hours.

At the end of the reaction period the product is transferred to a separatory funnel and the lower aqueous layer removed. The upper layer, containing the ester, is washed successively with several 200-ml. portions of 5% aqueous sodium hydroxide; two or three such washes usually suffice to extract all of the unreacted benzoic acid and are followed by two water washes of about 200 ml. each. The combined aqueous layers are extracted with 50 ml. of carbon tetrachloride or benzene, and this organic layer is added to the total organic product layer.

The combined organic product layers are then stripped of all volatile materials down to 5 mm. of mercury pressure, and the still residue, consisting almost entirely of the desired benzyl benzoate, is analyzed for ester content (by saponification), chlorine content, and amount of residual free benzoic acid. Its refractive index and melting point are also determined. The combined aqueous extracts are acidified by the addition of concentrated hydrochloric acid, whereupon unreacted benzoic acid is precipitated. It is filtered off with suction, dried in air, and weighed.

The reaction data obtained, together with any deviations from the general procedure given above, are found in Table I and Figures 1 and 2.

Amine-Catalyzed Nonaqueous Double Decomposition. One half mole of dry sodium benzoate powder and 0.7 mole of benzyl chloride are placed in a 500-ml., three-neck, round-bottom flask, equipped with a thermometer, a mercury-seal stirrer, and a reflux condenser terminating in a calcium chloride trap. The mixture is stirred for a few minutes to a homogeneous slurry, and about 1 ml. or 1 gram of an amine is added. With constant and rapid stirring, this viscous mixture is brought to 90–130° C. (depending upon the catalytic activity of the amine used) in about 10 minutes by means of a Glas-Col electric heating jacket. Sufficient heat is generated, after the reaction begins, to raise the temperature of the reaction mixture to 140–155° C. This temperature rise continues for about 5 minutes. External heat is applied to the reaction flask so that the temperature is maintained somewhere between 100° and 140° C. The over-all reaction periods vary from 0.5 to 2.0 hours.

When the reaction is complete, the product is poured into 0.5–1.0 liter of water and is thoroughly shaken. The lower organic layer, after separation, is washed with two 250-ml. portions of water.

The combined aqueous washings are extracted with two 50-ml. portions of carbon tetrachloride, and the extract is added to the organic product layer. Without further treatment this product is stripped in vacuo. In some runs the stripped benzyl benzoate residue was distilled for purification. The results are given in Table II.

Assay of Ester by Saponification. Fifty milliliters of 0.25 *N* potassium hydroxide are pipetted into each of three 600-ml. Erlenmeyer flasks. To two of these flasks, 1.500 to 1.750 grams of the ester are added; the third flask remains for the blank determination. The flasks are fitted with air-cooled reflux condensers 90 cm. in length, and the contents are refluxed for 45 minutes on a steam bath. After refluxing, 125 ml. of carbon-dioxide-free distilled water are added to each flask, and the contents are immediately titrated with 0.3 *N* sulfuric acid, using 5 drops of phenolphthalein solution as indicator. The two determinations should check each other with a precision of 2%:

$$\text{percentage of ester} = (21.224 \times A \times B)/C$$

where A = (ml. of acid required for blank) minus (ml. of acid required for sample)
B = normality of acid
C = weight of sample

Melting Point of Benzyl Benzoate. The melting point of each sample is determined by the conventional method of allowing a solidified sample to warm up gradually in an air-jacketed tube. The time-temperature data obtained are plotted, the best straight lines are drawn through the two slopes of the curve, and the point of intersection is taken as the melting point of the product.

Chlorine in Benzyl Benzoate. It was found that benzyl chloride gives lower values for chlorine by determination after refluxing with alcoholic sodium hydroxide than by determination after combustion in the Parr bomb. The values obtained for the total chlorine content of benzyl benzoate samples subjected to hydrolysis with alcoholic sodium hydroxide in pressure bottles are also consistently lower than those obtained by the Parr bomb method. Consequently, since the chlorine contents of the products are believed to arise mainly from traces of benzyl chloride and sodium chloride, the Parr bomb procedure was adopted for the determination of total chlorine in all benzyl benzoate samples.

YIELDS

Figures 1 and 2 show that the yield of benzyl benzoate depends upon two factors other than reaction temperature—namely, the ratio of benzyl chloride to sodium benzoate and the reaction time. An excess of sodium benzoate greatly reduces the formation of benzyl alcohol from the hydrolysis of benzyl chloride. This fact, together with the mass action effect imparted by an excess of sodium benzoates, favors higher yields of the ester. The optimum reaction period was found to be about 6 hours. As Figure 2 shows, refluxing of the reaction mixture for 8 hours results in lower yields of benzyl benzoate. This is probably caused by saponification of the ester after maximum yield has been reached. Benzyl alcohol produced through the hydrolysis of the chloride was identified, after isolation by fractionation, by its refractive index, (n_D^{20} 1.5392), and its urethan (melting point 76° C.) was prepared in the usual manner from phenyl isocyanate (*8*).

Tables I and II indicate that most of the benzyl benzoate samples prepared were not distilled but merely stripped in vacuo of all unreacted materials and by-products. This was done because the development was considered as preliminary to

Table II. Reaction Data on Amine-Catalyzed Nonaqueous Preparation of Benzyl Benzoate from Benzyl Chloride and Sodium Benzoate

Expt. No.	Sodium Benzoate, Mole	Benzyl Chloride, Mole	Amine Added	Max. Temp. Reached, ° C.	Av. Reaction Temp. after Max., ° C.	Total Reaction Period, Hours	Benzyl Chloride Recovered, Mole[a]	Benzyl Benzoate Obtained			Analysis of Ester					
								Grams	Mole	Yield, %	Ester content by saponification, %	Refractive index, n_D^{20}	M. P., ° C.	Chlorine content as Cl, %	Nitrogen content as N, %	Color of product
1	0.5	0.7	1 ml. triethylamine	125	110–115	1	Not measured	96.8[b]	0.46	91.2	100.6	1.5685	18.6	0.24	..	Water white
2	0.5	0.7	Same	127	110–115	1	0.14	104.2[c]	0.49	98.2	100.4	1.568	18.3	0.38	..	Light amber
3	0.5	0.7	Same	145	130–140	0.5	0.18	103.2[c]	0.49	97.3	100.5	1.5685	18.1	0.25	0.03	Light amber
4	0.5	0.7	1 g. hexamethylene tetramine	155	100–130	1	0.18	92.3[c]	0.43	87.0	103.4	1.5675	16.4	0.20	0.14	Light amber
5	0.39	0.54	0.77 g. hexamethylene tetramine	143	130–140	1	0.15	76.9[c]	0.36	94.1	101.8	1.567	13.6	0.32	..	Light amber
6	0.5	0.7	0.5 g. hexamethylene tetramine	144	120–130	2	0.18	97.5[c]	0.46	91.9	101.6	1.568	16.5	0.14	0.06	Light amber
7	0.5	0.7	1 ml. *N*-methylmorpholine	130	120–130	1	0.20	98.1[c]	0.46	92.5	100.5	1.5685	18.6	0.13	..	Very light amber
8	0.5	0.7	1 ml. pyridine	134	120–130	1	0.20	92.6[b]	0.44	87.3	101.4	1.5685	18.5	0.35	..	Slightly yellow
9	0.5	0.7	Same	140	130–140	1	0.16	90.4[b]	0.43	85.0	100.6	1.5685	18.4	0.57	..	Slightly yellow
10, 11	0.5	0.7	1 ml. triethanolamine	140	130–140	1					No appreciable visible reaction					
12	0.5	0.7	1 ml. diethylamine	143	135–145	1	0.25	73.5[d]	0.35	69.3	100.2	1.5683	18.0	0.14	0.04	Amber
13	0.5	0.7	1 ml. morpholine	135	125–135	1	0.51	22.3[d]	0.11	21.0	Not analyzed					Dark amber

[a] This fraction contains a small percentage of benzyl alcohol.
[b] Of distilled product. [c] Of stripped residue. [d] Of stripped product.

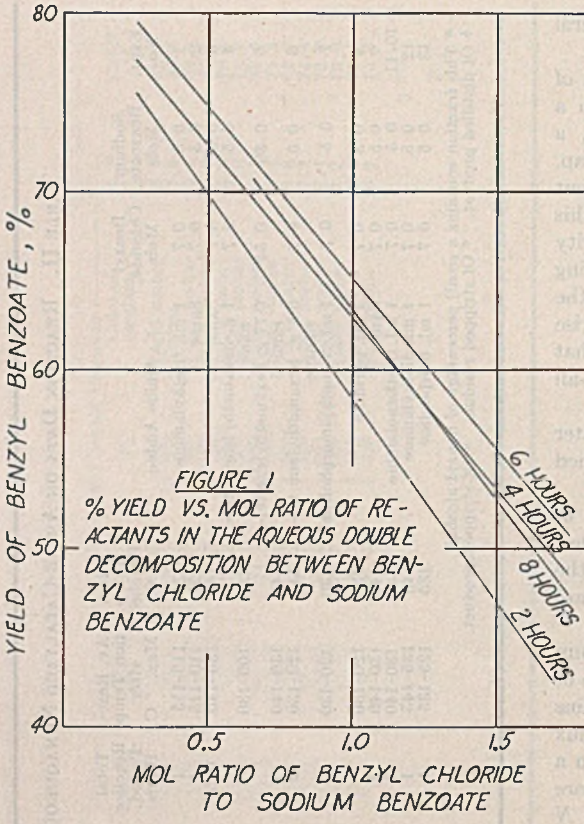
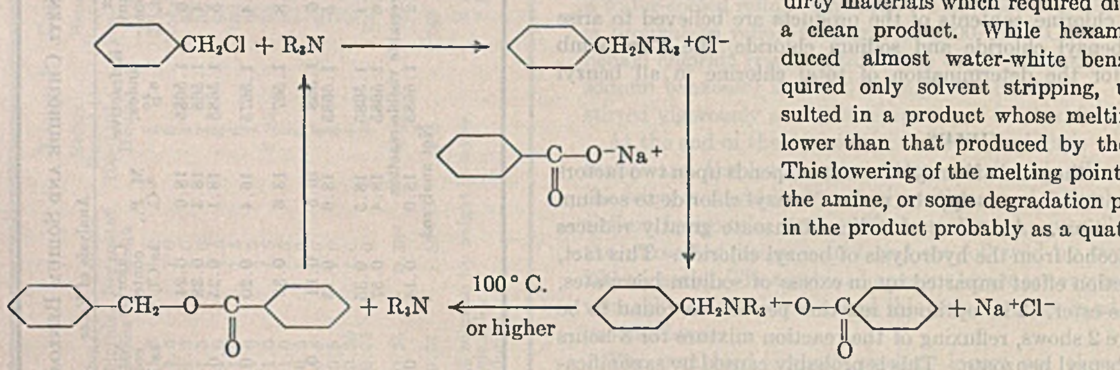


FIGURE 1
% YIELD VS. MOL RATIO OF REACTANTS IN THE AQUEOUS DOUBLE DECOMPOSITION BETWEEN BENZYL CHLORIDE AND SODIUM BENZOATE

larger-scale operation in which distillation of the final product would be undesirable because of the high boiling point of the product and unnecessary for the purposes of manufacture. One distillation of the combined stripped products (Table I) through a 6-inch unpacked column of 1-inch diameter produced a water-white grade of benzyl benzoate having the properties given in column 1 of Table III. When samples of the same stripped benzyl benzoate samples were washed twice before distillation with an equal volume of 5% aqueous sodium hydroxide, followed by two water washes of twice the ester volume, the resulting water-white benzyl benzoate was found to have somewhat superior properties (column 2).

It may be postulated that the amine-catalyzed formation of benzyl benzoate proceeds by formation of quaternary ammonium intermediates. Schematically, the course of the reaction may be written as follows:



This theory is based upon the fact that trialkyl benzyl ammonium salts thermally decompose contrary to Hofmann's rule (*9*) to produce a trialkyl amine and a benzyl derivative depending upon the negative ion in the parent salt.

Tertiary amines such as triethylamine, *N*-methylmorpholine, hexamethylenetetramine, and pyridine are all effective catalysts.

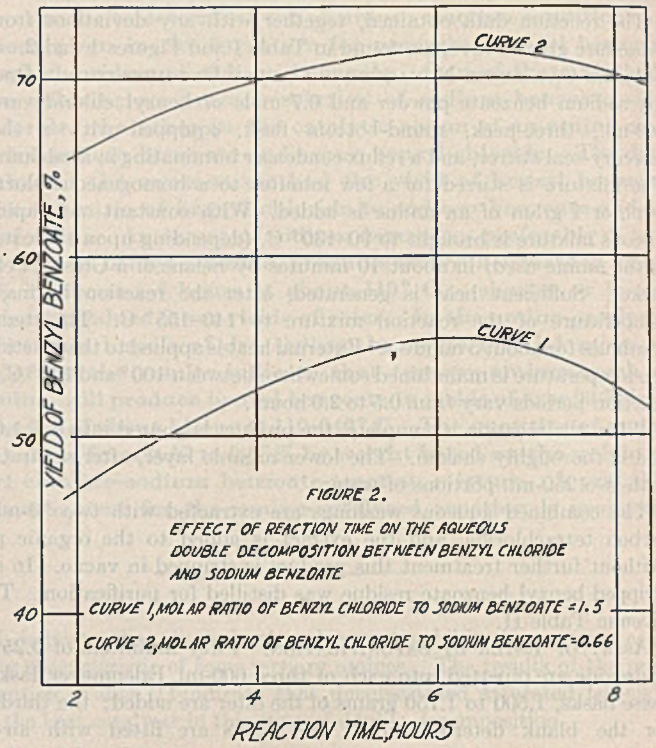


FIGURE 2.
EFFECT OF REACTION TIME ON THE AQUEOUS DOUBLE DECOMPOSITION BETWEEN BENZYL CHLORIDE AND SODIUM BENZOATE

Table III. Properties of Distilled Benzyl Benzoate

	Without Caustic Wash	After Caustic Wash
Melting point, ° C.	18.5	18.7
Boiling range at 2.5 mm. Hg, ° C.	131–133	132
Refractive index, n_D^{20}	1.5687	1.5687
Specific gravity, d_4^{25}	1.113	1.114
Ester content, %	99.0	99.7
Chlorine content, %	0.28	0.00
Free benzoic acid, %	<0.01	<0.01
Odor	None	None

On the other hand, triethanolamine and secondary amines such as morpholine were found to be virtually inert, whereas diethylamine exhibited only moderate activity. While most of the tertiary amines tried gave good results, hexamethylenetetramine and pyridine were found to be less desirable than triethylamine or *N*-methylmorpholine. Pyridine consistently produced blackish, dirty materials which required distillation for isolation of a clean product. While hexamethylenetetramine produced almost water-white benzyl benzoate which required only solvent stripping, use of this catalyst resulted in a product whose melting point was decidedly lower than that produced by the other tertiary amines. This lowering of the melting point was undoubtedly due to the amine, or some degradation product thereof, included in the product probably as a quaternary ammonium salt.

Cooperative research has been carried out at the Pennsylvania State College with emphasis on reaction conditions using triethylamine as catalyst. If the sodium benzoate contained even small amounts of free benzoic acid, the catalyst was correspondingly neutralized and the reaction would not take place at steam bath temperature. More catalyst or a higher temperature (about 165° C.) was then needed. For the same reason the reagents had to be dry (*11*).

In the products from the amine-catalyzed reaction, the ester content, as determined by the saponification method described above, consistently exceeded 100%. This discrepancy was probably caused by the presence in the product of another neutralizable compound, which consumed an equivalent amount of sodium hydroxide and thus falsely appeared as ester in the results.

In the preparations presented in this paper, no attempts were made to produce a chlorine-free grade of benzyl benzoate. However, both the aqueous process as well as the amine-catalyzed nonaqueous process can produce a virtually chlorine-free product. It is necessary to use a grade of benzyl chloride free of nuclear chlorine—for example, that obtained from the chloromethylation of benzene (*2*, *6*), and to include washing procedures which will remove all unused chloride as well as sodium chloride or nitrogen compounds present in the reaction product.

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PRODUCTION OF DDT . . .

Condensing Action of Chlorosulfonic Acid on Chloral Hydrate and Chlorobenzene

A new method of producing technical-grade DDT in 77% yield by the reaction of chlorosulfonic acid with chloral hydrate and chlorobenzene is presented. Although a yield of DDT greater than 90% is obtainable when chloral and chlorobenzene are condensed in an excess of sulfuric acid–oleum mixture, the process here described is carried out with the metathetical quantity of chlorosulfonic acid on chloral hydrate and chlorobenzene. Laboratory as well as best pilot plant procedures are outlined with a discussion of purification methods. The effects of reaction time and temperature on yield are shown. Since the process, on account of its low acid requirement, is apt to produce rather viscous products of DDT, a modification of the method using inert, recoverable solvents is described. Material costs for the chlorosulfonic acid and the conventional sulfuric acid–oleum processes, based on available published data, are compared.

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AT PRESENT 1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, the insecticide commonly called DDT, is being produced in large quantities, both in this country and abroad, by condensing chlorobenzene with chloral in the presence of a large excess of concentrated sulfuric acid (*2*, *5*, *7*, *8*). Inasmuch as some of the present commercial producers of DDT also possess facilities for the chlorination of ethanol, it has in some instances been found more economical to use chloral alcoholate, the end product of the ethanol chlorination, in place of chloral or its hydrate. This method of condensation and its many variations are based upon the work of Zeidler (*10*), who was the first to synthesize DDT.

For the manufacturer using chloral hydrate as a raw material, an alternate condensing agent was sought, in order to avoid the many troublesome operations connected with the handling of large volumes of sulfuric acid. It was found that halosulfonic acids of the type XSO_3H (where X = halogen) and, more specifically, chlorosulfonic acid, $ClSO_3H$, are excellent agents when used in metathetical quantities (2 moles) for the condensation of chloral hydrate (1 mole) with chlorobenzene (2 moles). Extensive laboratory and pilot plant investigations have proved the feasibility of the method.

Since halosulfonic acids, and specifically chlorosulfonic acid, are known to react with aliphatic alcohols (*9*) to form alkyl sulfates, the following over-all reaction mechanism for the condensation between chloral hydrate and chlorosulfonic acid is deemed likely:

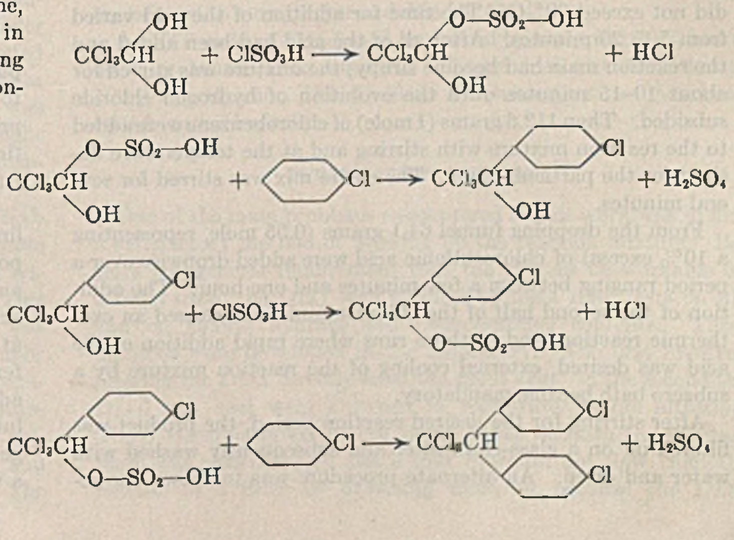

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TABLE I. RESULTS OBTAINED WITH CHLOROSULFONIC ACID (10% EXCESS) AS CONDENSING AGENT BETWEEN CHLORAL HYDRATE (0.5 MOLE) AND CHLOROBENZENE (1.0 MOLE)

Time for Adding 2nd Half of $ClSO_3H$, Min.	Reaction Time after Adding Acid, Hours	Reaction Temp., ° C.	Yield of Crude Product, %	Setting Point, ° C.	Sulfur Content, %
60	3	0	47.1	94.0	0.04
60	7	0	51.0	96.8	0.04
10	2	10	40.2	95–98[a]	...
About 10	6	10	57.2	94–98[a]	...
20	2	20	52.9	93–95[a]	...
60	3	20	62.6	90.0	0.23
23	6	20	69.1	92.4	0.16
60	7	20	74.5	82.8	0.32
60	1	30	58.7	90.0	0.16
60	3	30	74.0	80.5	0.75
60	5	30	72.0	84.6	0.29
60	6.5	30	74.0	85.1	0.27
60	5	40	72.3	80.0	0.28
60	4	50	63.8	72.0	0.55
60	5	60	72.3	75.6	1.04

[a] Melting point.

TABLE II. RESULTS OBTAINED WITH CHLOROSULFONIC ACID (10% EXCESS) AS CONDENSING AGENT BETWEEN CHLORAL HYDRATE (0.5 MOLE) AND 100% EXCESS CHLOROBENZENE (2.0 MOLES)[a]

Time for Adding 2nd Half of $ClSO_3H$, Min.	Reaction Time after Adding Acid, Hr.	Reaction Temp., ° C.	Yield of Crude Product, %	Setting Point, ° C.	Melting Point, ° C.	Sulfur Content, %
10–15	4	0	49.1	88.0	87–92	0.36
10–15	6	0	54.5	88.3	89–92	0.41
5–10	6	0	52.2	...	87–95	...
5–10	6	10	56.7	...	86–95	...
10–15	6	10	63.5	85.8	85–90	0.46
10	6	20	71.8	...	...	...
5–10	4	20	68.5	...	80–93	...
5–10	6	25	76.1	82.8	80–95	0.49
5–10	4	30	72.1	83.8	80–90	0.52
5	6	30	74.4	84.6	87–89	0.47

[a] 2.0 moles chlorobenzene added at one time before second $ClSO_2H$ addition.

The intermediates indicated in this scheme have been shown to exist, experimentally (*1*, *3*, *6*, *8*). The fact that secondary and tertiary alcohols will condense with benzene and its analogs in the presence of chlorosulfonic acid (*8*) is believed to lend considerable support to this scheme.

APPARATUS AND PROCEDURE

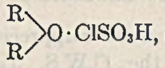
The apparatus consisted of a 500-ml. or a 1000-ml. three-neck flask, equipped with thermometer, mercury-seal stirrer, dropping funnel, and gas exit tube terminating in a calcium chloride trap.

Chloral hydrate, 82.7 grams (0.5 mole), was placed in the reaction vessel of the apparatus described above. From the dropping funnel 58.3 grams (0.5 mole) of chlorosulfonic acid were added dropwise at a rate such that the temperature of the medium did not exceed 20° C. The time for addition of the acid varied from 5 to 20 minutes. After all of the acid had been added and the reaction mass had become sirupy, the mixture was stirred for about 10–15 minutes until the evolution of hydrogen chloride subsided. Then 112.6 grams (1 mole) of chlorobenzene were added to the reaction mixture with stirring and at the temperature desired for the particular run. The entire mix was stirred for several minutes.

From the dropping funnel 64.1 grams (0.55 mole, representing a 10% excess) of chlorosulfonic acid were added dropwise over a period ranging between a few minutes and one hour. The addition of the second half of the chlorosulfonic acid caused an exothermic reaction, and in those runs where rapid addition of the acid was desired, external cooling of the reaction mixture by a subzero bath became mandatory.

After stirring for the desired reaction period, the product was filtered off on a glass-cloth filter and subsequently washed with water and dried. An alternate procedure was to drown the reaction mixture with excess ice water (about 300 ml.) in the reactor itself with external cooling, or by pouring the mixture into ice water.

Inasmuch as the described procedure resulted in rather heavy and viscous products, it was found convenient to conduct the reaction in the presence of an inert solvent. Excess chlorobenzene or carbon tetrachloride was found to be a satisfactory reaction medium. The excess solvent could be added initially—that is, along with the required chlorobenzene as described above, or it could be added in the later stages of the reaction when thickening of the reaction mass became apparent. In all runs where an excess of solvent was employed, the products were subjected to steam distillation after washing. Unreacted materials were thus recovered from the steam distillate.

The results obtained from a number of runs are given in Tables I, II, and III. In three runs diethyl ether, employed as the $ClSO_3H$ complex, was tried as a reaction medium without success. This complex,  $\begin{matrix}R\\R\end{matrix}\!\!>O\cdot ClSO_3H$, is stable at low temperatures and has been found to be an excellent sulfation agent for alcohols.

The crude products produced in the laboratory ranged in color from pure white to slightly grayish white. One recrystallization of the crudes from *n*-hexane or ethanol resulted in the recovery of about 65–70% (from *n*-hexane) of a snow-white crystalline product, melting at about 106° C. (uncorrected). A second recrystallization afforded a product with a melting point of about 108° C.

ANALYSIS. For $C_{14}H_9Cl_5$: % C found 47.51, calculated 47.45; % H found 2.68, calculated 2.56%; % Cl found 49.53, calculated 49.99.

The method of condensation described here has been successfully applied to a large variety of other aryl hydrocarbons (substituted as well as unsubstituted), other aldehydes, and to secondary and tertiary aliphatic alcohols (*8*). Fluosulfonic acid, FSO_3H, when used in place of chlorosulfonic acid, was found to give correspondingly good results (*8*).

TABLE III. RESULTS OBTAINED WITH $ClSO_3H$ (10% EXCESS) AS CONDENSING AGENT BETWEEN CHLORAL HYDRATE (0.5 MOLE) AND CHLOROBENZENE (1.0 MOLE) IN PRESENCE OF 200-ML. CARBON TETRACHLORIDE AT 15–20° C.

Time for Adding 2nd Half of $ClSO_3H$, Min.	Reaction Time, Hr.		Yield of Crude Product, %	Setting Point, ° C.	Sulfur Content, %
	Before adding CCl_4	After adding CCl_4			
90	0.5	30	57.9	87.2	0.60
60	5.5	85	71.3	87.1	...

PILOT PLANT PROCEDURE

Because of the inherent differences between laboratory and plant operations, and because the pilot plant product was required to meet army specifications, several changes in the laboratory procedure outlined above were found to be necessary. A description of the equipment and procedure for a typical pilot plant batch follows.

The reactions were carried out in a 50-gallon Pfaudler glass-lined reactor with a 45 r.p.m. anchor-type agitator. Forty pounds of chloral hydrate crystals were poured into the reactor and the agitator was started. Twenty-eight pounds of chlorosulfonic acid were then run into the reactor from a steel feed tank at a steady rate of 2 to 3 pounds per minute. With no cooling, a temperature rise of about 5° C. occurred. After the acid was added, the liquid was agitated for about 5 minutes until the evolution of hydrogen chloride had substantially ceased. The hydrogen chloride was sucked to a sodium carbonate scrubber through a vent line.

Sixty and one half pounds of chlorobenzene were next added. An immediate drop in temperature of about 5° C. occurred. The solution was milky in appearance immediately after the addition of chlorobenzene, but after 5-minute stirring it became clear. Experiments carried out on a small scale showed that two layers were present at this stage.

Thirty-three pounds of chlorosulfonic acid were added. Brine at −5° to −10° C. in the reactor jacket was required to remove the heat of reaction. Approximately one fourth of the acid was added during the first 5 minutes. No great change in temperature occurred, and little hydrogen chloride was evolved. However, the remaining three fourths of the acid was added over a 40–50 minute period. This rate of addition was the fastest possible without exceeding the 20° C. operating temperature desired. Within 5 minutes after all of the acid had been added, a decided increase in viscosity occurred, and DDT was suddenly precipitated as a crystal slurry. This occurrence was accompanied by a sharp increase in temperature caused by the latent heat of crystallization and by the decreased rate of heat transfer from the reactor charge to the brine. If the charge temperature was held below 20° C., a smooth, even, crystal slurry was formed which stiffened to the consistency of cold cream after 13 hours of stirring to complete the reaction. However, if the temperature was appreciably above 20° C., the DDT lumped up into balls as large as 1.5 inches in diameter. Little cooling was required after all of the acid had been added.

PURIFICATION

At the end of the reaction period, 200 pounds of carbon tetrachloride were added to the reactor. An immediate drop in temperature occurred as the DDT dissolved. To offset this drop and to increase the solvent power of the carbon tetrachloride, the temperature of the batch was brought up to 30–35° C. with warm water in the reactor jacket. After stirring for the 15–20 minute period required to dissolve the DDT completely, the agitator was stopped to permit the spent acid to settle. This required 15 minutes. The spent acid was then drawn off from beneath the DDT solution.

Neutralization of the DDT solution was accomplished by adding 15 to 20 gallons of warm water and sufficient 10% sodium hydroxide solution so that the pH of the aqueous layer was 11 or higher after 5-minute stirring; 1 to 1.5 gallons of caustic solution were usually required.

Washing was necessary to remove ferric hydroxide (from the chlorosulfonic acid lines) precipitated during the neutralization. This was done by introducing a continuous stream of water approximately at the level of the carbon tetrachloride–water interface. The water completely filled the reactor and overflowed through a sight glass to the sewer. Sufficient steam was admitted to the reactor jacket to maintain a temperature of 35° C. The agitator was operated during washing. The water rate was adjusted to the highest rate at which no drops of the solvent layer appeared in the overflow sight glass. The washing period lasted 15–20 minutes, the duration being determined by the appearance of the exit wash water. After washing, the DDT solution was again withdrawn from the reactor for weighing. A loss in weight of 8 to 10 pounds usually occurred during washing and neutralization. The washed solution weighed about 267 pounds.

The DDT solution was now ready for steam distillation, which was carried out by admitting steam through the bottom nozzle of the reactor. Some water was initially added and its pH adjusted to 11 or higher with 10% sodium hydroxide solution. This pH had to be checked every half hour, and more caustic was added if required. The steam and carbon tetrachloride vapor were condensed, and the condensate flowed by gravity to a separating tank. The first distillate came over at a pot temperature of 70° to 72° C. and was 90 to 95% carbon tetrachloride by volume. After one hour the pot temperature reached 100° C., and about 90% of the carbon tetrachloride had been distilled. The carbon tetrachloride contained less than 1% chlorobenzene and could be re-used without further treatment. About 2 hours more were required to remove the rest of the carbon tetrachloride and the traces of chlorobenzene which were dissolved in the molten DDT.

When the distillation was nearly complete, the granulating tank, a 150-gallon wooden vessel with two Lightnin' agitators, was prepared to receive the DDT. About 40 gallons of cold water were heated to 95° C. in the tank with live steam. The pH of this hot water was adjusted to 11 or higher with 10% sodium hydroxide, and 30 cc. of Tergitol 7 were added. When the distillation was complete, the reactor agitator was stopped to permit the molten DDT to settle. After settling, the DDT was dropped directly into the violently agitated hot water in the granulating tank. The water from the steam distillation was retained in the reactor since it contained some dirt. The temperature of the granulating tank was reduced to 65° C. in 5 minutes by the addition of cold water. When the temperature reached 75° C. (about 15° C. below the setting point of DDT), the DDT solidified at small granules ranging in size from 1/32 to 1/4 inch in diameter. In general, larger particles were obtained when the setting point of the DDT was high. The agitators were shut off as soon as the 65° C. temperature was reached and the DDT was washed to a filter. After a short cold-water wash on the filter, the DDT was transferred to a tray dryer and dried at 55° C.

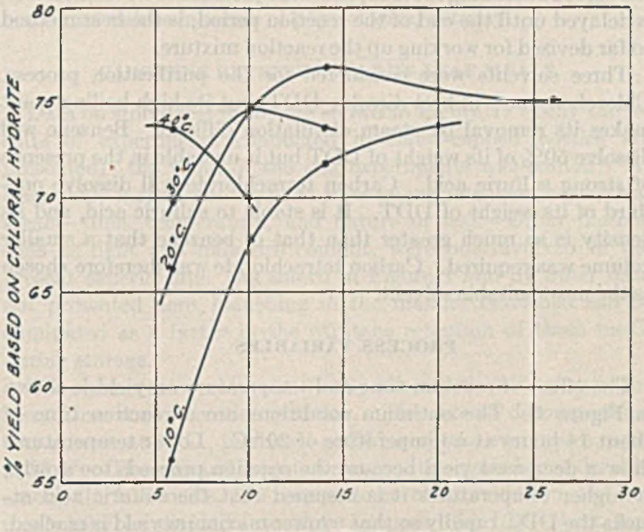


Figure 1. Effect of Reaction Time and Temperature on Yield of DDT

A DDT yield of 77% based on chloral hydrate and 70% based on chlorobenzene was obtained. The product met Joint Army-Navy Specification JAN-D-56 in all particulars and has been tested entomologically.

PURIFICATION METHODS

One of the main problems encountered in this work was to find a satisfactory method of working up the reaction mixture. Besides the general requirement that the process be workable on a large scale, the DDT was required to meet rigid tests on pH and on chloral hydrate and chlorobenzene contents. Three methods were developed in the laboratory. The first involved filtering the DDT directly from the spent acid; in the second the DDT and acid were drowned in cold water before filtration. These methods failed in the plant either because the reaction mass was such a heavy paste that it would not flow from the reactor to a filter or drowning tank, or because the DDT was in such large balls that they plugged the reactor outlet. Furthermore, no simple method was found of washing filtered or drowned DDT with caustic which gave a product meeting the pH specifications. Filtered or drowned material of specification grade can be made by melting the DDT under water with a pH of 11 or higher, but this required almost as much equipment as the steam distillation method and much more caustic.

In the third laboratory method the reaction was carried out in a solvent, but lower yields were obtained in both the plant and the laboratory. The low yield was avoided by delaying the addition of the solvent until the end of the reaction period. The mechanical difficulties encountered with the drowning and filtration methods were avoided by the use of a solvent, and the separation of spent acid from the DDT was much more complete so that less caustic was required for neutralization. Chloral and chlorobenzene can be easily removed from the DDT to any desired degree in the washing and steam distillation steps. Thus the solvent handling method, in which the addition of the solvent is delayed until the end of the reaction period, is the best method so far devised for working up the reaction mixture.

Three solvents were considered for the purification process. Chlorobenzene will best dissolve DDT, but its high boiling point makes its removal by steam distillation difficult. Benzene will dissolve 50% of its weight of DDT but is unstable in the presence of strong sulfuric acid. Carbon tetrachloride will dissolve one-third of its weight of DDT. It is stable to sulfuric acid, and its density is so much greater than that of benzene that a smaller volume was required. Carbon tetrachloride was therefore chosen as the most suitable solvent.

PROCESS VARIABLES

The effect of reaction time and temperature on yield is shown in Figure 1. The optimum conditions are a reaction time of about 14 hours at a temperature of 20° C. Lower temperatures show a decreased yield because the reaction proceeds too slowly; at higher temperatures it is assumed that the sulfuric acid attacks the DDT rapidly so that a lower maximum yield is reached.

In Figure 2 the same data are plotted for the yield of the desired *p,p′*-isomer of DDT as determined by the method of Cristol, Hayes, and Haller (*4*). Technical DDT as produced by the sulfuric acid–oleum process usually contains about 70 to 75% of the *p,p′*-isomer. The graph shows that the conditions producing the maximum yield of technical DDT are very close to those giving the maximum yield of the *p,p′*-isomer.

There is no marked effect of reaction time on setting point, but the effect of reaction temperature is important. The average setting points for several runs at each of the reaction temperatures studied follow:

Reaction Temp., ° C.	Setting Point, ° C.
10	88.9
20	88.5
30	87.4
40	84.0

The materials (pounds) required to produce a ton of specification grade DDT are listed below; there are no unusual steam, water, or refrigeration requirements for the chlorosulfonic acid process.

Chloral hydrate	1215
Chlorobenzene	1835
Chlorosulfonic acid	1850
Carbon tetrachloride	6075
Less recovered CCl_4	5840
Net CCl_4 used	235
Caustic, 100%	25
Anhydrous HCl produced[a]	315
Sulfuric acid produced[b]	2100

[a] Could be reconverted to chlorosulfonic acid.

[b] Has a total acidity equivalent to 58% sulfuric acid.

Based on the individual cost of each of the above items as of February, 1945, it is calculated that the material cost per ton of DDT amounts to $886.

COMPARISON OF PROCESSES

The data just listed indicate that the material cost in the chlorosulfonic acid process amounts to approximately $0.44 per pound of DDT. Neither the utilization of anhydrous hydrogen chloride produced nor the re-use of spent sulfuric acid, both of which if used would tend to lower the ultimate cost of DDT, has been considered in the computations.

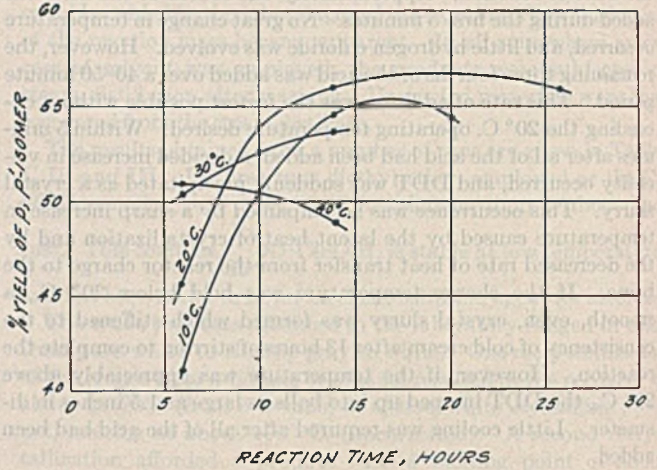


Figure 2. Effect of Reaction Time and Temperature on Yield of *p,p′*-Isomer of DDT

From the data obtained in this laboratory, it appears that, based on a 90% yield of DDT from chloral hydrate and chlorobenzene, the material cost in the sulfuric acid–oleum process amounts to approximately $0.39 per pound of product. This figure again does not take into consideration the possible re-use of spent sulfuric acid. Callaham (*2*) estimated that the Brothman continuous process will be capable of producing DDT in a sulfuric acid–oleum medium at an over-all production cost of about $0.30 per pound.

In retrospect it appears that the chlorosulfonic acid process, although not entirely competitive with the sulfuric acid–oleum process, does hold several advantages for the smaller manufacturer. Despite the fact that yields of technical-grade DDT are some 12–15% lower than those encountered in the conventional sulfuric acid process, the subject method is capable of producing an almost equivalent amount of DDT per unit reactor space even when inert solvents are employed. One particular advantage is that condensation is carried out in the presence of a minimum of acid. The chlorosulfonic acid process also affords a source of gaseous hydrogen chloride which is utilizable for other purposes.

ACKNOWLEDGMENT

The authors wish to acknowledge the technical assistance and cooperation rendered by the many members of the C.W.S. Technical Command who were associated with this project.

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Carotene Loss in Stored Leaf Meals and Extracts

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Carotene retention in vegetable leaf meals depends primarily on the storage temperature. Of the three temperatures used in these tests (5°, 24°, and 37.5° C.), the greatest carotene stability was at 5° and the least at 37.5°. Retention varied with the species of leaf, and a high oxalic acid content of the leaf seemed to be favorable. Carotene concentrates from leaf meals dissolved in oils are more stable than crystalline carotene in the same oils, possibly owing to the tocopherol in the concentrate. Levels of carotene up to 1000 micrograms per gram are more stable than the 5000- and 15,000-microgram levels. Oil solutions of carotene, of whatever source and at any concentration, are in most cases more stable at 5° C. than at higher temperatures. Addition of *d*-isoascorbyl palmitate and soybean lecithin to the carotene solution is ineffective in reducing loss of carotene.

CERTAIN dry vegetable leaf meals can be prepared which contain large amounts of carotene (*6*). These meals can be used as poultry feed supplements (*15*) or as starting material for carotene concentrates (*18*). Since both the leaf meals and oil solutions of the carotene concentrate may often be held in storage for considerable periods, the carotene losses of these products under various storage conditions were investigated.

Leaves of beet, carrot, broccoli, lima bean, rhubarb, spinach, and sweet corn were dried to a residual moisture content of 5% and ground 30 to 40 mesh in a Wiley mill. Prior to drying, portions of each material were blanched with steam at 100° C. or hot water at 90° to 100° for 5 minutes. The ground leaf meals were stored in 4-ounce screw-capped bottles; some were also stored in cloth bags. The meals were kept in the dark at 5°, 24°, and 37.5° C.

A carotene concentrate was prepared from a mixture of a number of leaf meals. The mixture was extracted with Skellysolve B; the extract was saponified to remove chlorophyll, and finally purified with hydrated lime according to the procedure of Wall, Kelley, and Willaman (*18*). Removal of the solvent gave the carotene concentrate used for all the "concentrate" experiments.

Aliquots of the concentrate, dissolved in Skellysolve B, were mixed with crude soybean and peanut oils; refined cottonseed, corn, soybean and peanut oils; lard, Crisco (a commercial shortening made from hydrogenated vegetable oil), and mineral oil. Aliquots were taken to give 100, 1000, 5000, and in some cases 15,000 micrograms of carotene per gram of oil. The solvent was removed on a warm water bath under nitrogen and vacuum. The oil solutions were stored in screw-capped vials in the dark at 5°, 24°, and 37.5° C. In the concentration range 100 to 5000 micrograms, 5 grams of oil solution were stored in 60 × 17 mm. vials. At the 15,000-microgram range concentration, 2 grams of oil solution were stored in 45 × 15 mm. vials. Samples were analyzed for carotene over a period of 6 months, using single determinations. Similar studies were made with oil solutions of crystalline carotene prepared in the same manner as the carotene concentrate solutions.

The source of crystalline carotene was S.M.A. Corporation's 90% beta, 10% alpha carotene. The crystalline carotene solutions were prepared from carotene stored in vacuum-sealed vials and were used at once. In all cases carotene was determined by the method of Wall and Kelley (*17*). Since some isomerization of carotene conceivably occurred during storage, and since some of these products may not be separated from beta carotene by the method used, the points in the curves probably represent maximum values in terms of physiological activity.

CAROTENE RETENTION IN DRY LEAF MEALS

Data on stored leaf meals are shown in Figure 1. Only the results of experiments conducted in screw-capped bottles are presented; the trend of the bag experiments was similar. At least three factors are involved in carotene retention in dry leaf meals—time, temperature, and nature of leaf. Other factors, such as light and moisture content, were not involved in the present experiments. As shown in Figure 1 and by other data not presented here, blanching in the manner described can be eliminated as a factor in the carotene retention of these meals during storage.

The storage temperature markedly affected the rate of carotene loss; time was a secondary factor. The rate of decomposition was slowest at 5° C., increased at 24°, and was even more rapid at 37.5°. The rate and extent of carotene loss varied considerably among the leaf meals. In respect to carotene retention, the leaf meals may be divided into three groups: (*a*) high—beet top, spinach, and rhubarb; (*b*) medium—broccoli and sweet corn; (*c*) low—carrot and lima bean. After 6-month storage, group *a* retained 70% carotene at 5° C. and 40% at 24°; group *b*, 60 and 25%, respectively; and group *c*, 30 and 15%, respectively. There may be some significance in the fact that all three leaf meals showing maximum carotene retention were very high in oxalic acid, whereas the leaf meals in groups *b* and *c* contained little oxalic acid.

CAROTENE RETENTION IN OIL SOLUTION

The effects of time, temperature, concentration and source of carotene, and kind of oil were studied in determining carotene retention in oil solution. In addition, some studies were made of the effect of adding to the oil solutions an antioxidant consisting of a mixture of 0.06% *d*-isoascorbyl palmitate and 0.03% soybean lecithin. These factors will be discussed individually, but the stability of carotene depends on a combination of all of them.

The effect of length of storage on carotene stability is shown in Figures 2, 3, and 4. Under most conditions the rate of carotene loss increased as the storage period became longer. However, as will be shown later, under certain circumstances, such as low temperature and low carotene concentration, the time factor became negligible.

Figure 2 shows the effect of temperature on the stability of carotene concentrate in oils. As the temperature was increased from 5° through 37.5° C., the destruction of carotene in most cases became more rapid. Data for crystalline carotene in oil, not presented in Figure 2, indicate that temperature increments exerted even more effect on the rate and degree of carotene destruction. As shown in Figure 2 and by other data not presented, carotene in the range 100 to 1000 micrograms stored at

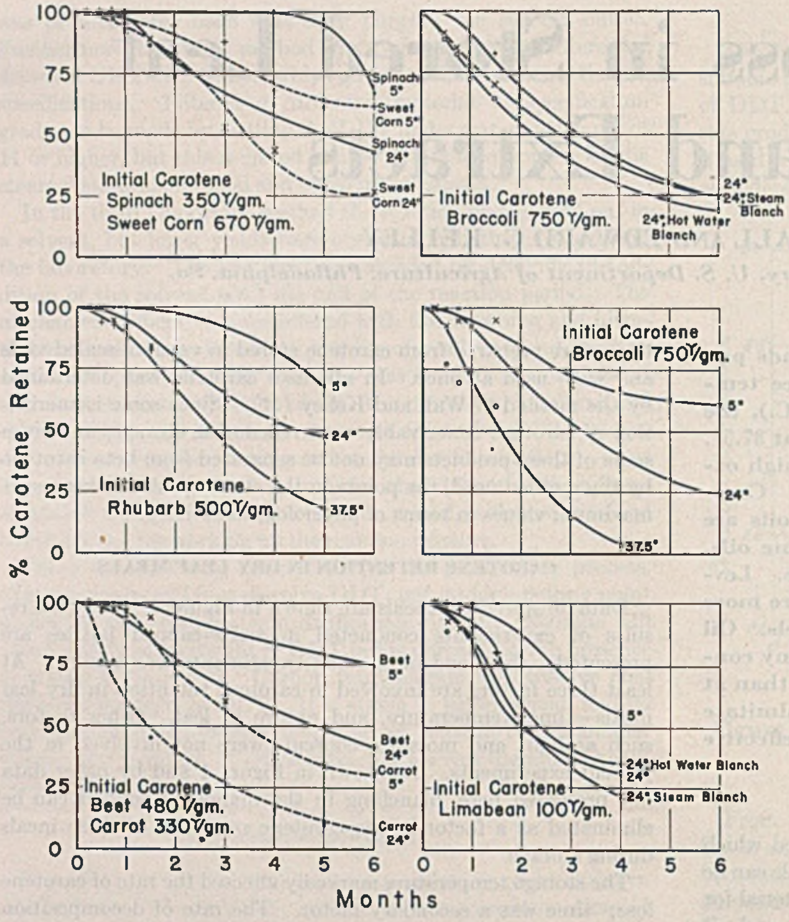

Figure 1. Effect of Storage Temperatures and Blanching on Carotene Retention in Dry Vegetable Leaf Meals

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5° C. was very stable; with few exceptions, 90 to 100% of the original carotene was retained at the end of 6 months.

Figure 3 illustrates the effect of carotene concentration on its stability in oils. Only the data for the carotene concentrate in oil at 24° C. are presented; results at other temperatures and with crystalline carotene showed similar trends. The low carotene samples, 100 to 1000 micrograms, were almost invariably more stable than the 5000–15,000 microgram series. The rate of carotene loss was slower at 5° C. and faster at 37.5°, but the general effect of concentration was the same at these temperatures. However, there was no regular concentration effect within the groups themselves. These irregularities may have been due to the nature of the various oils used, for the order of stability within the groups varied from oil to oil.

The data in Figure 4 show the effect of source of carotene on its stability in oils. The carotene concentrate was much more stable than the corresponding crystalline preparation. This was especially true with high carotene concentrations, such as 5000 micrograms per gram of oil. With lower concentrations this trend was not so regular, possibly because many of the oils may have contained sufficient natural antioxidants to give the crystalline carotene some protection. The superiority of the vegetable carotene concentrate is shown markedly in Figure 4, especially with mineral oil. The mineral oil used in this experiment contained no natural antioxidants. Crystalline carotene was completely decomposed at all temperatures and concentrations in one month, whereas the carotene concentrate was quite stable. These results indicate that the vegetable carotene concentrate contained natural antioxidants, the nature of which will be discussed later.

Figure 5 shows the percentage of carotene retained by the oil solutions of carotene concentrate and of crystalline carotene after 4-month storage at various temperatures. In most cases the nature of the oil was not significant. The carotene concentrate was stable in oils other than lard and even in mineral oil. Crystalline carotene, however, was very unstable in lard and mineral oil, and less stable than the concentrate in other oils.

In one series 0.06% *d*-isoascorbyl palmitate and 0.03% soybean lecithin were added to oil solutions of carotene. At 5°, 24° and 87.5° C. these additives had no significant effect on the stability of carotene.

DISCUSSION

The problem of carotene retention in vegetable leaf meals is one of preventing oxidation of a highly unsaturated and therefore relatively unstable compound. A number of workers (*4*, *10*, *13*, *19*),

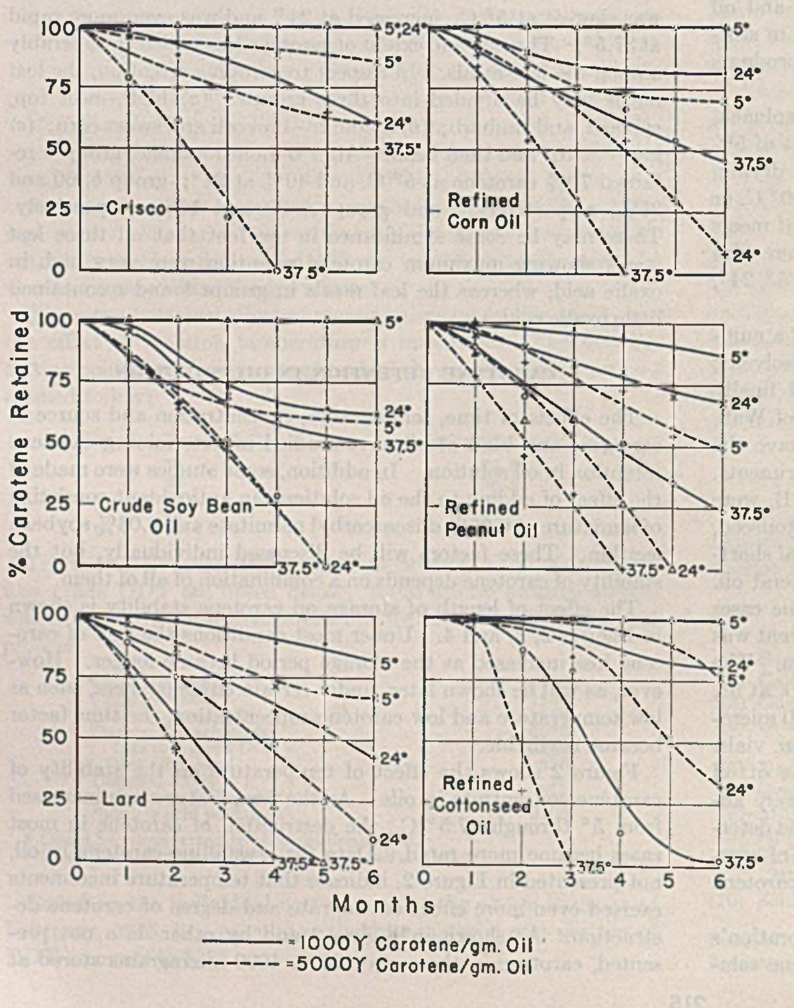

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Figure 2. Effect of Temperature on Stability of Carotene Concentrate in Oils

Figure 3. Effect of Carotene Concentration on Retention in Oils at 21° C.

Carotene concentrations in micrograms per gram of oil

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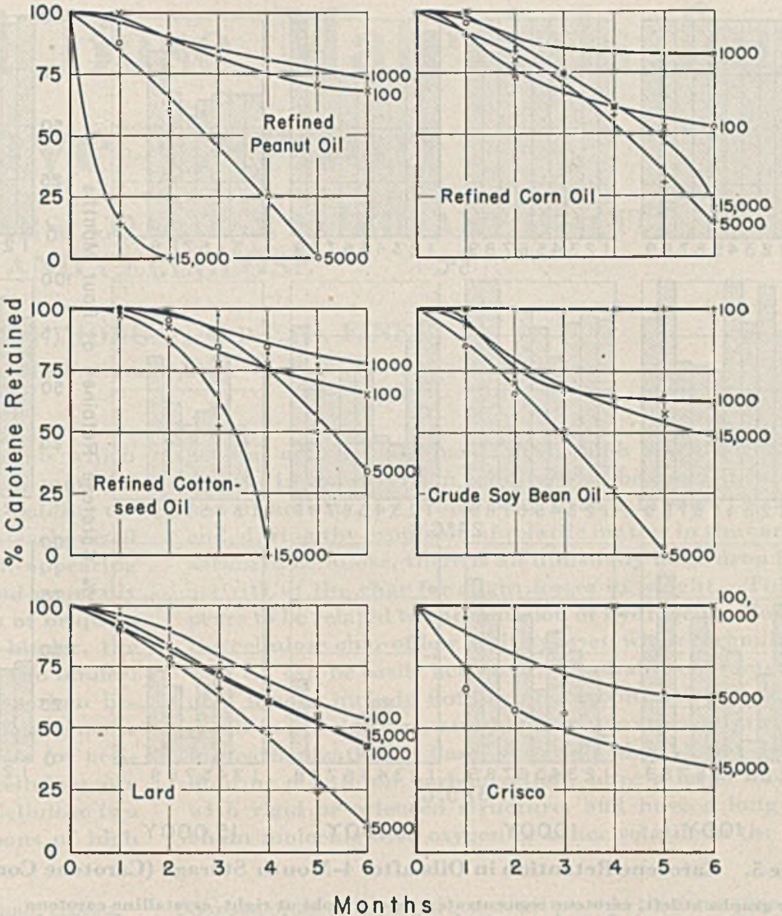

testing the stability of carotene in alfalfa, have found that losses increase with increased storage temperature. Dutton, Bailey, and Kohake (*3*), working with dehydrated spinach, demonstrated that carotene losses could be decreased by storage in an inert atmosphere such as carbon dioxide or nitrogen, and Taylor and Russell (*14*) reported no carotene losses in alfalfa stored in vacuum for 20 months at 0° to 5° C. Our findings that carotene losses in vegetable leaf meals increase with increased storage time and temperature are therefore similar to results obtained with alfalfa.

The fact that the vegetable leaf meals which had maximum carotene stability were very high in oxalic acid is of considerable interest. Mattill (*8*) emphasizes the fact that oxalic acid can act not only synergistically in the presence of phenolic antioxidants but as a stabilizer against rancidity when added alone to vegetable fats. It is conceivable that the increased carotene retention of these leaf meals is due, at least partially, to their high oxalic acid content.

The storage of carotene in oils presents problems similar to those encountered with leaf meals. A number of workers (*1, 7, 16*) have found that carotene losses of such oil solutions increase with lengthened storage periods and increased temperatures. The effect of wide variations in carotene concentration on carotene stability has not been extensively studied. Bickoff and Williams (*2*) showed that in pelleted mixtures of mineral oil and rice bran, carotene losses increased rapidly as the concentration rose from 200 to 1000 micrograms per gram. Morgal, Byers, and Miller (*9*) presented evidence that an alfalfa carotene concentrate is more stable in various media than is crystalline carotene.

Our conclusions therefore agree with those of other workers as to the effects of time and temperature on carotene losses in oil solution. In oils we found no significant differences from the results of Bickoff and Williams in the concentration range reported by them, but our carotene losses increased greatly at a concentration of 5000 micrograms per gram. Our comparison of the relative stability of carotene from a vegetable leaf concentrate and crystalline carotene shows that the concentrate was much more stable. This is similar to the results of Morgal *et al.* with an alfalfa concentrate. Unpublished data from this labora-

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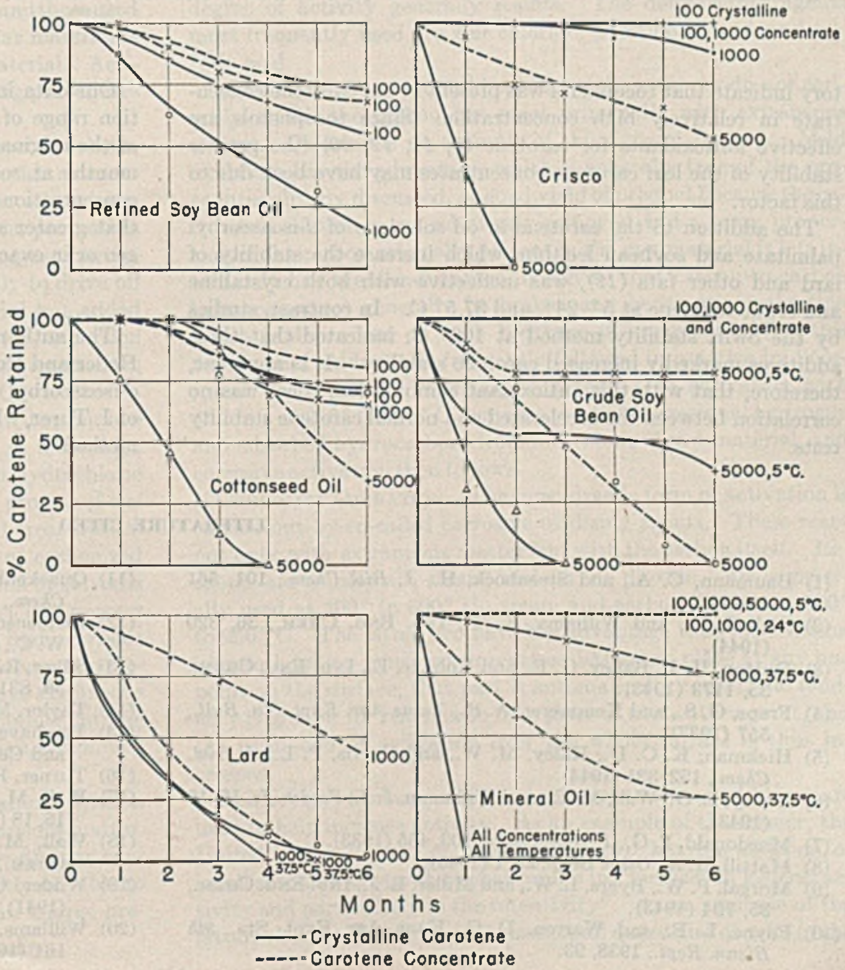

Figure 4. Effect of Source of Carotene on Retention in Oils

Carotene concentrations in micrograms per gram of oil; storage temperature, 24° C. unless stated otherwise

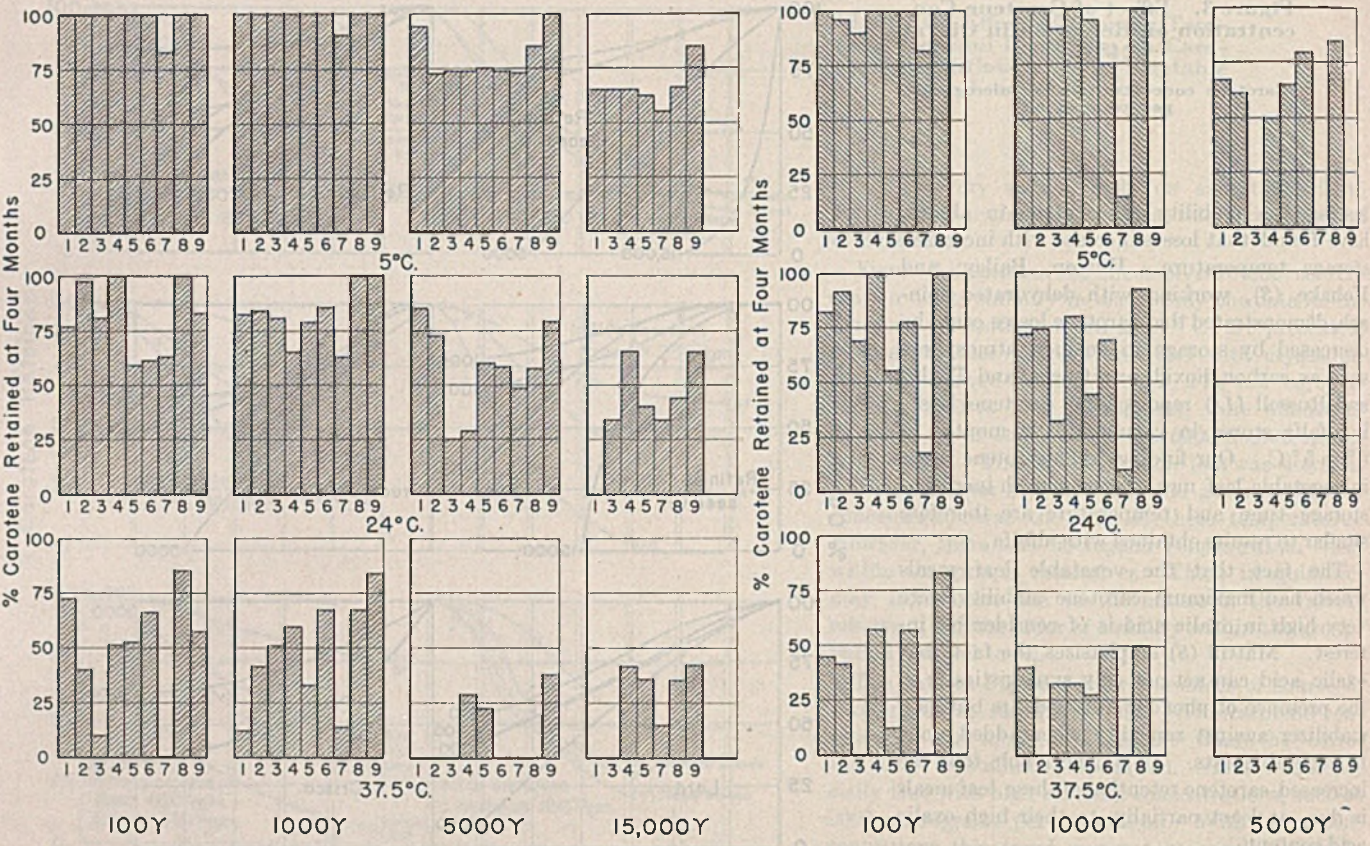

Figure 5. Carotene Retention in Oils after 4-Month Storage (Carotene Concentrations in Micrograms per Gram of Oil)

Four graphs at left, carotene concentrate; three graphs at right, crystalline carotene
1, refined cottonseed; 2, crude peanut; 3, refined peanut; 4, crude soybean; 5, refined soybean; 6, refined corn; 7, lard; 8, Crisco; 9, mineral oil

tory indicate that tocopherol was present in our carotene concentrate in relatively high concentration. Since tocopherols are effective antioxidants for carotene (*5*, *11*, *12*, *20*), the greater stability of the leaf carotene concentrates may have been due to this factor.

The addition to the carotene in oil solutions of *d*-isoascorbyl palmitate and soybean lecithin, which increase the stability of lard and other fats (*12*), was ineffective with both crystalline and crude carotene at 5°, 24°, and 37.5° C. In contrast, studies by the Swift stability method at 100° C. indicated that these additives markedly increased carotene stability. It is apparent, therefore, that with this antioxidant combination, there was no correlation between the accelerated and normal carotene stability tests.

Our data indicate that, in many oils and fats in a concentration range of 100 to 1000 micrograms per gram, at least 50% of the original carotene will be retained for storage periods of 6 months at room temperature (24° C.). With higher carotene concentrations the oils must be refrigerated, and it is possible that greater stability could be obtained by storage under nitrogen or in evacuated containers.

ACKNOWLEDGMENT

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Binders and Base Materials for Active Carbon

FUNCTIONS OF SUGARS, COAL TAR PITCH, ANTHRACITE, AND CELLULOSE

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Activated carbons are made from base materials which generally comprise the larger portion of the raw material and binders which are used to give strength by holding together the particles of base material. When carbonized alone, base materials shrink and give a dull-appearing char; binders swell, become macroporous, and generally yield a lustrous residue. Upon carbonization of briquets made from a mixture of base material and binder, the activity of the char is predominantly that of the binder; after activation the activity of the resulting carbon becomes chiefly that of the base material. Various glucose carbohydrates differ markedly as raw materials for activated carbons; dextrose behaves as a binder, cellulose as a base material, and starch is intermediate. Cellulose is a specially good base material. It yields carbons of high general activity and particularly high retentivity. Low density in carbons from cellulose can be avoided, without loss of activity, by briquetting with a binder. Near the end, during the expulsion of volatile matter in the carbonization of cellulose, there is an unusually large drop in the activity of the char for slight losses in weight. This appears to be related to the emission of hydrogen. However, the cellulose char of low activity, even when carbonized to 900° C., can be easily activated. Desirable characteristics of a binder include fluidity on carbonization, relatively small molecular size, and high temperature requirement for carbonization. Base materials should not become fluid or plastic on carbonization, have a large molecule with rigid or oriented structure, and have a long ring-chain molecule with oxygen or other volatile in the rings.

ACTIVATED carbons can be divided into two main classes—those used for adsorption of gases and vapors and those used in purification of liquids. For the former a granular material is generally employed, for the latter a powdered material. Activated carbons are usually made by one of the following procedures or combinations of several of them.

HEAT TREATMENT. The raw materials (wood, coconut shells, coal, etc.) generally contain hydrogen, oxygen, and other extraneous matter. The major portion is ordinarily driven off by heat. The main purpose of heat treatment is to reduce the proportion of extraneous matter; at the same time a certain degree of activity results. Heat treatment is also used occasionally to drive off extraneous material not present in the raw material but added during the processing; e.g., in the Urbain process (*38*) a portion of the phosphorus remaining from a phosphoric acid treatment is removed during subsequent carbonization at 1000° C.

SOLVENT EXTRACTION. This treatment may be used to remove extraneous matter or to produce activity. Thus in a German process (*23*) ash is extracted from brown coal with hydrochloric acid before carbonization and activation; in the process of the West Virginia Pulp and Paper Company (*36*) acid treatment is used before activation to reduce the ash content of carbonized waste liquor from the sulfite process. The utilization of solvents such as selenium oxychloride is claimed in at least one process (*26*) to induce activity, supposedly by dissolving hydrocarbons off the surface of the carbonized raw material. Solvent extraction, like heat treatment, is sometimes used to remove extraneous matter not present in the raw material; for example, in the Bayer process (*15*) zinc from a zinc chloride treatment is removed by washing with hydrochloric acid and water.

DEHYDRATING AGENTS. Treating the raw material with a dehydrating agent is another way of removing extraneous matter. Especially in those cases in which the raw material contains a considerable proportion of carbohydrates, it is frequently possible to remove hydrogen and oxygen selectively and retain a large portion of the original carbon structure. At the same time a high degree of activity generally results. The dehydrating agents most frequently used are zinc chloride, phosphoric acid, and sulfuric acid.

MILD OXIDATION. In mild oxidation the reagents do not seriously attack the carbon but react principally with extraneous matter. Chlorine is an example of this type of reagent. Mild oxidation has the advantage, which is generally true of the procedures already discussed, of good yield of product because the extraneous materials are selectively removed and a large proportion of the carbon originally present in the raw material is left intact. It has the disadvantage, however, that carbon-to-carbon linkages cannot generally be broken and hence any activation which is dependent on such breakage is impossible. For this reason mild oxidation is frequently followed in practice by "corrosive" activation. Thus in one process (*12*) activation with chlorine at 350° to 600° C. removes most of the residual hydrogen and adsorbed hydrocarbons from a carbonized raw material, and corrosive activation then follows.

CORROSIVE OXIDATION. The most drastic form of activation is carried out by so-called corrosive oxidizing agents. These react not only with extraneous matter but with the carbon itself. Reagents are usually air, steam, and carbon dioxide. Air is generally used at 400° to 600° C., steam and carbon dioxide at 700° to 950° C. The latter two have the advantage that the reaction is endothermic; hence when reaction has taken place at any one point on the surface, that part is automatically cooled, the tendency is greater for reaction to take place at some other point, and the likelihood of activation over the whole surface is thus increased.

ADDITIVES. Carbonaceous and noncarbonaceous additives are used to help increase activity. As an example of the former, the United States Bureau of Mines finds (*16*) that the addition of small amounts of starch to coal results in "increase in general activity and particularly in the retentivity". As an example of the latter, the Norit process (*35*) uses small quantities of salts of the

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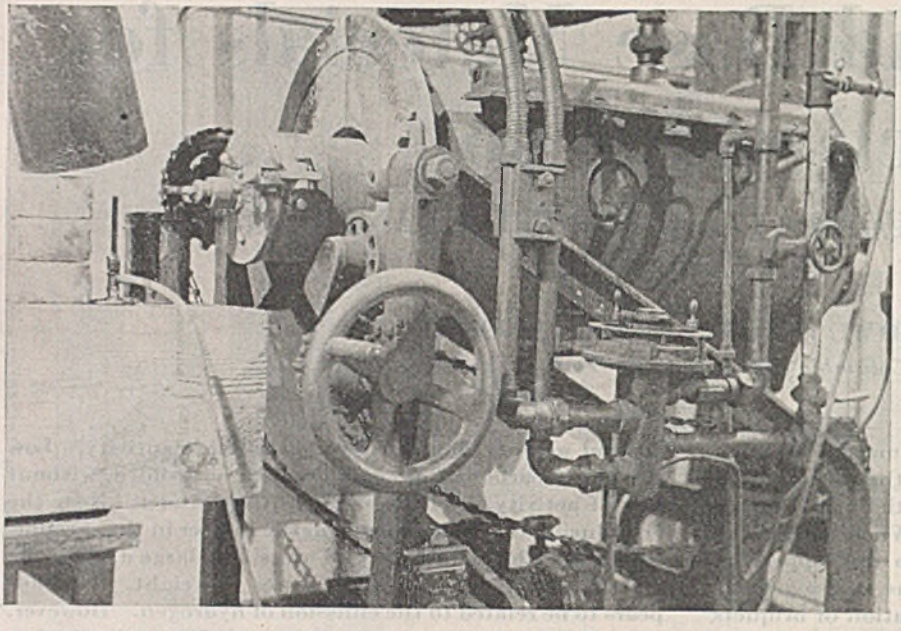


Figure 1. Rotary Furnace Used in Carbonizing

alkali and alkaline-earth metals to help produce activity. Materials added for purposes other than producing activity (usually in such large proportion that they cannot strictly be considered "additives") include binders to give mechanical strength and inert substances such as kieselguhr to provide a surface on which the carbonized raw material may deposit.

One part of the present investigation dealt with a study of pure chemicals as raw materials for activated carbons. Since activated carbon can be made from almost any carbon-containing material, many investigations have been directed toward the utilization of cheap and waste materials, most of which are chemically conglomerate mixtures. A survey of the literature indicated only a few studies on pure chemicals. Hence few data are available to show the fundamental relations between chemical and physical nature of the raw material (molecular structure, molecular size, physical aggolermation, etc.) and character of the resulting carbon. Most of the adsorptivity studies are reviewed by McBain (*27*), Adam (*1*), and Brunauer (*9*). Several papers are of particular interest in connection with the study of pure chemicals as raw materials (*3, 4, 5, 7, 14, 18–22, 29, 34*).

Another part of the investigation dealt with the role of binders in activated carbons, which is important in the preparation of granular carbons. Studies in connection with coke making had indicated that, during carbonization, the binder melts and flows among the particles to be bound and, after cooling, holds them together by a cementing or agglutinating action. Apparently no study had been made of binders in connection with the production of activated carbons in order to learn what happens to the binder during activation, whether the binder tends to contribute to the activity of the product, and what are the desirable characteristics in a binder for making activated carbons.

Stillman (*37*) has discussed binders in general. Binders in relation to activated carbons were reported by the Bureau of Mines (*16*) with the objective of evaluating American coals. A number of coals were briquetted and made into activated carbons, always with the same binder to obtain comparable information on the coals. A part of the present investigation included a similar study except that a single coal and a variety of binders were used.

The two properties generally required in granulated carbons (activity and mechanical strength) tend to work counter to each other. In so far as strength is due to specific adhesion (*28*) and activity to chemical adsorption (*9*), the one requires that primary valence forces be linked with one another to produce strength, and the other requires that there be great numbers of free primary valence bonds to induce activity. The optimum condition appears to be that in which the minimum number of bonds are used to produce the requisite strength and the rest are free, accessible, and so arranged as to give maximum activity.

The name "base material" is here defined as that part of the raw material which is generally present in greater proportion and is expected to contribute in high degree to the activity of the product; the term "binder" means that part which serves to give strength by holding together the particles of base material.

MATERIALS AND APPARATUS

Some of the raw materials are described sufficiently by their common names; for others, additional information is included:

Coal. Pennsylvania anthracite containing, on the dry basis, 8.5% volatile combustible matter, 77.9% fixed carbon, and 13.6% ash.

Coal Tar Pitch. Low melting (205–220° F.) and high melting (285–305° F.) pitches, both by cube-in-air method.

Lignite. A North Dakota lignite containing 7.0% ash on the dry basis, and the same material steam-treated by the Fleissner process (*25*).

Cellulose. Wood pulp cellulose of approximately the following composition: alpha-cellulose 93.0%, beta-cellulose 3.2%, gamma-cellulose 3.8%, and ash 0.08%.

Lignin. Purified fraction of the total lignin removed from hardwoods by the soda pulping process. Ultimate analysis: carbon 64.9%, hydrogen 5.9%, oxygen 29.2%; average molecular weight 870 for the repeating unit of the polymer, each unit of which contains six methoxyl and five hydroxyl groups.

Carbonization was carried out in a gas-fired rotary furnace (Figure 1). During carbonization, the furnace was sealed completely except for a small nozzle at one end, through which volatile products could escape. The heating was conducted so that the temperature rise was about 3° C. per minute. When maximum temperature was attained, the furnace was held at that point for exactly 2 hours. The nozzle was then plugged and the furnace allowed to cool.

Activation was carried out with superheated steam in a 2-inch i.d. silica tube surrounded by an electric furnace (Figure 2). Steam was generated in a boiler at the base of the tube and superheated to 925° C. while passing through approximately 2 feet of quartz packing. Approximately 100 grams of material were placed above the packing. A small quantity of quartz chips was placed over the charge to collect any undesired carbon resulting from gas cracking. The gases evolved passed through the top of the tube to a trap and gas meter.

Briquets were made in a Carver laboratory press. They were $1^1/_8$ inches in diameter and $^1/_4$ inch thick. As an aid to intimate mixing, the raw materials were ground to a fine powder. The coal was ground in a ball mill, and screen analysis indicated that more than 95% was finer than 200 mesh and all was finer than 48 mesh. The binders were usually ground with a mortar and pestle. In a few cases the binder was dissolved in a small amount of solvent, the base material added, and the whole mixed in a Werner and Pfleiderer mixer. Benzene was the solvent when phenol-formaldehyde, polystyrene, and ethylcellulose resins were used as binders; water was the solvent with sugar and dextrin.

All briquets were made at a pressure of 5000 pounds per square inch, either at room temperature or at a temperature approximately equal to the melting point of the binder used.

TESTS ON PRODUCTS

For the mechanical strength test the briquets were tested as such. For bulk density, toluene, and chloropicrin tests the material was ground to 8–14 mesh. For iodine, sugar decolorization, and x-ray tests a finely powdered material was used (over 90% through 200 mesh).

Mechanical Strength. An adaptation of a flexural strength test used in the plastics industry, the briquet was supported by two hardened steel blocks held $^3/_4$ inch apart by a spacer. Compressive force was applied from above by a rounded knife edge (a bar with a $^1/_8$-inch flat edge and sides tapering off at 45°). An Amsler testing machine applied and recorded the force required for breakage. The reproducibility of the test was usually within ±10%; errors of this magnitude were not significant because briquets of the widely varying materials used often differed by several hundred per cent. Strength is desired in granulated carbons so that they may stand handling in shipment and in use. In this test the breaking force is not applied in exactly the same way as the forces which cause breakage in handling, but a material which requires a large force for breaking in the test should also stand up well in handling.

Bulk Density. The Bureau of Mines test (*16*) was used, and results are reproducible within ±2%. Density data are important for granulated carbons because activity is frequently tested and reported on a weight basis, whereas the apparatus in which the carbon is used (gas mask canister or adsorption tower) has a definite volume.

Iodine Test. The Bureau of Mines method was used, but the final result was calculated as per cent of total iodine adsorbed. The reproducibility of the test was within ±0.5%.

Toluene Test. The toluene test (*16*) not only indicates the activity of a carbon toward toluene and similar hydrocarbons but also differentiates between portions of the adsorbate held tightly and loosely. Toluene adsorbed in the first part of the test was designated "total adsorption" and that retained after evacuation, "chemical adsorption". The difference between total and chemical adsorption was called "physical adsorption". Per cent retentivity was obtained by multiplying the ratio of chemical adsorption to total adsorption by 100, and represents the proportion of total adsorbate which is held tenaciously by the adsorbent. The reproducibility of the test was within ±2%.

Chloropicrin Test. The accelerated chloropicrin tube test of Fieldner *et al.* (*17*) is reproducible to about ±2 minutes. The method has been used to determine the suitability of a carbon for gas masks. It differs from other tests used here in that it is not an equilibrium test; that is, the test ends when the first traces of chloropicrin get through the carbon and before it is necessarily saturated. Also, the activity is expressed on a volume basis, and hence those carbons having high density will frequently show higher activity than in the other tests.

Sugar Decolorization. A 1-gram sample was shaken with 100 ml. of standard brown sugar solution at 70° C. The solution was filtered and compared with standards made by diluting portions of the original solution with various proportions of distilled water. Results are expressed as per cent of original color removed and were reproducible to about ±2%. The test is used to predict the utility of a carbon for removing large color-body molecules from liquids. As used here it gives only a rough classification of the carbons because the brown sugar solution was an arbitrary standard, and Freundlich isotherms, by which a complete evaluation can be made, were not determined.

X-Ray Photographs. A molybdenum anticathode and a powdered sample of carbon, enclosed in a small metallic frame, were used. X-ray photography is useful in showing the nature of crystallization because interference and reinforcement effects as the X-rays pass through the sample result in lines on the film; the intensity of these lines increases with the size of the crystals, and the spacing is dependent on the spacing of the units of the crystal. In general, a carbon which is highly crystallized will not be very active; but lack of activity is not necessarily caused by high degree of crystallization.

STRENGTH OF BRIQUETS

After Carbonization. Table I shows that carbonization increased the strength of briquets made with lignin, coal tar pitch, sugar, and sodium silicate. These binders have relatively small molecules and become fairly fluid on heating. Both coal tar pitch and lignin give off the major part of their volatile matter at higher temperatures than does cellulose, the base material with which they formed the strongest carbonized briquets. On the other hand, the strength of the briquets made with polystyrene, Pentalyn G, ethylcellulose, and urea-formaldehyde resins was decreased by carbonization, and the strength of carbonized briquets made with these resins was low. These resins yield large molecules on heating and do not attain much fluidity.

It appears, therefore, that strength generally increases if the molecules of the binder are small, if the binder becomes markedly fluid on heating, and if the binder carbonizes at relatively high temperature. Table II shows that the strength of carbonized briquets depends also upon the activity of the base material. Both sugar and coal tar pitch make stronger briquets with cellulose, which develops high iodine activity, than they do with coal, lignin, or carbonize coal tar pitch, whose iodine activity is lower.

After Activation. Tables I and II show that the strength of the briquets after activation was in all cases less than after carbonization. The loss in strength was almost always greater than would be anticipated from direct relation to weight loss.

During carbonization there can be either increase or decrease in strength because the binder is more or less mobile, and when unsatisfied bonds are produced by loss of volatile, the binder will in some cases attach to these points and hold the material together. At the end of the carbonization a rather rigid structure is left, and any unsatisfied bonds formed during activation will contribute to the activity of the final product; but these bonds usually cannot contact other unsatisfied bonds and add to the strength. Furthermore, some of the carbon chain linkages (residues from the carbonization and the

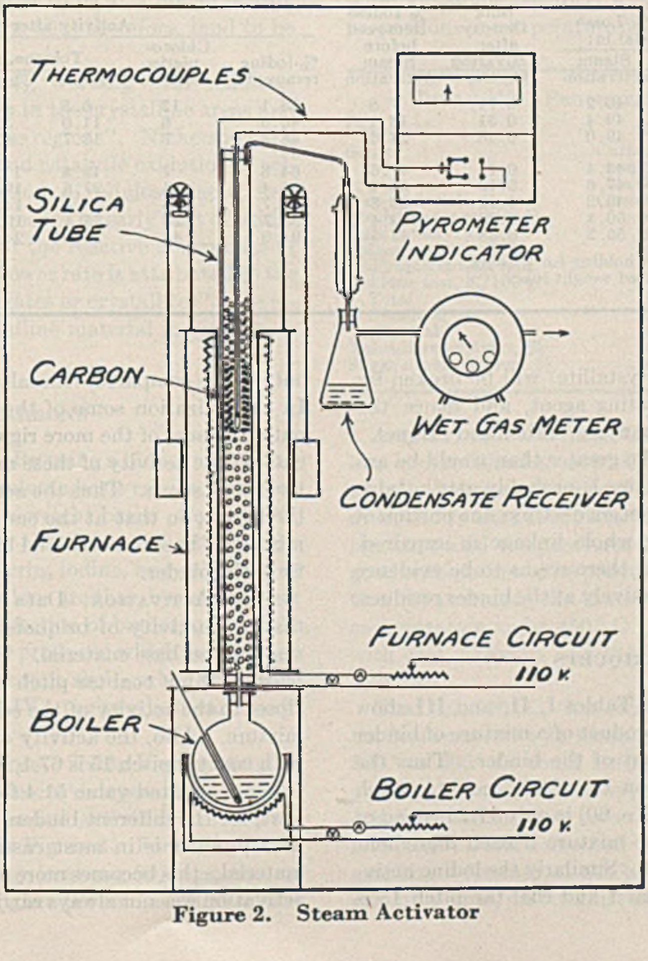


Figure 2. Steam Activator

TABLE I. ACTIVITY OF CARBONS[a] FROM POWDERED COAL AND BINDERS

Carbon No.	Binder Added (25% by Wt.)	Weight % Loss[b] (Dry Basis) in:		Mechanical Strength (Flexural Test) after:			Bulk Density after Activation, G./Cc.	% Iodine Removed before Steam Activation	Activity after Steam Activation						
		Carbonization	Steam activation	Briquetting	Carbonizing	Activating			% iodine removed	Chloropicrin, minutes	Toluene, g./100 g. Total	Toluene, g./100 g. Chem.	Toluene, g./100 g. Phys.	Toluene retentivity, %	% color removed from sugar
1	None[c]	6.7	43.9	0.9	0.7	0.4	0.51	16.7	58.5	21	18.2	12.0	6.2	65.9	64
2	Low m.p. pitch	13.5	48.4	30	53	7.3	0.43	4.4	67.1	27	22.6	14.6	8.0	64.6	73
3	High m.p. pitch	12.5	47.7	4.5	10.0	3.8	0.38	3.6	64.5	23	20.5	13.4	7.1	65.3	67
4	Lignin	17.4	50.0	17.5	57	1.6	0.42	13.2	65.5	25	23.4	15.1	8.3	64.5	68
5	Ethylcellulose	13.5	46.5	97	1.5	0.3	0.42	11.5	62.2	20	20.4	13.6	6.8	66.7	74
6	Polystyrene	25.5	43.6	133	0.8	0.1	0.42	10.6	52.0	23	19.4	13.5	5.9	69.6	78
7	Urea-formaldehyde	26.1	50.4	52	3.1	1.2	0.46	10.7	62.1	29	19.4	12.3	7.1	63.4	80
8	Phenol-formaldehyde	18.4	57.4	40	29	4.2	0.46	19.7	64.7	33	16.0	9.7	6.3	60.6	82
9	Sugar	23.0	45.9	27	36	5.5	0.50	12.4	62.3	28	20.2	12.2	8.0	60.4	68
10	Dextrin	27.5	43.6	8.3	7.1	2.9	0.48	13.8	61.0	26	20.2	13.4	6.8	66.3	72
11	Pentalyn G	26.2	50.3	11.2	0.1	0.0	0.40	14.1	57.1	20	18.4	11.6	6.8	63.0	76
12	Sodium silicate	6.9	44.9	7.3	8.7	1.2	0.57	14.6	46.1	20	14.9	9.6	5.3	64.4	62

[a] Carbonization carried out by heating to 700° C. and holding for 2 hours.
[b] Steam activation at 925° C. until indicated weight loss (usually 1/2 to 3/4 hour).
[c] Water used to aid in briquetting.

TABLE II. ACTIVITY OF CARBONS FROM VARIOUS RAW MATERIALS WITH LOW-MELTING COAL TAR PITCH AND SUGAR AS BINDERS

Carbon No.	Base Material[a]	Wt. % Loss (Dry Basis) in Carbonizing	Binder Added (25% by Wt.)	Weight % Loss[b] (Dry Basis) in:		Mechanical Strength (Flexural Test) after:			Bulk Density after Activation, G./Cc.	% Iodine Removed before Steam Activation	Activity after Steam Activation					
				Carbonizing briquets	Steam activation	Briquetting	Carbonizing	Activating			% iodine removed	Chloropicrin, minutes	Toluene, g./100 g. Total	Toluene, g./100 g. Chem.	Toluene, g./100 g. Phys.	Toluene retentivity, %
2	Coal (powdered)	...	Low m.p. pitch	13.5	48.4	30	53	7.3	0.43	4.4	67.1	27	22.6	14.6	8.0	64.6
13	Cellulose (carbonized)	81.1	Same	13.1	46.6	17.2	63	18.8	0.36	17.2	84.1	25	29.2	20.6	8.6	70.6
14	Lignin (carbonized)	64.2	Same	14.0	44.2	13.7	42	12.8	0.37	14.1	59.8	10	18.3	10.4	7.9	56.8
15	High m.p. pitch (carbonized)	48.7	Same	14.7	49.6	32	[c]	[c]	0.40	5.1	29.4	5	8.2	4.2	4.0	51.2
9	Coal (powdered)	...	Sugar	23.0	45.9	27	36	5.5	0.50	12.4	62.3	28	20.2	12.2	8.0	60.4
16	Cellulose (carbonized)	81.1	Same	18.4	53.2	16.3	44	5.0	0.31	12.8	91.9	27	36.2	26.7	9.5	73.7

[a] All except coal carbonized prior to addition of binder by heating to 700° C. and holding for 2 hours; all briquets carbonized similarly.
[b] Steam activation at 925° C. until indicated weight loss (usually 1/2 to 3/4 hour).
[c] Lost shape on carbonizing so that flexural test could not be made.

TABLE III. PROPERTIES OF ACTIVATED CARBONS[a] FROM MISCELLANEOUS RAW MATERIALS

Carbon No.	Carbonaceous Material	Weight % Loss[b] (Dry Basis) in:		Bulk Density after Activation G./Cc.	% Iodine Removed before Steam Activation	Activity after Steam Activation						
		Carbonization	Steam activation			% iodine removed	Chloropicrin, minutes	Toluene, g./100 g. Total	Toluene, g./100 g. Chem.	Toluene, g./100 g. Phys.	Toluene retentivity, %	% color removed from sugar
56	Coal (rice size)	6.4	40.2	0.71	7.8	38.1	12	6.5	4.0	2.5	61.5	60
57	Lignite	46.9	49.4	0.51	13.1	43.8	6	11.0	5.4	5.6	49.1	74
58	Lignite, steam-treated	42.9	49.0	0.48	24.6	48.3	7	13.7	6.9	6.8	50.4	77
59	Lignocellulose	78.9	43.4	0.19	47.6	64.8	7	19.8	11.2	8.6	56.6	88
60	Cellulose	81.1	47.6	0.13	34.4	85.4	14	27.6	19.9	7.7	72.2	89
61	Southern pine	77.0	49.2	0.12	33.3	74.7	6	23.4	14.6	8.8	62.4	86
62	Masonite	79.3	50.4	0.22	44.4	85.7	22	35.4	19.4	16.0	54.8	93
63	Coconut shell	73.2	56.2	0.38	41.5	91.0	42	36.0	24.0	12.0	66.7	80

[a] Carbonized by heating to 700° C. and holding for 2 hours.
[b] Steam activation at 925° C. to indicated weight loss.

linking across from crystallite to crystallite) will be broken by the corrosive attack of the activating agent, and hence the activated briquet will be weaker than the carbonized briquet.

That the loss in strength should be greater than would be anticipated by direct relation to weight loss is probably attributable to the fact that, when the corrosive action destroys one portion of the chain, the effectiveness of the whole linkage is impaired. Furthermore, as will be shown later, there seems to be evidence that the corrosive attack strikes selectively at the binder residues.

ACTIVITY OF BRIQUETS

AFTER CARBONIZATION. Data in Tables I, II, and III show that the activity of the carbonized product of a mixture of binder and nonbinder is predominantly that of the binder. Thus the iodine activity of the mixture (carbon 13) of 25% coal tar pitch binder (No. 15) and 75% cellulose (No. 60) is only 17.2 instead of 27.1, the activity calculated for the mixture if each ingredient contributed its proportional amount. Similarly the iodine activity of the mixture (carbon 2) of coal 1 and coal tar pitch 15 is only 4.4, as compared with calculated activity 13.8 for the mixture. In carbonization some of the mobile binder is adsorbed on the outer surfaces of the more rigid framework of the crystallites. It cuts off the activity of these more rigid portions and has little activity of its own. Thus the activity of the mass as a whole is relatively low, so that at the end of carbonization the activity of a mixture of base material and binder is predominantly characteristic of the binder.

AFTER ACTIVATION. Data from Tables I, II, and III also show that the activity of briquets after activation is predominantly that of the base material. The iodine activity of the mixture (carbon 13) of coal tar pitch 15 and cellulose 60 is 84.1, which is closer to the activity of the cellulose than 71.5 calculated for the mixture. Also, the activity of the mixture (carbon 2) of coal 1 with coal tar pitch 15 is 67.1, which is nearer to that of coal than to the calculated value 51.4 for the mixture. Table I also shows that, for the different binders used with coal, the activity of the final product is in most cases approximately that of the base material; this becomes more nearly correct if it is considered that activation was not always carried to exactly 50% weight loss.

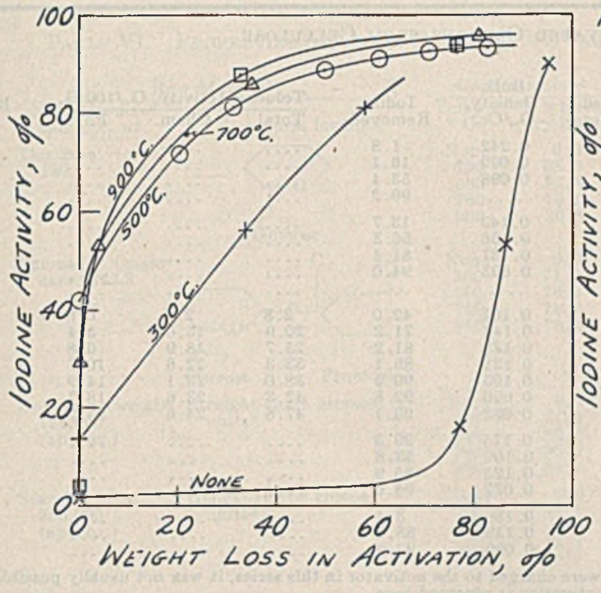


Figure 3. Activation Weight Loss of Cellulose Carbonized at Various Temperatures

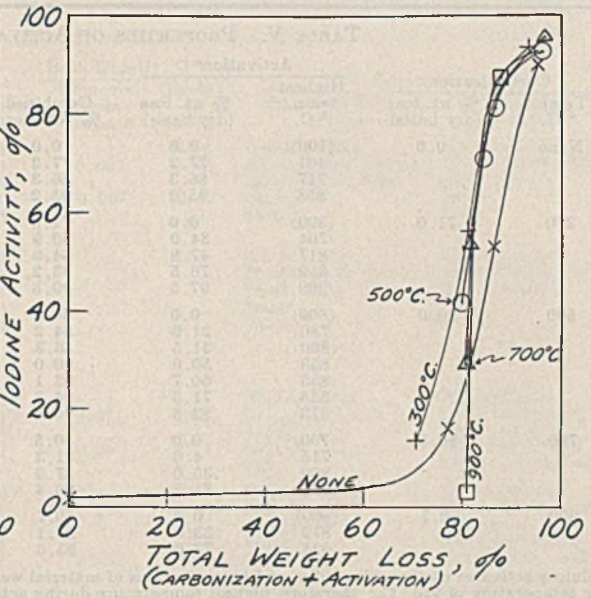


Figure 4. Total Weight Loss of Cellulose Carbonized at Various Temperatures

These facts indicate that steam activation tends to remove binder residues preferentially from carbonized mixtures of binder and nonbinder, probably because the binder residues tend to be nonoriented and disordered. They represent a brush-heap distribution of "bridges" between the more orderly crystallite sections of carbon from the base material. Penetration of the crystallite sections is more difficult for the activating agent than penetration of the nonoriented sections, and hence the latter are more readily available for reaction. Furthermore, brush-heap or amorphous sections are generally considered to be at a higher energy level than oriented crystallite sections and, therefore, tend to be more reactive.

Goldfinger, Mark, and Siggia (*24*), working with cellulose, found that "diffusion . . . is very slow in the crystalline areas and comparatively faster in the amorphous regions". Nickerson (*31*), reporting studies on the hydrolysis and catalytic oxidation of cellulose, stated that noncrystalline portions of cellulose reacted first and explained the rapid evolution of gas in the early part of oxidation as due "to the rapid cleavage of the reactive amorphous or expanded chain network; the final slower rate is attributed to the dense, less reactive crystalline aggregates or crystallites". He estimated the proportion of noncrystalline material in wood pulp cellulose to be about 10%.

CELLULOSE CARBONS

DENSITY AND VOLUME ACTIVITY. By using a binder with cellulose, its density and activity on a volume basis can be increased without impairment in activity on a weight basis. Carbons 13, 16, and 60 (Tables II and III) show that by use of a binder the volumetric activity toward chloropicrin, iodine, and toluene was approximately doubled. The indications are that, by using higher briquetting pressure, a different proportion of binder, or possibly a different binder, a carbon might be produced which would be as good as and perhaps better than coconut shell carbon 63 (Table III) and Columbia carbon I (Table IV), the two best carbons in this study.

IODINE ACTIVITY AND WEIGHT LOSS. Table V gives data on cellulose carbons carbonized at different temperatures and activated to various degrees. The iodine activities are plotted against weight losses in activation in Figure 3. For a weight loss in excess of 95%, the iodine activity is above 90, regardless of carbonization temperature. The higher the temperature of carbonization, however, the smaller the loss of weight in activation to give an iodine activity of 90.

The saving in material by high temperature carbonization is not so great as would appear from Figure 3 because the higher the carbonizing temperature, the higher the weight loss in carbonization. When iodine activity is plotted against combined weight loss in carbonization and activation (Figure 4), the curves are closer together. It appears that, as long as both carbonization and activation are used, the resulting activity will be approximately the same for any given total weight loss, regardless of the relative proportions or temperature of carbonization.

TABLE IV. PROPERTIES OF REFERENCE CARBONS

Carbon No.	I	II	III
Source	Carbide & Carbon (Columbia Grade G)	Universal Oil Products	Norit (decolorizing)
Raw material	Coconut shells	Petroleum	Vegetable matter
Mesh size (as received)	8–14	16–24	Powder
Bulk density, g./cc.	0.56	...	...
Iodine activity, %	86.9	77.3	62.9
Chloropicrin test, min.	41	...	...
Toluene test, g./100 g.	...	...	...
Total	32.2	...	...
Chemical	22.0	...	...
Physical	10.2	...	...
Toluene retentivity, %	68.3	...	...
Sugar decolorization, %	56	58	85

ACTIVITY OF CELLULOSE CARBONIZED AT 900° C. When cellulose is carbonized to 900° C., the activity of the product is extremely low, according to Table V (carbon 37). Figure 3, however, shows that this material is easily activated. Chaney (*11*) recommended temperatures below 600° C. for carbonization if good carbons are to be produced; the British Fuel Research Station (*8*) indicated the lowest possible temperature for practical carbonization to be 450° C. The latter work was done entirely with coal, however, and the former apparently does not include cellulose.

That this 900° C. char could easily be activated was proof that the loss in activity in passing from a carbonizing temperature of 500° to 900° C. could hardly be due to the formation of large graphitic crystals; moreover, this fact was checked by x-ray photographs of the cellulose carbons prepared by carbonization at 500° and 900° C., and compared with a similar photograph of natural graphite. Neither of the cellulose carbons showed evidence of graphitic lines, and it must be concluded that the loss in activity

Table V. Properties of Activated Carbons from Cellulose

Carbon No.	Carbonization		Activation[a]		Combined % Wt. Loss	Bulk Density, G./Cc.	% Iodine Removed	Toluene Activity, G./100 G.			Toluene Retentivity, %
	Temp., ° C.	% wt. loss (dry basis)	Highest temp., ° C.	% wt. loss (dry basis)				Total	Chem.	Phys.	
17	None	0.0	(100)	0.0	0.0	0.242	1.8	....	....	....	....
18			401	77.2	77.2	0.099	16.1	....	....	....	....
19			717	86.3	86.3	0.098	53.4	....	....	....	....
20			858	95.2	95.2	....	90.2	....	....	....	....
21	300	71.0	(300)	0.0	71.0	0.143	13.7	....	....	....	....
22			704	34.0	80.9	0.156	56.3	....	....	....	....
23			817	47.8	84.9	0.137	81.4	....	....	....	....
24			859	76.5	93.2	0.093	94.0	....	....	....	....
25			900	97.5	99.3	....	....	....	....	....	....
26	500	80.0	(500)	0.0	80.0	0.161	42.0	2.8	2.0	0.8	71.5
27			780	21.0	84.2	0.144	71.2	20.9	15.6	5.4	74.6
28			800	31.5	86.3	0.138	81.2	25.7	18.9	6.8	73.5
29			853	50.0	90.0	0.121	89.1	33.3	22.6	10.7	67.8
30			855	60.7	92.1	0.105	90.9	38.0	23.1	14.9	60.8
31			858	71.3	94.3	0.090	92.8	42.3	23.6	18.7	55.7
32			873	82.5	96.5	0.082	93.1	47.8	24.6	23.2	51.4
33	700	80.5	(700)	0.0	80.5	0.175	29.3	....	....	....	....
34			715	4.0	81.3	0.169	53.8	....	....	....	....
35			809	35.0	87.3	0.125	85.9	....	....	....	....
36			925	81.3	96.4	0.077	96.0	....	....	....	....
37	900	80.7	(900)	0.0	80.7	0.186	3.4	....	....	....	....
38			872	33.0	87.1	0.139	88.4	....	....	....	....
39			925	77.0	95.6	0.099	93.9	....	....	....	....

[a] Since cellulose activates easily and rapidly, and only 40 grams of material were charged to the activator in this series, it was not usually possible to attain an activating temperature of 925° C.; therefore, highest temperature during activation is reported here.

in going from 500° to 900° C. cannot be due to the formation of large graphitic crystals.

The indication is that, if steam activation is to be used later, the optimum temperature of carbonization is 900° C. or above, assuming that the fuel costs at this temperature are not prohibitive. Under these conditions the weight loss of material for a given activity tends to be less (Figures 3 and 4), and the density (Table V) tends to be greater. The latter is an advantage when activity is to be expressed on a volume basis.

Carbonization in Superheated Steam. A series of runs was made in which cellulose was activated without first being carbonized. This is the equivalent of carbonizing in an atmosphere of steam or carrying out the carbonization and activation steps simultaneously. The results (Table V, carbons 17, 18, 19, 20, and Figures 3 and 4) indicate that, although carbons of good activity can be made in this way, it is usually at a sacrifice of raw material; hence in commercial operation it would probably be best to carry out the process in two steps.

CARBOHYDRATE CHARS

Table VI gives data on chars made by carbonizing various carbohydrates. Three (dextrose, cellulose, and starch) are made up of glucose units in various degrees of polymerization. The fourth, sucrose, is composed of a glucose unit combined with a fructose unit. Sucrose was included for comparison with other data in the literature where sugar was used as a raw material. The chars differ not only in appearance and physical structure but also in density and adsorptive qualities. Of the three carbohydrates composed entirely of glucose units, dextrose appears to be a typical binder, cellulose is a typical base material, and starch has intermediate characteristics even though it is higher in molecular weight than either dextrose or cellulose. Sucrose was found to resemble dextrose.

General Appearance. Dextrose and starch swelled and became macroporous on carbonization while cellulose shrank and did not become macroporous, regardless of carbonization temperature. Most of the dextrose chars were black, lustrous, and flaky; the 300° C. char, however, was brownish black, iridescent, and spongy before being ground. In contrast, the cellulose chars were all dull and none was flaky; the color was always black or gray black, and when ground to powder, the higher temperature products appeared to become lighter gray.

Starch did not swell or become macrorporous to so great an extent as dextrose. The starch chars were only semilustrous as compared with the dextrose chars, resembled the cellulose charts in color, and were never flaky. The intermediate characteristics of starch, even though it is not intermediate in molecular weight, may be due to the fact that the glucose units are not arranged with the CH_2OH groups on alternate sides of the chain, as in the case of cellulose. Hence, according to Plunguian (*32*), the starch molecule rolls up as a sort of helical spring and does not have so much rigidity as the straight-chain cellulose molecule. The rigidity of the cellulose molecule appears to help it resist liquefaction; hence it does not "blow up" into a macroporous structure.

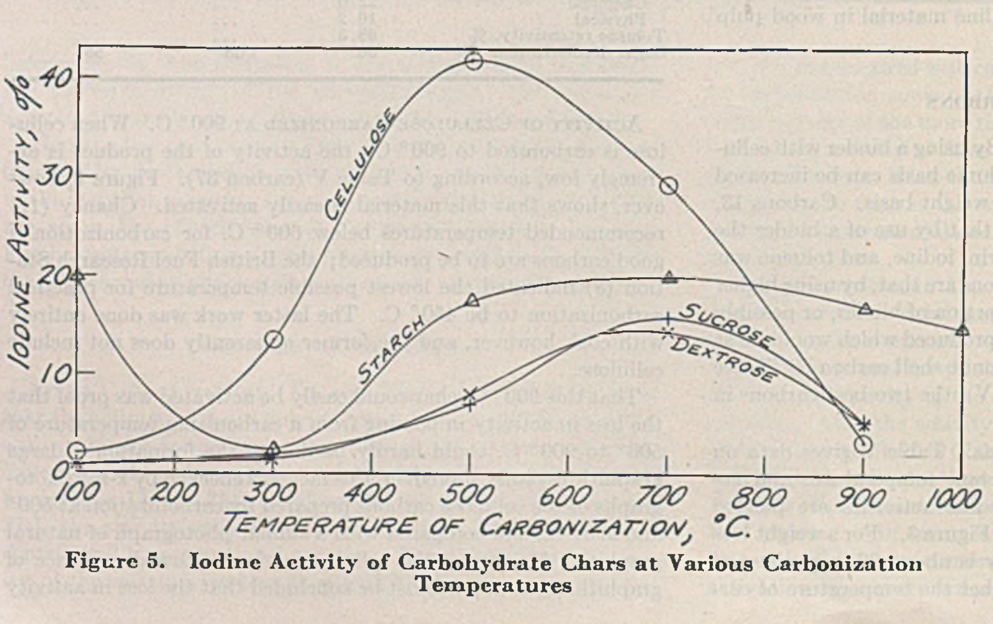
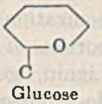
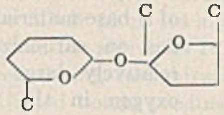


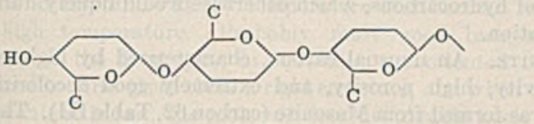
Figure 5. Iodine Activity of Carbohydrate Chars at Various Carbonization Temperatures

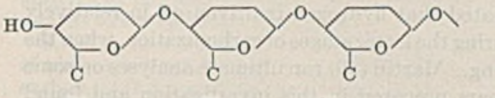
Table VI. Properties of Chars Produced by Carbonizing Carbohydrates at Various Temperatures

	Raw Material[a]		Carbonization[b]		Bulk Density, G./Cc.		Appearance		
Carbon No.	Name (source) and mol. wt.	Structural formula	Temp., ° C.	% wt. loss (dry basis)	Removed from furnace	Ground to powder	Removed from furnace	Ground to powder	% Iodine Removed
40	Dextrose (corn) 180.1		None	0.0	...	0.71	White powder	White powder	0.9
41			300	68.8	0.005	0.48	Brown-black, spongy	Brown-black, shiny	1.4
42			500	76.8	...	...	Black, shiny, flaky	Black, shiny	8.0
43			700	79.0	0.007	0.60	Same	Same	14 4
44			900	80.3	...	...	Same	Same	5.6
45	Sucrose (sugar cane) 342.3		None	0.0	...	...	White powder	White powder	1.0
46			300	71.9	...	...	Brown-black, spongy	Brown-black, shiny	1.8
47			500	76.2	...	...	Black, shiny, flaky	Black, shiny	6.8
48			700	78.8	...	...	Same	Same	16.0
49			900	79.4	...	...	Same	Same	5.3
17	Cellulose (wood) 125,000 (approx.)	Straight-chain glucose units[c]	None	0.0	...	[c]	White fibrous	White fibrous	1.8
21			300	71.0	0.07	0.47	Gray-black, dull	Dead black, dull	13.7
26			500	80.0	...	...	Same	Black, dull	42.0
33			700	80.5	0.09	0.54	Same	Gray-black, dull	29.3
37			900	80.7	...	...	Same	Lt. gray-black, dull	3.4
50	Starch (corn), 250,000 (approx.)	Helical-spring glucose units[d]	None	0.0	...	0.76	White powder	White powder	20.0
51			300	64.1	0.012	0.55	Gray-black, semi-shiny	Dead black, semi-shiny	2.6
52			500	75.1	...	...	Same	Black, semishiny	17.4
53			700	77.7	0.012	0.61	Same	Gray-black, semi-shiny	20.1
54			900	78.9	...	...	Same	Lt. gray-black, semishiny	17.2
55			1000	79.4	...	...	Same	Same	14.8

[a] Molecular weights estimated from Plunguian (*32*, p. 71) and from a communication of National Starch Products, Inc.; structural formulas from Conant (*13*, p. 159) and Plunguian (*32*, pp. 68–9).

[b] Carbonization carried out by heating to indicated temperature and holding for 2 hours, except for carbon 55, held for 5 hours.

[c] 

[d] 

[c] It was not possible to grind the uncarbonized cellulose to powder; the density of a sheet of uncarbonized material was found to be 0.84.

Density. Table VI shows that the density of cellulose chars as formed is about ten times as great as that of dextrose chars; but when ground to powder, the densities are approximately the same. The low density of the dextrose char as it is removed from the furnace is due to large voids which are eliminated when the material is ground. The considerable increase in the density of cellulose char on grinding is due principally to the fact that the squares of carbonized cellulose as removed from the furnace do not pack well, and not to any considerable voids in the char itself. The density of starch char on removal from the furnace is intermediate between those of dextrose and cellulose chars, although nearer the dextrose char; after grinding it is approximately the same as that of the other two. In general, the density of a given char increases as carbonization is continued to higher temperature.

Weight Loss. The major part of the volatile matter is driven off even at the lowest carbonizing temperature employed (300° C.). The amount varies, however, for the various carbohydrates, and the small additional amount that can be expelled by continued heating to higher temperature also varies. Volatile matter is most easily driven off from cellulose; that is, for any given carbonization temperature cellulose usually suffers the greatest weight loss. This may be due to the fact that the vapors do not have to pass through a liquid or viscous mass. Of the three remaining materials, each of which becomes fluid on carbonization, volatile content was lost with increasing difficulty as molecular weight became higher. Starch, even after carbonization for 5 hours at 1000° C., lost less material than cellulose carbonized for 2 hours at 500° C.

Iodine Activity. Figure 5 shows iodine activity of the carbohydrate chars plotted against temperature of carbonization. The dextrose, sucrose, and starch chars reach maximum activity at 700° C. and then decrease. This agrees with the findings of Riley (*34*), who concludes that many of the properties of chars, including adsorptivity, change in the neighborhood of 700° C. In the case of cellulose, which apparently Riley (*4, 5*) did not investigate, the char with greatest activity was made at 500° C. This further emphasizes the fact that certain properties of cellulose char are unique.

Figure 5 shows also that, for the major part, the sucrose and dextrose chars are low in activity, the cellulose char is high, and the starch char intermediate. The cellulose char drops off rapidly in activity after reaching a peak, and the others taper off slowly. The latter would seem to indicate that the viscous nature of dextrose, sugar, and starch chars does not so readily allow the readjustment in structure necessary for decreased activity on continued carbonization.

The iodine activities listed in Table VI are also plotted against weight loss in carbonization (Figure 6). Extreme changes in adsorptive capacity take place for relatively small losses in volatile matter while last portions are being expelled. Thus for the first 60 or 70% lost, the increase in activity is relatively slight. From approximately 70 to 80%, however, the activity increases manyfold; the removal of an additional 1 or 2% toward the end of this range generally results in correspondingly great decrease in activity.

While the exact nature of the phenomena involved is not known, it seems likely that a portion of the unsatisfied bonds produced in the early part of the loss of volatile may be used up in reformation of the carbon structure. That cellulose attains the highest activity is believed due to the fact that cellulose is composed of large, rigid molecules. These have less mobility than smaller dextrose and sucrose molecules and less flexibility than the more plastic starch molecules. Hence when unsatisfied surface bonds are formed by driving off volatile, the opportunity for utilization of these bonds in structural rearrangement is not so great.

The sudden drop in activity near the end of the curves of Figure 6 is noteworthy. In the case of cellulose, for a weight loss of

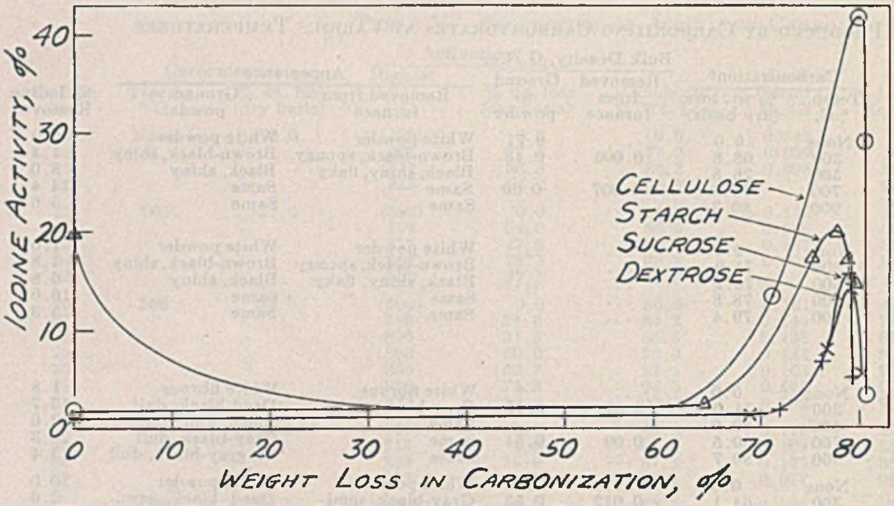


Figure 6. Variation of Iodine Activity of Carbohydrate Chars with Weight Loss

less than 1% of the original charge or less than 4% of the material remaining, more than 90% of the activity was lost. Figure 3 has already shown that this same char, by loss of an additional 4% or less in activation, was again restored to high activity.

Riley (*33*) indicated that hydrogen is driven off in relatively high proportion during the latter stages of carbonization, when the activity is decreasing. Martin (*30*) ran ultimate analyses on some of the cellulose chars prepared in this investigation and found that the hydrogen content did decrease in relatively high proportion during the later stages of carbonization. During activation, however, the loss in weight which results in increased activity is mainly gasification of carbon. With steam as the activating agent, it seems certain that hydrogen, removed coincident with the loss of activity in the latter stages of carbonization, is not restored to the carbon mass during the restoration of activity in the activating step; either oxygen or carbon dioxide can be substituted for steam in activation, and both the hydrogen and oxygen contents of the charcoal decrease during activation (*6*).

In one experiment a smaller charge of cellulose than usual was carbonized at 900° C. in the rotary furnace, and no precaution was taken at the end of the run to seal the furnace; the product showed a weight loss of approximately 82%, and the iodine activity was above 35, presumably on account of activation by air drawn in during cooling. When this experiment was repeated with conventional procedure, the results checked those in Table VI within experimental error.

This extreme sensitivity to slight weight loss seems important in the light of carbon activity. X-ray photographs showed that the loss in activity is not caused by growth of large graphitic crystals, and the char could easily be activated. There is the possibility that very small graphitic crystallites might have been formed by a sort of thermal readjustment or high-temperature "tempering"; there is the possibility, too, that the hydrogen being freed might have played an important role in any such readjustment.

MISCELLANEOUS CARBONS

Coal and Pitch. In view of the fact that most coals contain about 10% or more of ash, which is of questionable value as a raw material for activated carbon, it might be supposed that coal tar pitch would be a better raw material for activated carbon than coal. However, Table II (carbons 2 and 15) shows that coal carbon, in spite of its high ash content, has better activity than the carbon made from coal tar pitch. Coal tar pitch is a binder or plastic type of material and becomes liquid on carbonization. Lack of activity was not due to the formation of large graphitic crystals, as shown by x-ray photographs.

Cellulose and Lignin. Data on carbons 13 and 14 (Table II) show that the cellulose carbon has higher activity than the lignin carbon. Lignin is a plastic material and becomes liquid on carbonization; lignin also has a smaller proportion of oxygen in the ring structure. Lignin, generally considered a binder, does possess some of the characteristics of a base material. Thus, while it liquefies on carbonization, the molecule is relatively large and does have some oxygen in the ring structure. Compared with coal tar pitch, it gives off a relatively large proportion of volatile matter. These characteristics are reflected in the activity, and the lignin carbon was found to be more active than that from coal tar pitch.

Steam Treatment of Lignite. Steam-treated lignite was found to be slightly better as a raw material for activated carbon than ordinary lignite (Table III, carbons 57 and 58). Steam treating is used principally to reduce moisture content; any improvement in activity probably results from the incidental removal of hydrocarbons, which otherwise would liquefy during carbonization.

Masonite. An unusual carbon, characterized by high general activity, high porosity, and extremely good decolorizing ability, was formed from Masonite (carbon 62, Table III). These properties are believed to be due to the explosion process of manufacture, together with the washing and compressing which follow. Masonite is compact, but its fibers have been thoroughly separated, and it is composed of very fine particles of homogeneous, porous material washed free of natural impurities.

Retentivity. Tables I, II, and III show that for a large number of carbons made by similar procedure from widely different raw materials, the ratio of material held by chemical adsorption to that held by both chemical and physical adsorption (toluene retentivity) appears to be directly related to the raw material. For carbons made from coal, the figures are between 60 and 70. The only values above 70 are for cellulose carbons. Those below 60 include the carbons made from lignin, coal tar pitch, lignocellulose, Masonite, and lignites. In general, base materials usually give carbons of higher retentivity than binders. The particularly high retentivity of the cellulose carbons seems to be due to the fact that the raw material has a rigid oriented structure and a high proportion of volatile to be expelled.

BINDERS AND BASE MATERIALS

Appearance after Carbonization. Binders, in general, whenever carbonized alone gave products having approximately the same characteristics. Coal tar pitch, dextrose, and sugar swelled, became macroporous, and gave shiny chars. The shiny appearance indicates that the material was liquid or plastic during carbonization and cooled to the viscous state. The swelling and macroporous condition apparently resulted from effervescence of the viscous mass as volatile matter escaped.

Base materials, particularly cellulose and anthracite, did not expand on carbonization. Although anthracite retained most of its shiny appearance, it did not lose much volatile matter and did not gain much in activity. Good base materials are of rigid or oriented structure and do not melt on carbonization.

Binders seem to lose volatile content by destructive distillation; base materials lose volatile by "destructive" sublimation. Mixtures of base materials and binders may, on carbonization, take on the appearance of either of the two ingredients. Coconut shells, southern pine, Masonite, and lignocellulose shrank and became dull during carbonization. It is well known that certain bituminous coals cake in carbonization and others do not, that some swell and others do not.

Activity. Both base materials and binders increase in activity while volatile is being lost, and base materials usually attain higher activity than binders. The degree of activity appears to be related also to the proportion of volatile matter that can readily be expelled. For the two base materials cellulose and anthracite (Nos. 60 and 1), the amounts of volatile driven off were 81.1 and 6.7 and the corresponding activities 34.4 and 16.7. For the two binders, lignin and coal tar pitch (14 and 15), the volatile losses were 64.2 and 48.7 and the activities 14.1 and 5.1, respectively. Activity produced during carbonization is believed to result largely from unsatisfied bonds produced on the surface when volatile matter is driven out. In the case of binders, which are mobile or flexible, a higher proportion of these bonds are used up in re-formation of the surface structure. Lignin has some of the characteristics of a base material and hence attains a relatively high degree of activity.

Cellulose can attain a high degree of activity in carbonization probably as a result of its rigid structure. Mark (*10*) considers cellulose an example of the fiber type of molecule in comparison with the rubber and the plastic types. The fiber (crystalline or oriented) type is defined as one which shows high degree of crystallizability; the rubber type shows small tendency to crystallize; and the plastic type is an intermediate variety, which tends to crystallize at low temperature and become rubberlike at high temperature. Probably most good base materials belong to the fiber type, in that they are oriented or "crystallized". This gives them a rigid structure, and when the volatile content is lost, the molecule does not double back on itself and use up the unsatisfied bonds. Binders, on the other hand, belong to the plastic type, and when heated, melt and lose rigidity.

Another feature of cellulose appears to be that it is a long-ring chain type of molecule, with oxygen in the ring. The long molecule means that it has a high proportion of surface to volume, which is a desideratum in activated carbon. Oxygen in the ring means that, when this oxygen is driven out in carbonization, possibly dragging a carbon with it, at least two carbons are left behind with unsatisfied bonds. That there can be ring cleavage in the cellulose molecule without necessarily shortening the length of the chain was recently indicated by Ott (*10*), who stated that cellulose is "one of the most rigid high polymers known".

Mixtures Containing Excess Binder. Since binders carbonized alone give carbons low in activity, and swelling causes the product to be low in density and strength, it follows that a material composed of binder, or containing too high a proportion of binder, does not make the best raw material for activated carbon. The Bureau of Mines (*16*) found that anthracite of low volatile content makes a better activated carbon than bituminous coal. As most of the cheap raw materials available commercially for activated carbon manufacture are mixtures of base materials and binders, this is an important consideration. The solution of the commercial problem appears to lie in the addition of base material or binder to make up for any deficiency or the proper blending of various raw materials. An alternative procedure might be to destroy excess binder by heat treatment, either by prolonged heating at preplastic temperatures or by using a slow rate of heating. Atkinson, Brewer, and Davis (*2*) reported that by prolonged preplastic heating it is possible to destroy the binder in fuel briquets.

CONCLUSIONS

1. Raw materials for activated carbons seem to divide themselves naturally into base materials and binders. Intermediate materials possess some of the characteristics of each group. Anthracite, which is high in fixed carbon, and cellulose are typical base materials, starch and lignin are intermediate, sugar and coal tar pitch are typical binders.
2. On carbonization base materials differ from binders principally in that the former do not liquefy. Base materials usually shrink during loss of volatile matter and give a dull char; binders swell, become macroporous, and leave a lustrous residue.
3. When carbonized separately, the activities of both base materials and binders increase during loss of the major portion of volatile matter. Base materials usually attain a higher degree of activity than binders, but base materials which contain a relatively small proportion of volatile matter attain a lower activity.
4. The activity of the carbonized product of mixtures of base material and binder is predominantly that of the binder; on activation with steam the activity becomes predominantly that of the base materials.
5. The properties of chars obtained by carbonizing carbohydrates such as dextrose, cellulose, and starch (composed of glucose units) are markedly different. Dextrose appears to be a typical binder, cellulose a typical base material, and starch an intermediate.
6. Cellulose is a specially good base material; activated carbon made from it has high general activity and particularly high retentivity. Its density is normally low but can be increased by briquetting with a binder, which results in increase in activity on a volume basis without loss of activity on a weight basis.
7. Cellulose can be carbonized in the presence of steam so that, in effect, carbonization and activation are carried out together. However, the weight loss of material for a given degree of attained activity is greater than when the operations are conducted separately; commercially the process will probably be more economical if carried out in two steps.
8. Near the end, during the expulsion of volatile matter in the carbonization of cellulose, there is an unusually large drop in the activity of the char for slight loss in weight. This appears to be related to the emission of hydrogen.
9. The fact that cellulose carbonized to 900° C. in the absence of air has low activity does not preclude its use for making active carbon, as this material is easily activated.
10. For carbons made of similar procedure from various raw materials, the toluene retentivity appears to be directly related to the materials used. For materials carbonized at 700° C. and activated to about 50% weight loss, the per cent retentivity of cellulose carbons is in excess of 70, that of coal carbons between 60 and 70, and those of lignin, Masonite, coal tar pitch, and lignite carbons follow in that order with values ranging from 57 to 49.
11. A binder for making activated carbon should (*a*) liquefy and become very fluid on carbonization, (*b*) have a relatively small molecule, and (*c*) require high temperature for carbonization.
12. A base material for making activated carbon should (*a*) not become plastic on carbonization, (*b*) have a large molecule of rigid or oriented structure, and (*c*) have a long ring-chain molecule with oxygen or other volatile in the ring.

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PURIFICATION OF LACTIC ACID

Production of Methyl Lactate from Aqueous Solutions of Crude Acid

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Difficulties involved in the purification of fermentation lactic acid are outlined, and a new method for purifying this acid or preparing methyl lactate directly from crude aqueous lactic acid is described. The method comprises passing methanol vapor through aqueous lactic acid and condensing the effluent vapors. The condensate, a mixture of methanol, water, and methyl lactate, can be distilled to recover the methyl lactate or hydrolyzed to obtain purified lactic acid. Other esters of lactic acid can be prepared similarly with appropriate alcohols. The effect of variables on the volatilization of lactic acid (principally as the methyl ester) with methanol vapor has been studied. The time required to volatilize a given amount of lactic acid decreases as the rate of methanol addition is increased. Increasing the catalyst concentration (concentrated sulfuric acid) accelerates the operation. Approximately 9 moles of methanol are required to volatilize 1 mole of lactic acid from an 82% solution of the acid (kept at 92–100° C.) over a wide range of methanol addition rates. Although dilute lactic acid can be used, less time and less methanol are required to volatilize a given quantity of lactic acid from the more concentrated solutions.

A CONSPICUOUS feature of the lactic acid industry (*18, 24*) is that this acid is sold as several different grades and at prices considerably higher than the cost of the sugars used as raw materials in its fermentative production (*19*). Although the sugars in whey, molasses, and starch hydrolyzates sell for about 1 to 4 cents per pound (*27*) and yield almost one pound of lactic acid (*25*) for each pound of sugar, the crude and U.S.P. grades of lactic acid are quoted at 11 and 43 cents per pound (100% basis), respectively (*15*).

Since lactic acid, as it occurs in dilute fermentation liquors, is inexpensive, the high cost of relatively pure lactic acid may be attributed largely to difficulties encountered in purification. The purification of fermentation lactic acid is difficult because of its low vapor pressure, tendency to undergo self-esterification (*5*), similarity in solubility characteristics to water, and presence of troublesome impurities (*1, 9, 17, 19, 24*), such as dextrins, proteins, inorganic salts, and unfermented sugars.

Six types of purification procedures were reviewed recently by Smith and Claborn (*24*), who recommended conversion (*32*) of calcium lactate into methyl lactate, purification of the methyl ester by distillation, and hydrolysis of the ester (*33*). Other proposed purification methods comprise crystallization of the calcium (*3, 13, 16, 31*), aniline (*2*), or zinc salt (*24, 30*), extraction (*8, 28, 29*) with a solvent such as isopropyl ether (*7*), and distillation (*24*). Some of the impurities in lactic acid produced by fermentation can be removed or destroyed by treatment with oxidizing agents (*24*) such as hypochlorites, chromates, permanganates, nitric acid, peroxides, chlorine, and ozone.

Distillation procedures have been studied by previous investigators to determine their merit in the purification of lactic acid. Distillation in a vacuum (*10, 26*), steam distillation under reduced pressures (*6, 11, 12, 21, 22*), distillation in a stream of gas (*14*), and passage of superheated steam through condensation polymers of lactic acid (*17*) have been described as purification procedures. Since lactic acid of good quality is still relatively expensive (*15*), it appears that the distillation and other purification methods are not entirely satisfactory in their present stage of development and that improved purification procedures are needed.

Previous communications (*5, 20*) from this laboratory have shown that methanol reacts readily with condensation polymers of lactic acid, methyl lactate is readily volatilized in a stream of methanol vapor, and methyl lactate and water distill azeotropically. These facts seemed to warrant an investigation of the preparation and removal of methyl lactate from aqueous solutions of lactic acid by passing methanol vapor through the solution. The present paper indicates that this technique is advantageous in several respects for preparing methyl lactate (or

Table I. Volatilization of Lactic Acid with Alcohol Vapors

Expt. No.	Lactic Acid		Alcohol	H_2SO_4, Ml.	Tower Temp., °C.	Time, Hours	Available Lactic Acid[a], %	
	Moles	Concd., %					Volatilized	Retained in tower[b]
1	1.0	82[c]	Methyl	1	93–112	1.6	99.5	..
2	1.0	82[c]	Methyl	0.5	97–102	2.0	91	..
3	1.0	82[c]	Methyl	0.25	99–106	2.5	103	..
4	1.0	82[c]	Ethyl	0.5	102–113	3.75	97	..
5	1.0	82[c]	Isopropyl	0.5	97–108	7.0	86	..
6	1.0	82[c]	Methallyl	0.5	97–108[d]	4.0	78	..
7	0.5	35[e]	Methyl	0.5	84–109	4.66	88	6
8	1.13	57[f]	Methyl	1	96–100	4.75	74	..
9	1.0	57[f]	Methyl	1	98–107	3.2	87	9
10	0.93	26[g]	Methyl	1	98–107	4.23	86	..
11	0.93	26[g]	Methyl	1	98–105	3.91	93	..
12	1.0	26[g]	Methyl	1	106–112	4.0	81	..
13	1.0	26[g]	Methyl	1	ca. 100	4.0	95	..
14	1.0	26[g]	Methyl	1	64–128	5.0	100	..
15	1.0	26[g]	Methyl	1	98–106	4.42	95	..
16	2.0	26[g]	Methyl	2	95–105	8.1	95	..
17	2.0	56[h]	Methyl	2	118–127	2.83	91	..
18	2.0	103[i]	Methyl	2	94–100	5.66	97	..
19	1.0	26[g]	Ethyl	1	98–127	3.67	82	..
20	1.0	26[g]	Ethyl	1	98–125	7.25	85	..
21	1.0	26[g]	Isopropyl	1	117–126	11.33	52	..
22	1.0	48[j]	Ethyl	1	96–118	4.75	82	13
23	1.0	81[k]	Methyl	1	94–104	3.0	96	..
24	1.0	89[l]	Methyl	None	94–101	9.33	64	30
25	1.0	89[l]	Methyl	None	121–127	5.0	76	16
26	1.0	89[l]	Methyl	None	144–154	4.0	82	13
27	1.0	89[l]	Isoamyl	1	101–106[m]	5.25	45	46
28	1.0	89[l]	Methyl	[n]	95–107	4.0	69	26
29	1.0	91[l]	Methyl	0.5	97–105	4.0	70	..
30	1.0	91[l]	Methyl	1	97–104	2.33	74	21
31	1.0	91[l]	Methyl	1	101–109	6.0	77	20
32	1.0	91[l]	Methyl	2	101–108	2.75	82	17
33	1.0	91[l]	Methyl	2	101–108	2.67	85	15
34	1.0	91[l]	Methyl	3	99–109	3.16	90	13
35	1.0	91[l]	Methyl	3	91–108	3.0	92	9
36	1.0	91[l]	Methyl	4	92–106	2.66	94	9
37	2.0	89[l]	Methyl	4	88–105	3.2	97.5	..
38	1.0	91[l]	Ethyl	1	99–107	3.25	73	25
39	1.0	91[l]	Ethyl	1	96–107	4.75	78	19
40	1.0	91[l]	Ethyl	[o]	96–107	6.0	78	16
41	1.0	91[l]	Isopropyl	1	97–109	9.9	59	40

[a] No correction made for possible presence of acidic compounds other than lactic acid and its esters.

[b] Tower washed with water or methanol at end of experiment, and washings titrated.

[c] Almost colorless edible lactic acid obtained from the Du Pont Company.

[d] Reaction tower operated under pressures of 110 to 114 mm. of mercury.

[e] Fermentation liquor, furnished by Du Pont, was acidified with sulfuric acid and filtered; filtrate was concentrated to 35% lactic acid.

[f] Crude lactic acid supplied by Sealtest, Inc.

[g] Crude lactic acid supplied by Sheffield Farms Company, Inc.

[h] Prepared by concentration of 26% crude lactic acid used in experiments 10 to 16.

[i] Prepared by concentration and filtration of 26% crude lactic acid used in experiments 10 to 16.

[j] Crude lactic acid supplied by American Maize-Products Company.

[k] Technical lactic acid supplied by Clinton Company.

[l] Prepared by concentration and filtration of 22% crude lactic acid obtained from Clinton Company.

[m] Reaction tower operated under a pressure of 60 to 65 mm.

[n] 2.5 grams of H_3BO_3 as catalyst.

[o] 3.5 grams of *p*-toluenesulfonic acid as catalyst.

certain other lactic esters) from crude, dilute lactic acid and for purifying lactic acid through its methyl ester. Wenker (*33*) and Schopmeyer and Arnold (*23*) also purified lactic acid by passing alcohol vapor through the crude acid; their patents appeared after the completion of this investigation.

PURIFICATION PROCEDURE

Alcohol vapor was passed through the crude lactic acid, which was maintained at a temperature above the boiling point of the alcohol. The lactic ester thus formed was volatilized in the stream of alcohol vapor, and the mixture of alcohol, water, and alkyl lactate was condensed. The fact that some of the lactic esters distill azeotropically (*20*, *32*) with water may facilitate volatilization of the ester. When purified lactic acid was desired, the condensate was heated to hydrolyze the lactic ester and distill the alcohol. In some experiments the condensate was distilled, usually in a vacuum, to recover the lactic ester.

In one series of experiments (Table I), lactic acid and alcohol vapor (usually methanol) were passed countercurrently through a tower. This comprised a Pyrex tube, 1 inch in diameter and 4 feet long, packed with $^1/_4$-inch Berl porcelain saddles. The top of the tower had an inlet tube for introducing the crude lactic acid and an outlet tube for removing vapors. The base of the tower was provided with a side arm for introducing the alcohol vapor. The tower was heated electrically, and the temperature was controlled and recorded automatically. The crude lactic acid, with or without an esterification catalyst, was fed in at the top of the tower, and alcohol vapor was introduced at the base. The vapors from the tower, composed essentially of alcohol, water, and lactic ester, were led to a continuous stripping still, and the major portion of alcohol was separated and automatically returned through a liquid seal to the alcohol vaporizer. The purified lactic acid–lactic ester solution was collected at the base of the stripping still. Titration and saponification data were obtained to estimate the amount of lactic acid that had been carried over, principally as an ester, by the alcohol vapor. The condensate, when slowly distilled to hydrolyze the lactic ester and remove the alcohol, yielded a purified aqueous solution of lactic acid. During hydrolysis, the virtually colorless lactic acid sometimes became pale yellow or amber. It was found, however, that the color can be almost completely removed by treatment with a fraction of 1% of decolorizing carbon.

Operation of the tower may be illustrated by experiment 9 (Table I). To 159 grams (1 mole) of crude 57% lactic acid was added 1 ml. of concentrated sulfuric acid. The resulting mixture was fed into the top of the tower, and methanol vapor was introduced at the base. The condensate, collected at the base of the stripping still, was refluxed during the run to accelerate hydrolysis. The temperature of the tower was 98° to 107° C. After 3 hours and 10 minutes, over 87% of the lactic acid in the crude had reacted with methanol, and the product had distilled and collected at the base of the stripping column. The hydrolysis of the lactic ester in the purified solution was completed by slow distillation until the vapor temperature reached 97° C. under total reflux. A virtually colorless aqueous lactic acid solution of approximately 57% concentration was obtained.

The effect of certain variables was determined with an almost colorless edible 82% lactic acid, using a cylindrical Pyrex vessel with a fritted glass plate at the bottom. One mole of the 82% lactic acid (containing sulfuric acid) was placed in the cylindrical vessel (8.5 inches high and 2.75 inches in diameter), which was surrounded by a boiling water bath. Methanol, contained in a

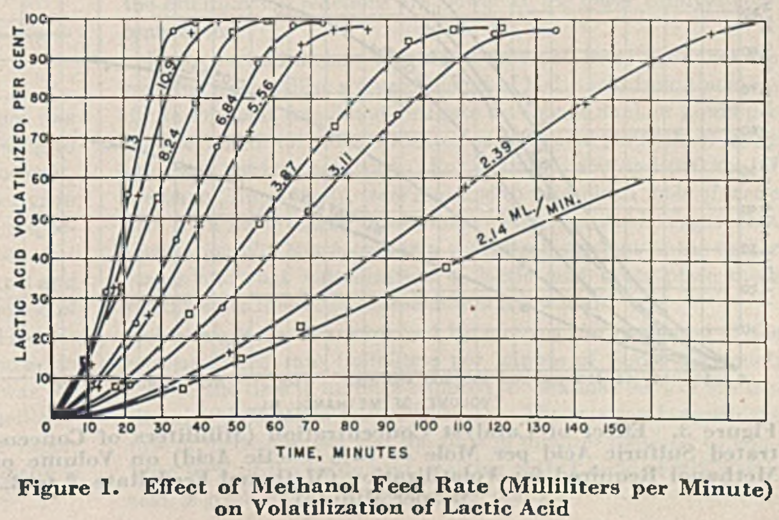

Figure 1. Effect of Methanol Feed Rate (Milliliters per Minute) on Volatilization of Lactic Acid

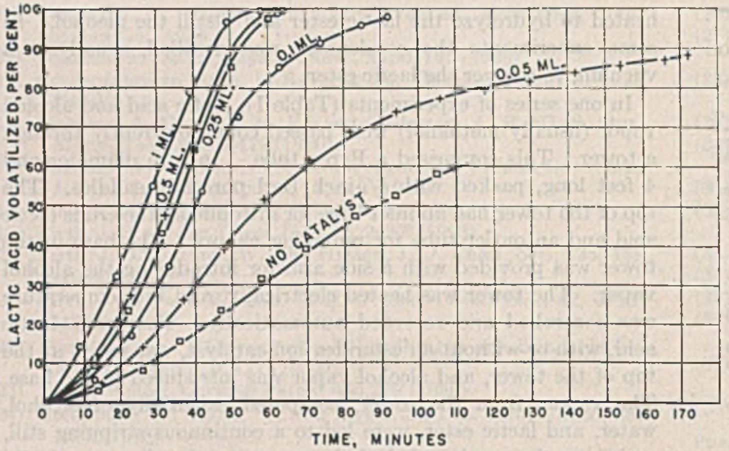

Figure 2. Effect of Catalyst Concentration (Milliliters of Concentrated Sulfuric Acid per Mole of 82% Lactic Acid) on Rate of Volatilization of Lactic Acid

graduated cylinder, was pumped with a constant-rate bellows pump (*4*) through a steam-jacketed preheater into the bottom of the lactic acid solution. The vapors withdrawn from the top of the cylindrical reaction chamber were condensed in approximately 100-ml. portions. These portions were titrated to determine the lactic acid volatilized principally as methyl lactate. In some instances the condensates were distilled to recover the methyl lactate. A suitable distillation procedure consisted in distilling most of the methanol, adding an entraining agent such as benzene, distilling water azeotropically, and then distilling the methyl lactate under reduced pressure.

The temperature of the lactic acid solution rose sharply to approximately 108° or 109° C. in the first minute or two of these experiments, although heat was supplied by a boiling water bath. This elevation of temperature may have been due to esterification of the carboxyl groups or to heat of solution. After the initial increase, the temperature of the mixture dropped to approximately 92–95° (depending on the feed rate) and then gradually rose to 100° C. at the end of the experiment.

Methyl lactate was isolated from the condensates in 85 to 90% yields by adding a small quantity of sodium acetate, distilling the methanol at atmospheric pressure, adding benzene, distilling water and benzene, and finally recovering the methyl lactate by vacuum distillation. When calculated on the basis of the lactic acid not recovered as polylactic acid in the distillation residues, the yields of methyl lactate were over 90%.

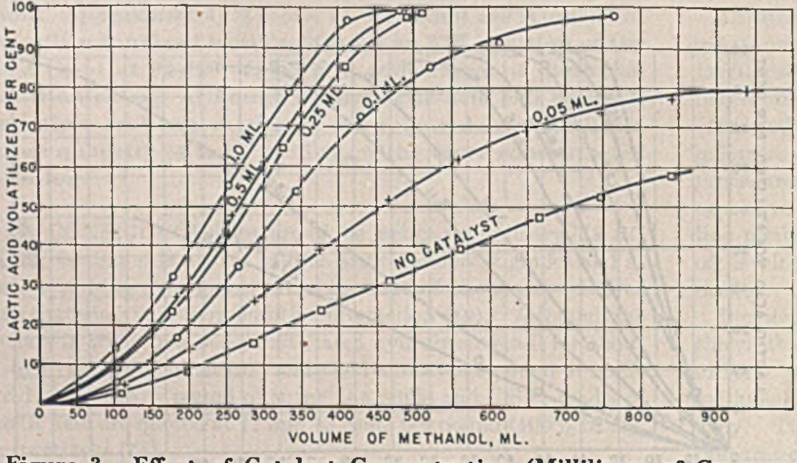

Figure 3. Effect of Catalyst Concentration (Milliliters of Concentrated Sulfuric Acid per Mole of 82% Lactic Acid) on Volume of Methanol Required for Volatilization (Methanol Feed Rate, 8 to 8.3 Ml. per Minute)

PACKED TOWER EXPERIMENTS

Results obtained by passing crude lactic acid and alcohol vapors countercurrently into a packed tower show that lactic acid can be readily volatilized as ester in high yields by this procedure (Table I). The method is applicable to different types of crude lactic acid and to various concentrations. This and the fact that either methyl lactate or purified lactic acid can be produced illustrate the flexibility and usefulness of the method.

The crude lactic acid used may be the dilute aqueous solution obtained by liberation of lactic acid from the fermentation liquor, or the product obtained by concentration of such a solution to any convenient content of lactic acid. One advantage in first concentrating the dilute aqueous solution lies in the fact that the more concentrated solution appears to react more rapidly with alcohol vapors than does the dilute solution. Furthermore, the inorganic salts and other solid impurities precipitated by concentration can be removed by filtration, although this is not necessary. Crude lactic acid solutions ranging in acid content from 26 to 103% (by weight) of lactic acid have been used with 90 to 100% of the acidity esterified by methanol vapor to form a volatile product. The lactic acids of higher concentration, which contained some condensation polymers of lactic acid, were prepared by removing water from the more dilute solutions.

In the purification of lactic acid, the alcohol vapors may be reacted with the crude acid either in the presence or absence of esterification catalysts. In the absence of esterification catalysts, the reaction is much slower. By using relatively large amounts of esterification catalyst, the yield of acid volatilized was considerably improved. The yield was raised to 97% by use of 4 ml. of concentrated sulfuric acid per mole of crude lactic acid (experiments 24, 25, 29–37). Boric acid and *p*-toluenesulfonic acid were effective as catalysts, but they had no obvious advantage over sulfuric acid. It was noted that some of the catalyst, either as such or as a derivative, was carried over by the alcohol vapor when boric acid or sulfuric acid was used. Hence, in making edible grades of lactic acid, it may be advisable to purify the lactic acid in the absence of a catalyst, use a harmless catalyst, neutralize the mineral acid in the purified product, or revolatilize the lactic acid in a second tower.

In experiments 24 to 26 the use of higher temperatures increased the yield of volatilized acid in the absence of a catalyst. Less time was required for the volatilization at the higher temperatures.

Different types of alcohol may be employed. Methanol or ethanol vapors seemed equally satisfactory. Isopropyl alcohol was not so suitable as methanol or ethanol (experiments 5, 21, and 41). When methallyl and isoamyl alcohols were used, the experiments were conducted at reduced pressure, mainly to avoid the use of high temperatures.

FERMENTATION LIQUOR

That the process can be used even with crude unfiltered fermentation liquors was shown by the experiments of Table II, conducted as follows: The crude liquor, acidified with sulfuric acid, was placed (with or without filtering) in a flask having an entrance tube extending to the bottom of the flask and an exit tube attached to a condenser. The flask was immersed in a boiling water bath. Methanol vapor, produced by vaporizing methanol in another flask, was led in through the entrance tube. The exit vapors, composed essentially of methanol, water, and methyl lactate, were condensed. Saponification of the condensate,

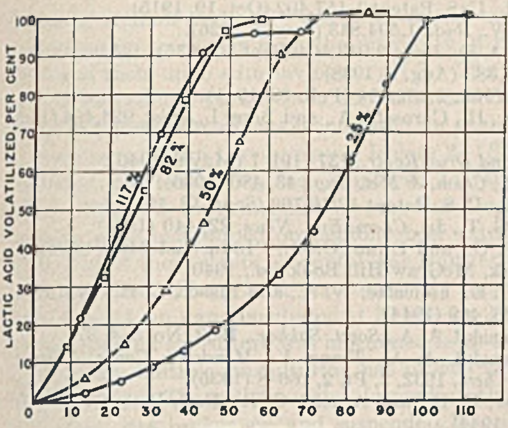

Figure 4. Effect of Lactic Acid Concentration on Rate of Volatilization (Methanol Feed Rate 8 to 8.3 Ml. per Minute)

which was colorless, showed that most of the lactic acid, mainly as its ester, had been volatilized by the methanol vapor. To the condensate was then added 0.25 to 0.5 gram of sodium acetate, and methanol was distilled at atmospheric pressure (vapor temperature, 85–90° C.). Then 100 ml. of benzene were added, and water was removed by continuous entrainment using a modified Dean and Stark trap. After all the water had been removed, the benzene was distilled at atmospheric pressure, and then methyl lactate was recovered by distillation under approximately 30 mm. pressure.

TABLE II. METHYL LACTATE AND PURIFIED LACTIC ACID FROM FERMENTATION LIQUORS[a]

Expt. No.	Fermentation Liquor: Batch	% Ca lactate	Amount	Lactic acid equivalent	H_2SO_4, Ml.[b]	Reaction Time, Hours	Temp., ° C.	% Lactic Acid Volatilized[c]	Methyl Lactate %[d]
1	A	ca. 10	510 cc.	0.5	0.5	3.0	98	75	..
2	A[e]	ca. 10	510 cc.	0.5	0.5	4.6	84–109	88	..
3	B[e]	10.2	1070 g.	1.0	2.0	4.5	80–95	87	78
4	C	10.5	1037 g.	1.0	1.0	7.6	90–96	82	56
5	C	10.5	1037 g.	1.0	10.0	7.0	88–95	93.5	81
6	C[e]	10.5	1037 g.	1.0	1.0	2.5	90–97	96	91
7	C[e]	10.5	1037 g.	1.0	1.0	2.5	90–97	93	85

[a] Kindly supplied by Du Pont Company.

[b] In excess of that required to liberate lactic acid from calcium lactate.

[c] Determined by titration and saponification of condensate.

[d] Isolated by distillation; based on lactic acid originally present in fermentation liquor.

[e] The acidified liquor was filtered, and the filtrate concentrated (to approx. 35% in expt. 2 and 3, and over 90% in expt. 6 and 7) prior to treatment with methanol.

In experiments 4 and 5, where dilute fermentation liquor was used, lactic acid instead of methyl lactate was obtained owing to hydrolysis of the ester during the removal of water. However, a second treatment of this lactic acid with methanol vapor gave the yields of methyl lactate indicated—i.e., 56 and 81%, respectively.

The data of Table II show that volatilization of lactic acid and formation of isolable methyl lactate are facilitated by the use of considerable excess of sulfuric acid; a high yield of methyl lactate resulted when 10 ml. of sulfuric acid in excess of that required to neutralize the calcium lactate were used. A high yield was obtained also by filtering the acidified fermentation liquor and concentrating the filtrate prior to treatment with methanol vapor. The latter procedure has the advantage that most of the water is distilled only once.

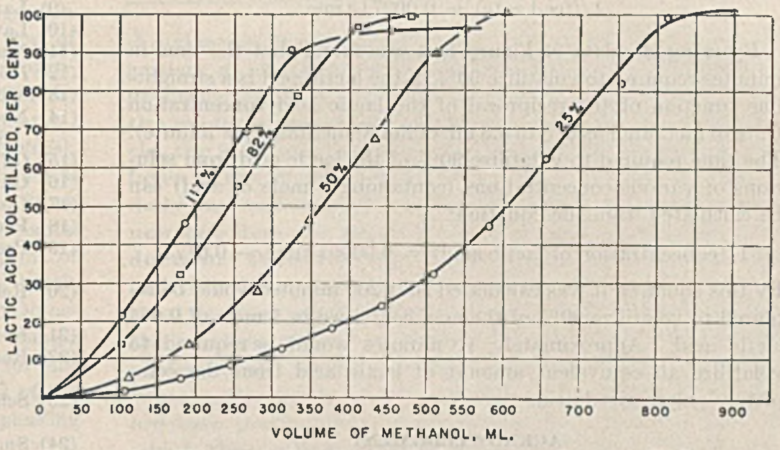

Figure 5. Effect of Lactic Acid Concentration on Volume of Methanol Required for Volatilization

EFFECT OF VARIABLES

Data on the effect of quantity of methanol used, methanol feed rate, concentration of lactic acid, and concentration of catalyst were obtained by pumping methanol through lactic acid contained in a gas-washing cylinder. Figure 1 shows that the rate of volatilization of lactic acid from an 82% lactic acid solution containing 1 ml. of concentrated sulfuric acid increases with increase in the rate of methanol addition. Probably the limiting factors are the rates of esterification and alcoholysis (of polylactic acid), which apparently occur rapidly when lactic acid and methanol are the reactants.

Figure 2 indicates that, when the concentration of the catalyst is below 0.2 ml. of concentrated sulfuric acid per mole of lactic acid, the rate of volatilization is materially retarded. In these experiments the methanol was passed into the lactic acid mixtures at the fairly rapid and constant rate of 8.0 to 8.3 ml. of liquid per minute. Probably volatilization at the lower catalyst concentrations was limited by lower rates of esterification. A virtually constant amount of methanol (approximately 9 moles) is required to volatilize lactic acid from its 82% solution (with 1 ml. of concentrated sulfuric acid per mole of lactic acid as catalyst) except at extremely low rates of methanol feed and presumably at certain high rates of feed.

The catalyst concentration affects the volume of methanol required to volatilize lactic acid (Figure 3). When the catalyst concentration is below 0.25 ml. of sulfuric acid per mole of lactic acid, considerably more methanol is required to carry over the lactic acid. No doubt the explanation is found in the fact that the esterification reactions are slower at the lower catalyst concentrations.

Figures 4 and 5 show that more time and more methanol are required to volatilize a given amount of lactic acid from the more dilute solutions (methanol feed rate was about 8 ml. of liquid per minute, and 1 ml. of concentrated sulfuric acid per mole of lactic acid was used as catalyst). For example, 450 and 600 ml. of methanol, respectively, were required to volatilize 1 mole of lactic acid from its 82 and 50% solutions. Figures 4 and 5 suggest that distillation of water occurs to a considerable extent in the earlier stages and that volatilization of lactic acid takes place more readily after the water concentration is lowered.

A straight line was obtained by plotting the reciprocal of the methanol feed rate (milliliters per minute of liquid methanol) against the time in minutes required to volatilize 90% of the lactic acid (data taken from Figure 1). The relation between the rate of methanol feed and the time in minutes required to volatilize 90% of the lactic acid, starting with 1 mole of 82% lactic acid, is given by the equation which follows.

$$1/(\text{feed rate}) = 0.00271 \text{ time}$$

By using the data of Figure 4, it was found that the time in minutes required to volatilize 90% of the lactic acid is a straight-line function of the reciprocal of the lactic acid concentration (rate of methanol feed, 8 to 8.3 ml. of liquid methanol per minute). The time required to volatilize 90% of the lactic acid from solutions of various concentrations (containing 1 mole of acid) can be calculated from the equation:

$$1/(\text{concentration of lactic acid}) = 0.00061 \text{ time} - 0.0174$$

By this equation it was calculated that 200 minutes would be required to volatilize 90% of the acid contained in 1 mole of 9.6% lactic acid. Approximately 41 minutes would be required to volatilize an equivalent amount of lactic acid from the completely polymerized acid.

ACKNOWLEDGMENT

The authors are grateful for the samples of crude lactic acid generously supplied by the manufacturers and for assistance rendered by other members of this laboratory.

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BACTERIAL AMYLASES . . .

Production in Thin Stillage

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BECKORD, Kneen, and Lewis (*2*) described a method which can be adapted commercially for producing bacterial amylase on a semisolid medium prepared from wheat bran. In the commercial production of bacterial amylases, the prevailing practice has been to employ liquid culture media. Methods for preparing these media have been described by Boidin and Effront (*3*), Wallerstein (*11*), and Schultz, Atkin, and Frey (*9*). In all of these procedures, proteinaceous materials such as soybean, peanut, or cottonseed cake are utilized. Preparation of the media may involve preliminary hydrolysis of the material by acid or enzymic digestion to render the protein more readily available to the organism.

In this investigation thin stillage, an alcohol fermentation by-product, was selected as the culture medium for all experiments. This material was convenient to use in the laboratory since it proved to be an acceptable nutrient without any preliminary treatment other than adjustment of the hydrogen-ion concentration. Thin stillage contains the water-soluble nutrients from the original grain as well as those arising from the added malt and yeast and from their enzymic actions plus some grain fines and suspended dead yeast cells. Although the composition of thin stillage can be expected to vary somewhat from batch to batch, the nutritive value is reflected in the data of Bauernfeind and co-workers (*1*); the composition of the dried solubles from thin stillage indicates that the liquid could support certain types of bacterial growth.

This report presents the technical details involved in producing bacterial amylase in a liquid medium prepared from thin stillage. Similar details can be expected to pertain in amylase production whenever culture media of the liquid type are employed.

STILLAGE AND ORGANISM

Preparation of Thin Stillage for Culture Medium. Thin stillage resulting from either the fermentation of corn, a mixture of corn and wheat, or a mixture of sorghum and rye was used to prepare the culture media for all experiments. Availability determined the thin stillage utilized.

The hydrogen-ion concentration of the thin stillage, as received, was pH 4.0 to 4.5. Since this reaction was unfavorable for the growth of the organisms used, anhydrous sodium carbonate was added to adjust to a favorable pH level. However, after the addition of sodium carbonate, autoclaving raised the pH level approximately one unit. For example, the addition of 2

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grams of sodium carbonate per liter caused the hydrogen-ion concentration to change from the proximity of pH 4 to that of pH 6 and then, upon autoclaving, to pH 7. The final hydrogen-ion concentration of the adjusted, sterilized (autoclaved at 121° C. for 30 minutes) thin stillage is indicated for each experiment.

INOCULATION AND INCUBATION. Isolate 23 (*Bacillus subtilis*), described previously (*2*), was employed for the experimental work. The following inoculation procedure was used. Stock cultures were maintained on peptone-beef extract-agar slants. From one of these slants, a loopful was transferred to 50 ml. of adjusted thin stillage in a screw-capped, square glass bottle (6 × 6 × 14 cm.) and incubated at 37° C. for 24 hours. On occasion a second subculture was inoculated from the first. Single rather than multiple subculturing has proved adequate for this organism (*2*). The pellicle which formed on the surface of the subculture was broken up and suspended by vigorous shaking before the inoculum was withdrawn.

Incubation temperature and time varied with the purpose of the experiment and with the type of apparatus.

SAMPLING AND TESTING. Progress of amylase production was determined by testing samples withdrawn from the cultures. Conventional sampling with sterile pipets was both time consuming and conducive to contamination. To eliminate these two factors, the sampler illustrated in Figure 1 was inserted into each culture vessel. Parts *A*, *B*, and *E* were constructed from 6-mm. glass tubing, and *C* (capacity 5-8 ml.) and *F* from 16-mm. tubing. To withdraw a sample, cotton plug *G* was removed, the rubber tubing pinched shut at *D*, and suction applied by mouth to a length of rubber tubing slipped over *B*. When suction was released, excess liquid in tube *A* was forced back into the flask, and the collected liquid in *C* was drained into a sample bottle.

A 20-ml. aliquot was withdrawn from each culture for testing. Thin stillage cultures, like water extracts of wheat bran cultures (*2*), contained suspended material which resisted centrifugation and filtration and obscured the end point in the iodine test for dextrinizing activity. Each 20-ml. sample was clarified for testing as follows: 1 ml. of phosphate buffer (1.5 grams of KH_2PO_4 and 3.5 grams of $K_2HPO_4.3H_2O$ per liter) and 0.25 to 0.5 ml. of 20% $CaCl_2.2H_2O$ solution were added. The sample was shaken and cleared of the precipitate by centrifugation.

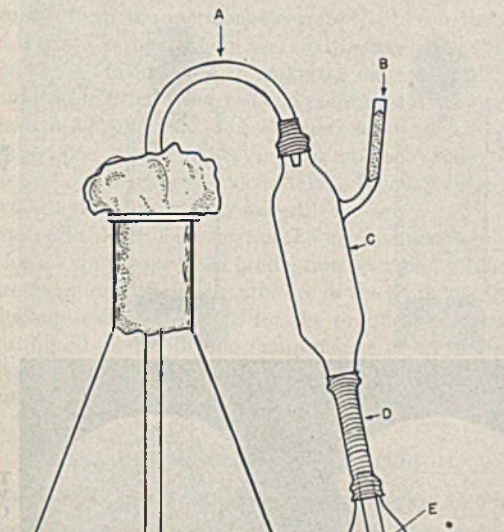

Figure 1. Device for Aseptic Sampling of Bacterial Cultures in Liquid Medium

Amylase is produced in thin stillage by the same organism as on wheat bran (*Bacillus subtilis*). The pellicle produces amylase and secretes it into a narrow layer of the medium underneath this pad. For a quiescent pellicle, the total amylase produced is greatest when the liquid layer of the medium is 2.5 to 3.8 cm. Shaking a culture daily and submerging an old pellicle in order to re-form a new one does not result in increasing total amylase production. Daily renewal of the medium underneath the pellicle neither prolongs amylase production nor increases total production but does accelerate the rate at which the maximum level of amylase is attained. Circulation of deep layers of the medium underneath the pellicle increases the mass of the pellicle as well as the total amylase production. Application of a drip method in which thin stillage trickles over wood chips covered with pellicle growth results in active amylase solutions after a short incubation period. Amylase production as well as pellicle formation ceases after 4 to 6 days, regardless of the manner of culturing. Replacing the functions of the pellicle by aeration results only in a low amylolytic activity of the cultures after a long incubation period. In the case of either an undisturbed pellicle or an aerated culture, a drop in the initial pH of the culture is followed by an abrupt rise. Neutralized thin stillage contains essentially adequate nutrients for the amylase-producing organisms employed. Culturing on thin stillage results in the same amylase as does culturing on wheat bran.

Routine evaluation of the amylase activity was by the dextrinization procedure described previously (*2*). Dextrinizing activity is expressed as the time in minutes required at 30° C. for 10 ml. of the thin stillage culture to convert 20 ml. of 1% boiled soluble starch (pH 6.0) to the point at which a red-brown color is given with iodine.

Enzymic conversion of boiled soluble starch to fermentable sugar was evaluated by a technique previously described (*2*). This method utilizes a closed system in which the pressure of carbon dioxide resulting from yeast fermentation of the sugars produced by enzymic action is measured as millimeters of mercury.

PELLICLE FORMATION

Isolate 23 is a pellicle former. (The ability to form pellicles is characteristic of members of the *Bacillus subtilis* group.) Figure 2 shows the manner in which the pellicle was progressively formed by isolate 23. To obtain some degree of photographic clarity, progression of pellicle formation was followed on a clear medium rather than on turbid thin stillage. After the first day of incubation, the pellicle was a thin, white, slightly wrinkled film. By the third day it became a thick white pad, heavily wrinkled with craterlike depressions over the surface. On the fifth day the physical characteristics of the pellicle were similar to that after 3-day incubation, but the color changed from white to light amber. Also by the fifth day a dark amber zone became apparent in the liquid immediately below the pellicle. As will be discussed later, this zone, in close proximity to the mat of organisms (i.e., the pellicle) is the region in which the secreted amylase is concentrated.

Boidin and Effront (*3*, *4*) obtained amylase in significant quantities only when pellicle formation occurred. The important role it plays in amylase production was demonstrated as follows: Two liters of corn thin stillage were adjusted to give pH 7.0 after sterilization and poured into a selected, cylindrical culture vessel so

Table I. Effect of Depth and Surface Area of Corn Thin Stillage on Amylase Production by Isolate 23

Depth of Medium, Cm.	Surface Area per Unit Vol., Sq. Cm./Ml.	Dextrinization Time, Minutes			
		1 day	2 days	3 days	4 days
0.6	1.67	36.5	11.5	9.0	8.5
1.3	0.77	26.0	9.0	7.8	6.8
1.9	0.53	49.0	10.0	8.5[a]	7.0[a]
5.1	0.20	60+	60+	33.0	25.0

[a] All dextrinization times except these two are averages of duplicate runs.

that the liquid depth was 8 cm. The medium was inoculated with the entire 50 ml. of a first thin stillage subculture. After 5-day incubation at 30° C., a 2.5-cm. amber-colored zone appeared just beneath the pellicle. A sample withdrawn from the amber-colored zone had a dextrinization time of 18 minutes, whereas one withdrawn from the bottom of the culture vessel had a dextrinization time of 120 minutes (considered negligible activity). Obviously, of the organisms in the culture only those in the pellicle were able to produce measurable quantities of amylase. The slow diffusion of the enzyme down into the medium resulted in a concentration in the amber-colored zone.

EFFECT OF DEPTH AND SURFACE AREA OF MEDIUM

Boidin and Effront (*3*), as well as Schultz, Atkin, and Frey (*9*), found that culturing in thin layers was requisite for producing maximum amylolytic activity. Since the amylase secreted by the pellicle diffuses down into a narrow zone beneath the pellicle, culturing in deep layers resulted not only in a practical waste of the medium but also in a diluted amylase solution. In order to obtain maximum activity per unit volume, isolate 23 was cultured in thin layers. To ascertain the appropriate depth for culturing, a constant volume of thin stillage at various depths was employed.

A quantity of corn thin stillage was neutralized with sodium carbonate (pH 7.0 after sterilization), dispensed in 1500-ml. amounts into 2-liter Erlenmeyer flasks, and sterilized. The content of each flask was inoculated with 50 ml. of a second thin stillage subculture and poured into a sterile porcelain pan which was covered with a sterile glass pane. Incubation was at 30° C. Four pans were selected to give liquid depths of 0.6, 1.3, 1.9, and 5.1 cm. for the constant volume of 1550 ml.

Table I shows that the dextrinization times after 4-day incubation were 8.5 minutes for a depth of 0.6 cm., 6.8 minutes for 1.3 cm., 7.0 minutes for 1.9 cm., and 25 minutes for 5.1 cm. In other words, the culture with a depth of 5.1 cm. was from a third to a fourth as active as the other three cultures of shallower depths.

Further, Table I shows that there was a limit to which the depth could be decreased (decreased depth resulted in increased surface area per unit volume) and still obtain efficient amylase production. A pellicle with an area of 1.67 sq. cm. (liquid depth 0.6 cm.) secreted no more amylase into 1 ml. of the medium than did a pellicle with an area of 0.53 sq. cm. (liquid depth 1.9 cm.). This confirms the finding of Boidin and Effront (*4*) that culturing in very thin layers resulted in only feeble amylolytic activity. When the depth of the medium was decreased beyond a certain limit, the potential amylase-producing capacity of the pellicle was not utilized fully or efficiently. In the selection of an appropriate depth for culturing, this experiment eliminated a depth of 5.1 cm. or more. Subsequent experiments indicated that a depth within the limits 2.5 to 3.8 cm. is satisfactory.

EFFECT OF INCUBATION CONDITIONS

The pellicle has the capacity for producing amylase. This capacity, however, is not retained indefinitely. The period during which amylase production occurred and the extent to which it took place were determined under various incubation conditions. The results are given in Table II. In the first instance (column *A*), amylase production by an undisturbed pellicle was determined at intervals. Four hundred milliliters of corn thin stillage were adjusted (pH 8.0 after sterilization), poured into a 1-liter Erlenmeyer flask (liquid depth, 3.8 cm.), fitted with a sampler (Figure 1), and sterilized. After inoculation with 20 ml. of a second thin stillage subculture, the flask was incubated at 37° C.

Amylase production by the quiescent (undisturbed) pellicle ceased after 6-day incubation (dextrinization time, 7.25 minutes); on the seventh day activity had begun to decrease (dextrinization time, 8.5 minutes). Further incubation beyond the seventh day resulted only in progressive loss of activity and partial or complete disintegration of the pellicle. In a supplementary experiment a culture incubated at 45° instead of 37° C. demonstrated the accelerating effect of high temperatures on the destruction of the pellicle. After 3-day incubation, amylase production ceased and pellicle disintegration began. The pellicle had completely dissolved, as if by autolysis after 5-day incubation at 45° C.

Whenever a culture flask was shaken, the pellicle was broken up and submerged and a new liquid surface exposed. Another pellicle would re-form over this new surface. In the second instance (column *B*, Table II), an inoculated flask, prepared in the same manner as described for the quiescent pellicle, was shaken

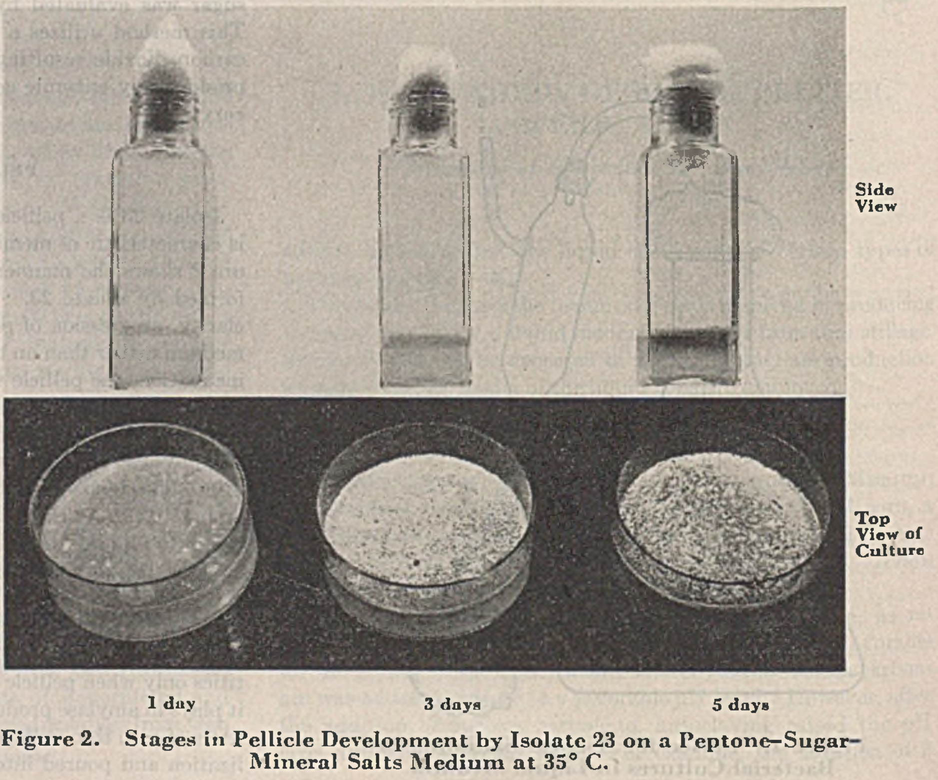

Figure 2. Stages in Pellicle Development by Isolate 23 on a Peptone–Sugar–Mineral Salts Medium at 35° C.

Table II. Amylase Production by Pellicle of Isolate 23 under Various Incubation Conditions

Incubation Period, Days	Dextrinization Time, Minutes Pellicle quiescent *A*	 Pellicle disturbed *B*	 Pellicle undisturbed, medium renewed daily *C*
1	180+	180+	18
2	101	41	7.5
3	35	24	9
4	15	17	30+
5	10	12	30+
6	7.25	14.5	30+
7	8.5	14	...

Table III. Effect of Circulation of Wheat-Corn Thin Stillage on Amylase Production by Pellicle of Isolate 23

Incubation at Room Temp., Days	Dextrinization Time, Minutes Stirred culture[a]	 Unstirred control[b]
1[c]	47	27
2	12.3	17
3	11.3	22
4	7.8	8.5
5	6.3	13.0
6	8.3	15.0

[a] Average of duplicate runs.
[b] Sampled only from the 2.5-cm. active zone underneath the pellicle.
[c] No stirring during first day.

daily. Thus, amylase production arising from a series of newly formed pellicles was compared with that from the undisturbed pellicle.

The data for the disturbed pellicle show that daily shaking did not enhance production. After 5-day incubation, amylase production was of the same order for both the quiescent pellicle (dextrinization time, 10 minutes) and the shaken flask (12 minutes). On the sixth day amylase activity had begun to decrease for the shaken flask (14.5 minutes) whereas for the quiescent pellicle amylase activity was still increasing (7.25 minutes). Visually, the type which re-formed from day to day after shaking changed from a heavy wrinkled pellicle to a thin delicate film by the fifth day.

The data in columns *A* and *B* of Table II indicate that shaking during the first 3 days enhanced amylase production. Part of this may be due to sampling errors. Shaking distributed the amylase secreted by the pellicle throughout the medium so that a representative sample was withdrawn from the disturbed culture. Obtaining a representative sample from underneath an undisturbed pellicle was difficult, especially early in the incubation period when all of the amylase was in the zone just under the pellicle and not distributed evenly throughout. In order to obtain a sample most nearly representative of the culture, a composite was withdrawn from underneath the quiescent pellicle as follows: one third of the sample from the bottom of the liquid layer, one third from the center of the layer, and one third from directly underneath the pellicle.

Amylase production by the quiescent pellicle ceased after 6-day incubation. In the third instance (column *C*, Table II), an attempt was made to prolong amylase production by replenishing the nutrients underneath the pellicle as well as removing possible toxic metabolites. To achieve this, a hole was bored through the bottom of a porcelain pan. A rubber stopper fitted with a glass tube was inserted into the hole so that the medium could be drained every 24 hours from underneath the pellicle. Two liters of wheat-corn thin stillage and 50 ml. of inoculum were introduced, and the whole was incubated at 30° C. The liquid depth was 2.5 cm. The data show that daily renewal of nutrients had no effect on prolonging the amylase-producing capacity of the pellicle. A dextrinization time of 18 minutes resulted from the increment of amylase secreted during the first day, 7.5 minutes from the increment secreted between the first and second day, and 9 minutes from the increment secreted between the second and third day. The increments secreted between the third and fourth, fourth and fifth, and fifth and sixth days were diluted by the medium to the extent that the end point in dextinization was not reached in 30 minutes. These experiments with respect to the incubation period showed that neither amylase production nor pellicle formation progressed indefinitely. When pellicle formation ceased, amylase production ceased.

The data of Table II demonstrate the marked decrease in time required for maximum amylase production effected by renewal of the culture medium without disturbance of the pellicle. It would appear that optimum conditions for the production of bacterial amylase in liquid media include maintenance of an undisturbed pellicle, liquid depths in the neighborhood of 2 to 4 cm., and frequent renewal of the nutrient.

EFFECT OF CIRCULATING THE MEDIUM

The effect of circulation was determined by using a cylindrical culture vessel (diameter 14.2 cm.) fitted with a mechanical stirrer. A glass stirrer (constructed of 8-mm. glass rod) was devised so that its revolving shaft did not disturb the pellicle. When a 2-liter portion of sterile wheat-corn thin stillage was adjusted (pH 7.0 after sterilization) and poured into the vessel, the liquid depth was 10.2 cm. (5.1 cm. was shown above to be too deep for efficient amylase production in a quiescent liquid by an undisturbed pellicle). The stirrer was adjusted to give a mild agitation (16 r.p.m.) in the region some 2.5 to 3.0 cm. below the liquid surface. After inoculating with 50 ml. of a second thin stillage subculture of isolate 23, the culture was undisturbed for 24 hours (incubation at room temperature) to establish a pellicle before the stirrer was started. A duplicate culture which served as the control was run simultaneously but not stirred.

In this experiment representative samples could be withdrawn for testing from the stirred culture. With the unstirred control, withdrawal of a representative sample was almost impossible; the method described above for sampling underneath a quiescent pellicle was satisfactory only for shallow liquid layers. Thus, to obtain a reasonable index of activity with the control, samples were withdrawn only from the 2.5-cm. active layer underneath the pellicle.

When interpreting the results of this experiment (Table III), the fact must be kept in mind that each dextrinization time listed for the stirred culture is representative of the activity throughout the total volume (2050 ml.) of the culture. For the control, each dextinization time represents the activity of the medium (approximately 400 ml.) only in the active zone—i.e., the activity of the medium if it were only 2.5 cm. deep.

The dextrinization times listed for the stirred culture and the control after 5-day incubation were 6.3 and 13.0 minutes, respectively, but owing to the larger volume of active liquid the total amount of amylase contained in the stirred culture was some ten times more than that contained in the unstirred control. Five-day incubation was sufficient to obtain the maximum pellicle development and, consequently, maximum amylase production. This markedly great increase of total amylase caused by the circulation of the medium coincided with a highly developed pellicle. The pellicles from a stirred and an unstirred culture incubated for 5 days as just described were skimmed off and weighed. The wet weight of the pellicle from the unstirred culture was 22.8 grams and from the stirred culture, 77.5 grams, or an increase in weight of almost 3.5 times due to circulation of the medium. The unstirred culture gave a pellicle like that pictured in Figure 2, but the stirred culture gave a thick pellicle, extensively wrinkled, piled high in ridges, and hanging down into the medium in heavy folds. After the stirrer was started, a visual increase in the size of the pellicle was apparent within 3 to 4 hours. Circulation provides an efficient culturing procedure. Large volumes of liquid can be handled with an economy of surface area. The amylase is distributed throughout the liquid, and fresh nutrients are brought in contact with the pellicle. Thus, the maximum

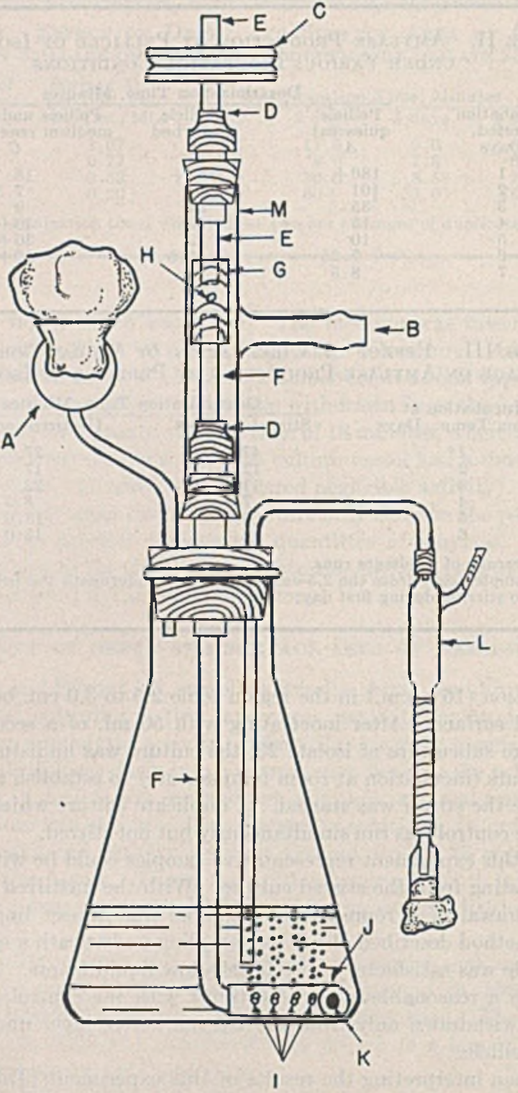

Figure 3. Apparatus for Aeration of Bacterial Cultures in Liquid Medium

amount of pellicle results from the nutrients available and a minimum of surface area is required.

DRIP METHOD

In the quick vinegar process (*7*) an alcohol solution trickles down over wood chips upon which acetic-acid-producing bacteria are clinging. Conversion to acetic acid occurs during its flow over the mass of organisms. An aerobic condition is maintained by passing air through the mass of chips and organisms. Likewise, the slow percolation of nutrient solution through a tower of shavings inoculated with a desired organism has been applied to penicillin production (*5*).

The feasibility of applying a similar technique to amylase production was tested. The study was not extensive and, for this reason, conditions selected for the experiment were arbitrary and not necessarily optimum. A glass tube (supported vertically), 60 mm. in diameter and 1.5 meters long, was loosely filled with moist poplar chips which had been boiled in water for one hour. The upper end of the tube was plugged with a rubber stopper containing an air outlet and four inlet tubes from which the medium dripped onto the chips. The lower end was plugged with a rubber stopper containing an air inlet and an outlet for the medium. This apparatus was sterilized in flowing steam at atmospheric pressure for 3 hours. A first wheat-corn thin stillage subculture was used to inoculate one liter of thin stillage. After incubation at 30° C. for 24 hours, 500 ml. were used to inoculate the chips. The tube and chips were incubated at room temperature for 24 hours to establish pellicle formation. Then 6 liters of sterile wheat-corn thin stillage (pH 7.0 after sterilization) were allowed to drip onto the chips at a rate of 3 liters per day. At the time the flow was started, a small current of sterile air was turned on and passed through the tube. After one day of flow the tube became packed with a heavy pellicle.

The dextrinization time was 10 minutes for the portion collected from one-day flow and likewise 10 minutes for the portion collected during the second day of flow. With this drip method, solutions with high amylase activity were obtained in a relatively short time. A 5-day incubation period was required with a quiescent pellicle (Table II) to obtain a culture which was as active as the portion collected after the first day's flow. The similarity between the rates of amylase production achieved by the drip method and by a replenishment of the nutrients below a quiescent pellicle (Table II) is obvious. Either procedure was greatly superior to that in which the total nutrients available were limited to the shallow layer supporting the initial development of the pellicle.

The portions collected during 2-day flow were recombined and dripped back through with the anticipation that a further increase in amylase activity would result. However, when they were recollected and tested, part of their activity had been lost; the dextrinization time was 14 minutes for the portion collected during the third day and 24 minutes for the portion collected during the fourth day. Apparently, both pellicle development and amylase production were complete after a short incubation period.

EFFECT OF AERATION

Boidin and Effront (*3*) bubbled air through their culture but found that only insignificant amylolytic activity resulted. Waldmann (*10*) employed aeration to enable organisms to produce amylase in a submerged condition. Although the supposition has not been fully substantiated, the growth of aerobic bacilli, such as isolate 23, occurs in a pellicle because such growth affords the organism an aerobic environment (*8*). An experiment was performed to determine whether aeration could replace pellicle formation by isolate 23 and thus permit amylase production in a submerged culture.

The effect of aeration was determined by adjusting 400 ml. of corn thin stillage (pH 8.0 after sterilization) and pouring it into a one-liter Erlenmeyer flask (liquid depth 3.8 cm.). An aeration device (Figure 3) was inserted into the flask and the entire apparatus sterilized in the autoclave. After sterilization, 20 ml. of a second corn thin stillage subculture were poured into the flask aseptically through funnel *A*. The apparatus was set up in a 37° C. incubator. Air-inlet *B* was connected to a source of sterile, humidified air, and pulley wheel *C* (16 r.p.m.) was attached to the reduction gear of an electric motor. When air entered inlet *B*, it passed into glass-enclosed chamber *M*. Air was entrapped in chamber *M* by rubber seals *D* around the shafts. Shaft *E* (6-mm. solid glass rod) and shaft *F* (6-mm. glass tubing) were joined by rubber coupling *G* which was pierced by hole *H*. Thus, the only escape for the entrapped air was through hole *H* down through shaft *F* and out the four glass capillary tubes *I*. Capillaries *I* were inserted into a piece of rubber tubing, *J*, which was

Table IV. Effect of Aeration of Culture[a] on Amylase Production by Isolate 23

Incubation Period, Days	Dextrinization Time, Min.	Incubation Period, Days	Dextrinization Time, Min.
1	180+	5	42
2	180+	6	41
3	150	7	25
4	66		

[a] Corn thin stillage used as culture medium.

plugged by a piece of glass rod, *K*. Funnel *A* served as air outlet. Air flow was regulated so that four streams of fine bubbles issued forth vigorously. Sample of the culture was withdrawn by sampler *L*. As the capillaries were revolved, air was distributed evenly throughout the medium, and the entire liquid surface was constantly disturbed by the bubbles so that pellicle formation could not occur on any portion of it.

The results of this experiment (Table IV) show that amylase production did occur without the presence of the pellicle but only after a relatively long period of incubation. After 3-day incubation, amylase activity was negligible (dextrinization time, 150 minutes). By the sixth day a dextrinizing time of 41 minutes was found for the culture and 25 minutes by the seventh day. Apparently the functions of the pellicle were not completely replaced by simply aerating the culture; an activity indicated by a dextrinization time of from 6 to 12 minutes would have indicated satisfactory amylase production.

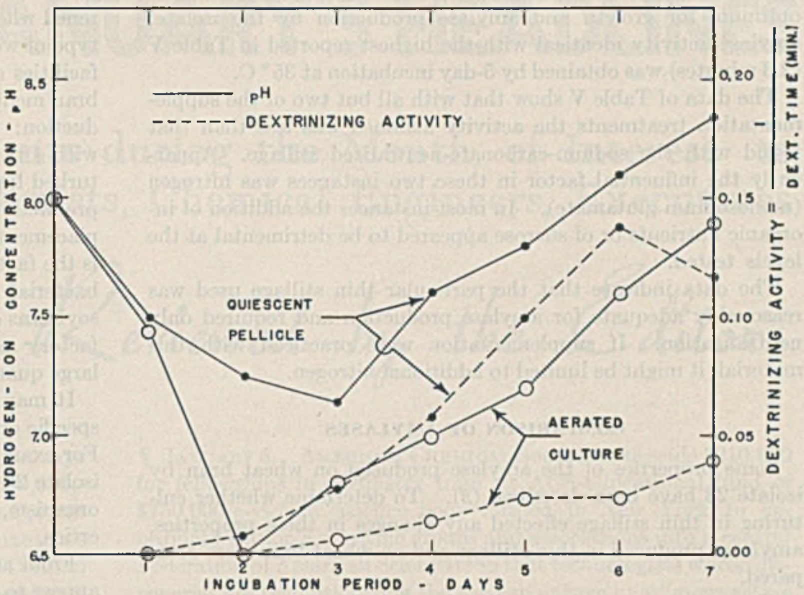

Figure 4. Changes in Hydrogen-Ion Concentration and in Dextrinizing Activity of Thin Stillage Cultures of Isolate 23 during 7 Days at 37° C.

HYDROGEN-ION CHANGES

Boidin and Effront (*3*) stated that bacterial amylase production occurred in an alkaline medium. In this investigation the thin stillage was adjusted so that the original hydrogen-ion concentration fell within the range of pH 7 to 8.

Figure 4 shows the changes in hydrogen-ion concentration as well as in amylase activity of a culture with a quiescent pellicle and of an aerated culture. All pH determinations were made with a glass electrode on the samples before clarification. The curves show that the same trend existed in both cultures—i.e., a drop in the initial pH level followed by an abrupt rise. During incubation of the culture with the quiescent pellicle, the pH dropped initially from 8.0 to 7.15 by the third day and had returned to 7.6 on the fourth day. At the end of the seventh day the pH had attained a level of 8.35. The amylase activity increased slowly and gradually as the pH dropped; when the pH rose, the activity increased at an accelerated rate. The curve shows that activity decreased between the sixth and seventh day whereas the pH value continued to rise.

As the aerated culture was incubated, the pH dropped from 8.0 initially to 6.5 on the second day. Boidin and Effront (*3*) likewise noted that aeration of an alkaline culture caused it to become slightly acid. On the third day the pH had returned to 6.8 and rose steadily to pH 7.9 by the seventh day. The amylase activity remained negligible during the pH drop and then slowly increased as the pH rose.

The amylase of isolate 23 is most resistant to thermal inactivation at about pH 7.0 and less resistant at pH 8.0 (*2*). This would indicate that it would be inadvisable to permit the reaction of the culture to become too alkaline. Figure 4 shows that a loss of amylase did occur after prolonged growth of the organism and when a high pH level had been reached. Therefore, to obtain a culture of maximum amylase activity, it is necessary to terminate the growth before any marked reduction in activity occurs.

SUPPLEMENTATION OF THIN STILLAGE

Thin stillage was used in the above experiments without enriching it nutritionally other than with sodium carbonate neutralization. To determine whether the nutritional value could be improved, it was variously supplemented. Thin stillage resulting from the fermentation of a mixture of sorghum and rye was utilized. The thin stillage cultures were inoculated with an amylase-producing organism (isolate 96) closely related to, but having a higher amylase-producing capacity than isolate 23. Each culture was prepared by pouring 250 ml. of the medium into a 2-liter bottle (liquid layer, 2.5 cm.), inserting a sampler (Figure 1), autoclaving, and inoculating with 5 ml. of washings from a 48-hour agar slant culture. Incubation was at 30° C. for 5 days.

Table V lists the various supplementations and the dextrinization times resulting after 5-day incubation. The first three treatments were neutralization studies and showed that sodium carbonate neutralization resulted in the most active culture. This type of neutralization had been employed in all previous work.

Table V. Effect of Supplementing Sorghum-Rye Thin Stillage on Amylase Production by Isolate 96

Supplementation	Dextrinization Time[a], Min.
Neutralization with NaOH (27 ml. of 2 *N* NaOH/liter)	6.5
Neutralization with $K_2HPO_4.3H_2O$ (23 grams/liter)	8.5
Neutralization with Na_2CO_3 (4.5 grams/liter)	3.5
Sucrose (5 grams/liter)[b]	7.0
Monosodium glutamate (5 grams/liter)	2.4
Sucrose + monosodium glutamate	4.5
Mineral salts (1 gram $K_2HPO_4.3H_2O$, 0.1 gram $MgSO_4.7H_2O$, 5 grams NaCl, 0.005 gram $CaCl_2$/liter)	7.0
Trace elements (2 mg. $FeSO_4$, 2 mg. $MnSO_4.7H_2O$, 2 mg. H_3BO_3, 0.2 mg. $CuCl_2$, 0.2 mg. $ZnCl_2$/liter)	13.0
Mineral salts + trace elements	14.0
Mineral salts + trace elements + sucrose	8.5
Mineral salts + trace elements + monosodium glutamate	10.0
Mineral salts + trace elements + monosodium glutamate + sucrose	2.3

[a] After 5-day incubation.

[b] Last nine supplementations made to a thin stillage neutralized with sodium carbonate.

Further supplements, in addition to the sodium carbonate used for neutralization, were sucrose, monosodium glutamate, mineral salts, and trace elements, individually and in combinations. The study was incomplete since ranges of the various additions were not used and modification of the results obtained would be anticipated with supplementation levels other than those employed. It should be noted that the combined supplements listed in the last experiment of Table V by themselves constitute an adequate nutrient for the organism. A nutrient composed of the same levels of salts and trace elements plus twice the levels of sucrose and monosodium glutamate (i.e., 1% of each) is close to optimum for growth and amylase production by the isolate; amylase activity identical with the highest reported in Table V (2.3 minutes) was obtained by 5-day incubation at 35° C.

The data of Table V show that with all but two of the supplementation treatments the activity attained was less than that found with the sodium-carbonate-neutralized stillage. Apparently the influential factor in these two instances was nitrogen (monosodium glutamate). In most instances the addition of inorganic nutrients or of sucrose appeared to be detrimental at the levels tested.

The data indicate that the particular thin stillage used was reasonably adequate for amylase production and required only neutralization. If supplementation were practiced with this material, it might be limited to additional nitrogen.

COMPARISON OF AMYLASES

Some properties of the amylase produced on wheat bran by isolate 23 have been described (*2*). To determine whether culturing in thin stillage effected any changes in these properties, amylases produced in thin stillage and on wheat bran were compared.

The high saccharifying activity manifested by the amylase of isolate 23 grown on wheat bran was deemed one of its significant properties. That this property was retained after culturing in thin stillage is indicated by the production of fermentable sugars. Pressure meters were employed as previously (*2*) except that the enzyme solution and water brought the final volume of the reaction mixture to 25 ml. The enzyme solutions were aliquots (dextrinization times, 14 minutes) from a corn thin stillage culture and from a water extract of a dried wheat bran culture. After the end of a 21-hour fermentation period, the pressures caused by the carbon dioxide evolved were closely comparable—manometer readings of 397 mm. of mercury for the thin stillage culture and 407 mm. for the wheat bran culture.

The amylase inhibitor of Kneen and Sandstedt (*6*) derived from wheat does not inhibit the action of high-liquefying commercial bacterial amylases but does inhibit the action of the high-saccharifying amylase of isolate 23. Equal amounts of inhibitor reduced by 48% the dextrinization rate of the amylase of isolate 23 produced either in corn thin stillage or on wheat bran.

The behavior of the amylases of isolate 23 derived from thin stillage and wheat bran were essentially identical with respect to saccharifying ability and response to inhibitor. For that reason it was considered that culturing in thin stillage had not affected the properties of the amylase.

DISCUSSION

The studies on production of bacterial amylase using thin stillage as a medium have several significant features. The relations found between pellicle production and amylase secretion are important. The formation of a pellicle appears to be a prime requisite for efficient production of amylase by the organism used. To utilize fully the capacity of this pellicle for amylase production, several techniques are practical. In addition to the customary shallow tray procedure, large volumes of nutrient liquid with relatively small surface area may be employed. To do this it is necessary to agitate the liquid in such a manner that (*a*) the amylase will be distributed through the body of the liquid, (*b*) fresh nutrients will be brought in contact with the pellicle, and (*c*) the pellicle itself will be relatively undisturbed and thus remain intact.

Further modification of the liquid culture procedure might well be the use of a method similar to that known as the quick-vinegar process. The nutrient liquid can be dripped onto wood chips packed into a vertical tower. Provision is made for preforming the pellicle on the surface of the chips and likewise for aeration.

A previous communication (*2*) demonstrated that amylase could be produced satisfactorily by culturing the organism on moistened wheat bran. A number of procedures are possible for this type of work. The utility of any one of them depends upon the facilities available and the product desired. A semisolid wheat bran medium has certain advantages as to speed of amylase production: Maximum activity was attained in 2 days as compared with 4 to 6 days for maximum amylase production in an undisturbed liquid medium. On the other hand, the rate of amylase production in a liquid medium can be greatly accelerated by replacement of the medium with fresh nutrient. Also emphasized is the fact that various natural materials have potential value as bacterial nutrients. In addition to the extract of hydrolyzed soybeans commonly used (*11*), neutralized thin stillage is a satisfactory medium and is available as an industrial by-product in large quantities.

It may be assumed that the type of amylase produced by a specific organism on all of these media will not vary appreciably. For example, when an extract of a dried wheat bran culture of isolate 23 was compared with a thin stillage culture of the same organism, the amylases produced had essentially the same properties.

From an industrial standpoint, the prime requirements would appear to be rapid production of a desirable type of amylase with a minimum of effort. The type of amylase is governed by the nature of the organism, and the quantity produced may be regulated by further selection to obtain better strains. Production features such as speed of turnover and the minimizing of contamination appear to be most satisfactorily achieved by the use of wheat bran. However, the production in liquid, either as customarily done or with one of the variants suggested, might meet industrial requirements with greater facility. Provided the importance of pellicle formation is kept in mind and the proper relation between the pellicle and source of nutrient is maintained, little difficulty should be involved in adapting any of these procedures in industry.

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(4) *Ibid.*, 1,227,525 (May 22, 1917).
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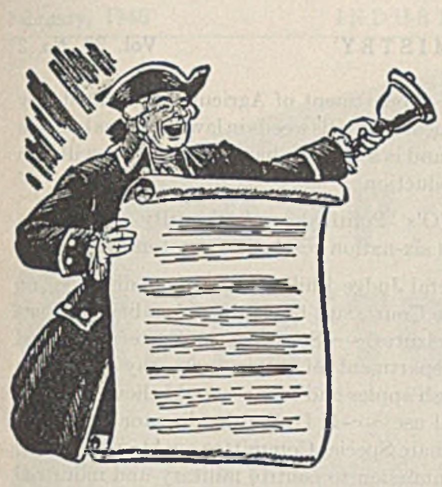
System of Distillation Equations—Correction

Attention has been called to a typographical error in my paper which appeared in the December, 1945, issue of Industrial and Engineering Chemistry. Equation 8 on page 1163 should read

$$G = \sqrt{(v - u)^2 + 4w}$$

The sign in front of $4w$ is, of course, plus rather than minus as printed.

W. D. Harbert



JANUARY'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ JANUARY 1. Herbert E. Smith, president U. S. Rubber, says rubber industry in 1946 expects to raise output to $1,500,000,000, a rise of 66% over 1939.~~Sun Oil Co. and Houdry Process Corp. develop methods for production in substantial quantities of carbon 13, and plan construction of two plants.~~Civilian Production Administration says demand for penicillin necessitates placing it under allocation.

¶ JANUARY 2. John D. Biggers, president Libbey Owens Ford Glass Co., says company is expanding its Plaskon plastics division and plans to invest $5,000,000.~~William H. Scott, president Aqua-sec Corp., says Alrose Chemical Co. has developed new finish for rayon said to reduce shrinkage and distortion to 1%.~~Sherwin Williams announces development of a new DDT concentrate, Pestroy.~~R. J. Dearborn, chairman Committee on Patents, NAM, says this year promises to be most critical for U. S. patent system.~~Shell Chemical Corp. incorporates in Delaware for purpose of taking over and continuing business of Shell Chemical Division of Shell Union Oil Corp. and will be a wholly owned subsidiary of Shell Oil Co., Inc.[1].

¶ JANUARY 3. B. F. Goodrich Co. breaks ground for new research center on 260-acre tract midway between Akron and Cleveland[2].~~Survey by M. W. Kellogg Co. shows that atomic research gives industry 5000 new products and techniques.~~George W. Merck, president Merck & Co. and special consultant on biological warfare to War Department, in report to latter sees germ warfare research vital to national defense[3].~~War Department reveals U. S. was prepared to combat and had surpassed Axis in poison-germ warfare.~~Board for Coordination of Malarial Studies, an arm of the Office of Scientific Research and Development, announces new drug, SN 7618, claimed to be superior to atabrine or quinine for malaria.~~Charles Seymour, president Yale University, warns of dangers of political control of universities in research or teaching and in annual report to 51,000 alumni says it would be disastrous if universities "scramble for the contents of a research pork barrel".

¶ JANUARY 4. Surplus Property Administration in report to Congress urges top preference be given to petroleum in disposal of Big and Little Inch lines.~~Department of Commerce, in report says vitamin oil trade in U. S. has grown into big business in 5 years.~~SPA reveals that U. S. will retain wartime patents, processes, and inventions indefinitely[4].~~National Wholesale Druggists Association and 23 member codefendants fined $87,000 for antitrust violations[1].~~Navy reveals details of death-laden mists developed during war in field of germ warfare.~~Miles A. Dahlen, assistant director technical laboratories of du Pont and just returned from government mission to Germany, tells American Association of Textile Chemists and Colorists I. G. Farben's work on dyes lags considerably behind U. S.

¶ JANUARY 5. AMERICAN CHEMICAL SOCIETY sets aside $210,000 for fellowships in chemistry from its ACS educational fund of $750,000.~~New science body formed in New York to coordinate Nation's scientific groups and associations into a central Federation of American Scientists so that technologists whose discoveries are revolutionizing the age can engage in a "more active political role".~~SPA accuses Aluminum Co. of America of obstructing disposal of government-owned aluminum plants to competitors.

¶ JANUARY 6. Aluminum Corp. tells Senator Mahoney, chairman Senate Military Affairs Subcommittee, that charges it had refused to grant licenses under its patents for benefit of operators of government plants were without foundation.~~Du Pont announces new series of research positions designed to make science as a career as attractive as the administrative field in industry.~~Maurice Holland, research adviser of New York, predicts 5-year manpower shortage of trained research managers and workers.

¶ JANUARY 7. Secretary of State Byrnes names special 5-member committee "to study the subject of controls and safeguards necessary to protect this Government" during the UNO atomic energy control commission study. Special committee is headed by Undersecretary of State Dean Acheson, and includes John J. McCloy, New York attorney and former Assistant Secretary of War, Vannevar Bush, James B. Conant, and Maj. Gen. Leslie R. Groves. Byrnes emphasizes that UNO commission will not have "authority to decide what information the U. S. or any government should place at its disposal".~~UNO General Assembly puts Senator Tom Connally on political and security committee which includes atomic bomb issues.

¶ JANUARY 8. International tin committee is organized[5].~~First tung oil shipment in 5 years arrives in San Francisco.~~Department of Commerce reports greatly expanded production of cinchona trees in India.~~George VI confers "most excellent order of the British Empire" upon six atomic energy research scientists.

¶ JANUARY 9. James G. Blaine, president Marine Midland Trust Co. of New York, at annual meeting of stockholders, says he is convinced atomic energy will prove greatest factor to insure continuing peace throughout world.~~Secretary of State Byrnes puts end to atomic bomb controversy within U. S. United Nations delegation and says no secrets of bomb will be given away without congressional approval.~~American-owned Trans-Arabian Pipeline Co. receives concessions to build 1000-mile oil pipeline across Palestine from Saudi Arabia to a Mediterranean port.

¶ JANUARY 10. Synthesis of biologically active vitamin A substances achieved by wartime research at Massachusetts Institute of Technology, Nicholas A. Milas, associate professor of chemistry there, announces at symposium on vitamins conducted by Northeastern Section, ACS.~~R. S. Reynolds, president Reynolds

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[1] *Chem. Eng. News*, 24, 236 (Jan. 25, 1946).

[2] *Ibid.*, 68 (Jan. 10, 1946).

[3] *Ibid.*, 229 (Jan. 25, 1946).

[4] *Ibid.*, 238 (Jan. 25, 1946).

[5] *Ibid.*, 234 (Jan. 25, 1946).

Metals Co., says company has leased world's largest aluminum plant at Hurricane Creek, Ark., with annual productive capacity of 1,555,000,000 pounds, and government-owned aluminum reduction plant at Jones Mill, Ark., 20 miles from Hurricane Creek[6]. ∼∼Aluminum Co. of America agrees to grant Government free use of all its aluminum production patents, SPA says[6].

¶ January 11. Vannevar Bush reveals details of efforts to synthesize penicillin under a $3,000,000 secret war research program.∼∼Justice Department says it will wait until competitors capture a significant share of aluminum market before easing its curbs on Aluminum Co. of America.∼∼Navy says cruiser *Prinz Eugen* will sail for U. S. over week-end to become "subject of study and experimentation", presumably for atomic bomb tests. ∼∼Navy releases official film "The Atomic Bomb Strikes".∼∼ Association of Manhattan Project Scientists and Association of N. Y. Scientists issue statement urging establishment by UNO of atomic energy commission to study international control.

¶ January 13. Reynolds Metals Co. leases government-owned aluminum extrusion plant in Grand Rapids, Mich.

¶ January 14. Attorney General Clark announces entry in U. S. District Court at Chicago of consent decree terminating civil antitrust suit against Wisconsin Alumni Research Foundation and 17 companies, and the freeing of vitamin D patents owned by foundation to public[6].∼∼S. D. Kirkpatrick, editor of *Chemical and Metallurgical Engineering*, says 7th award for chemical engineering achievement will be shared by approximately 100 companies, universities, and research organizations for their contributions to atomic bomb project.∼∼Maurice H. Lockwood, Eastern States Farmers Exchange, in address before Connecticut Valley Section, ACS, says enactment of three bills now before Congress would launch Government on paternalistic policy involving it inextricably in fertilizer business.∼∼American Association for Advancement of Science announces establishment of George Westinghouse Science Writers Award Fund to give national recognition to newspaper writers and newspapers contributing most to better popular understanding of achievements of science and technology.

¶ January 15. Committee on Fertilizers of Combined Food Board, in report to Department of Agriculture, predicts a million-ton world shortage of fertilizer.∼∼SPA recommends liberal leasing arrangements for the government's $233,000,000 aviation gasoline plants to private operators.∼∼P. W. Litchfield, chairman of board, Goodyear Tire and Rubber, says company plans $3,000,000 plant for conversion of vinyl chloride copolymers and other resins into films and sheets and a $1,000,000 Chemical Products Division Development Laboratory[6].

¶ January 16. SPA says government-owned synthetic rubber plants will not be sold until a national rubber policy has taken specific form.∼∼Owens Corning Fiberglas Corp. buys 35-acre industrial property in Kansas City, Kans., from RFC for plant expansion.∼∼Universal Oil announces it will help develop and establish a modern petroleum refining industry in China.

¶ January 17. Soviet Academy of Science, at annual meeting, demonstrates electron microscope which magnifies 50,000 times.

¶ January 18. Association of Los Alamos Scientists sends atomic bomb exhibit to mayors of 42 cities.∼∼Soviet Union calls on members of United Nations to accept Big Three's Moscow resolution on atomic energy.

¶ January 20. RFC says natural rubber is moving steadily to U. S. from French Indo-China.∼∼Big Five group in UNO meets in London on formation of atomic energy commission.∼∼ Americans United for World Organization make public statement by Association of Oak Ridge Scientists declaring no foolproof system of atomic bomb control and inspection is possible without world law.∼∼Department of Agriculture scientists say new hormonelike chemical that kills weeds in lawns, ripens bananas after they are picked, and is a boon to hay fever victims will soon go into large-scale production.

¶ January 21. UNO's Political and Security Committee unanimously approves six-nation resolution on atomic energy.

¶ January 22. Federal Judge Phillip L. Sullivan dismisses, on order of U. S. Supreme Court, suit to establish legality of Montgomery Ward plant seizures.∼∼Scientists at Eastern Regional Laboratory, U. S. Department of Agriculture, say they have bottled essences of fresh apples and tobacco and believe they will have large commercial use.∼∼H D. Smith, director Bureau of the Budget, before Senate Special Committee on Atomic Energy, recommends single commission to control military and industrial application of atomic energy and approves McMahon bill.

¶ January 23. J. R. Dunning, director Columbia University's division of war research, says Oak Ridge, Tenn., plants for making atomic bomb have become "technically obsolete" by development of new techniques.∼∼Secretary of Navy James Forrestal, testifying before Senate Special Committee on Atomic Energy, urges that no powers be given to the President to remove members of Atomic Energy Commission and asks that the Vice President, and the Secretaries of State, War, and Navy be added to commission as ex officio members.∼∼Secretary of Interior Ickes announces award of $249,000 contract to Girdler Corp. for designing, erecting, and placing in initial operation plant for production of hydrogen and synthesis of gases at new synthetic liquid fuels laboratory under construction by U. S. Bureau of Mines at Bruceton, Pa.

¶ January 24. UNO unanimously agrees to establish commission to study control of atomic energy.∼∼Admiral Blandy, deputy chief of naval operations for special weapons appearing before Special Atomic Energy Committee, discloses that tests of air-borne atomic bombs will be conducted against 97 ships at the Bikini Atoll in the Marshall Islands next May and July.

¶ January 26. Navy Department's Office of Research and Inventions begins wide program to encourage scientific research by financing research in colleges.

¶ January 27. National Bureau of Standards says ceramic heat-resistant coatings promise important peacetime applications.∼∼Hugh Cabot Memorial Fund announces plans to erect $2,000,000 penicillin research laboratory in Russia through voluntary contributions of U. S. citizens.∼∼War Department says 17 chemical experts who served as Chemical Warfare Service consultants and members of an industrial intelligence team in surveying German chemical plants have been given certificates of appreciation.∼∼Association of Manhattan Project Scientists endorse McMahon bill, S1717.

¶ January 28. State Department announces completion of price negotiations for purchase of natural rubber from British, Dutch, and French areas in Far East at $20^{1}/_{4}$ cents a pound.∼∼ U. S. Department of Agriculture announces that rutin, a drug with medicinal values, is ready for full-scale production for first time.∼∼Prime Minister Attlee says British Government has requested that its representatives observe atomic bomb test in Pacific.∼∼Harrison Davies, of atomic bomb project, tells Senate Special Committee on Atomic Energy that military men should be excluded from policy-making functions on proposed commission.∼∼Secretary Byrnes says President Truman agrees United Nations Atomic Energy Commission should be invited to observe atomic bomb tests in Pacific.

¶ January 30. Captain Eddie Rickenbacker urges bombing of Antarctic to get mineral deposits.

¶ January 31. President Truman gives approval for early substitution of civilian control for existing military guardianship of development and uses of atomic energy in U. S.

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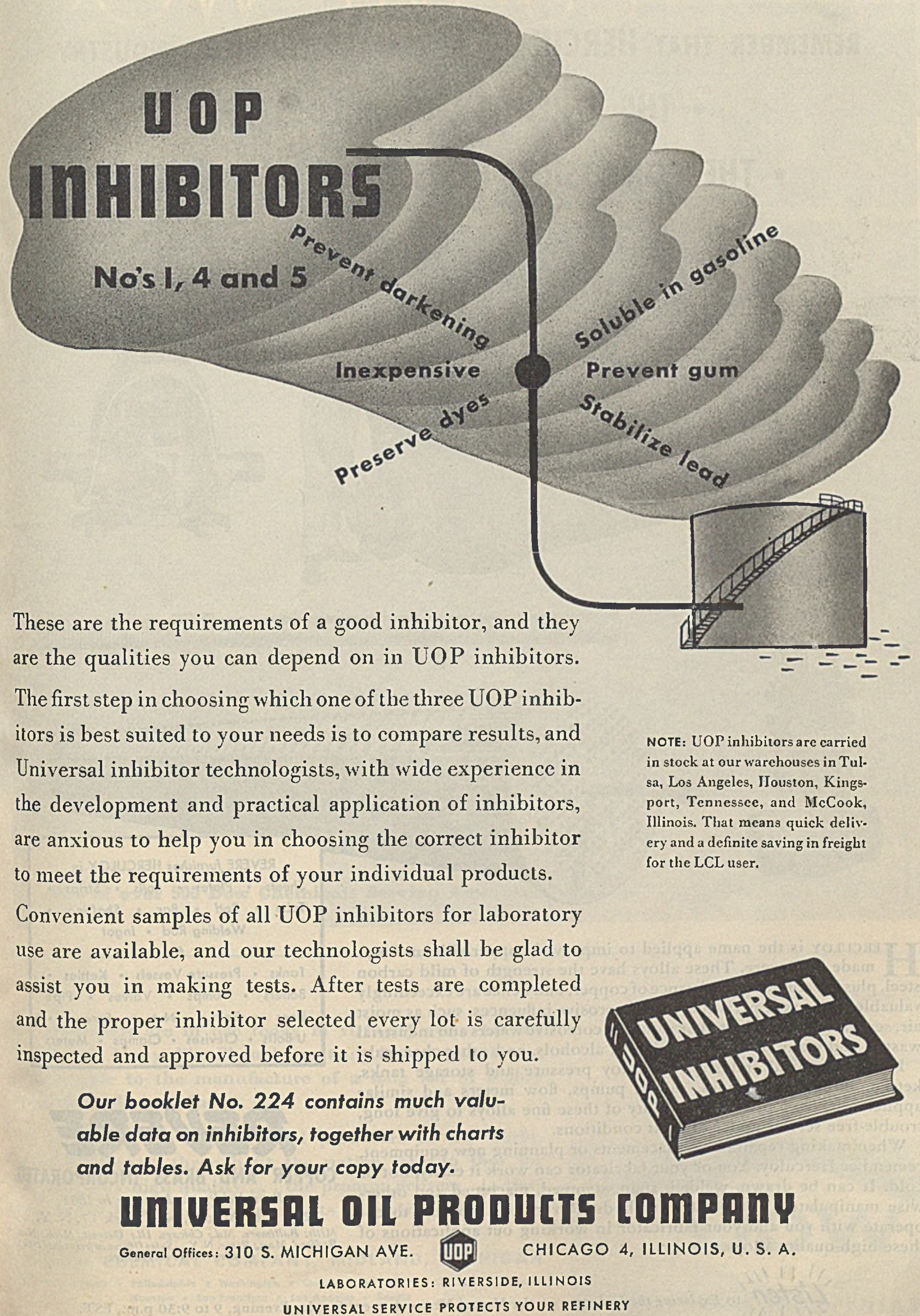
[6] *Chem. Eng. News*, 24, 233 (Jan. 25, 1946).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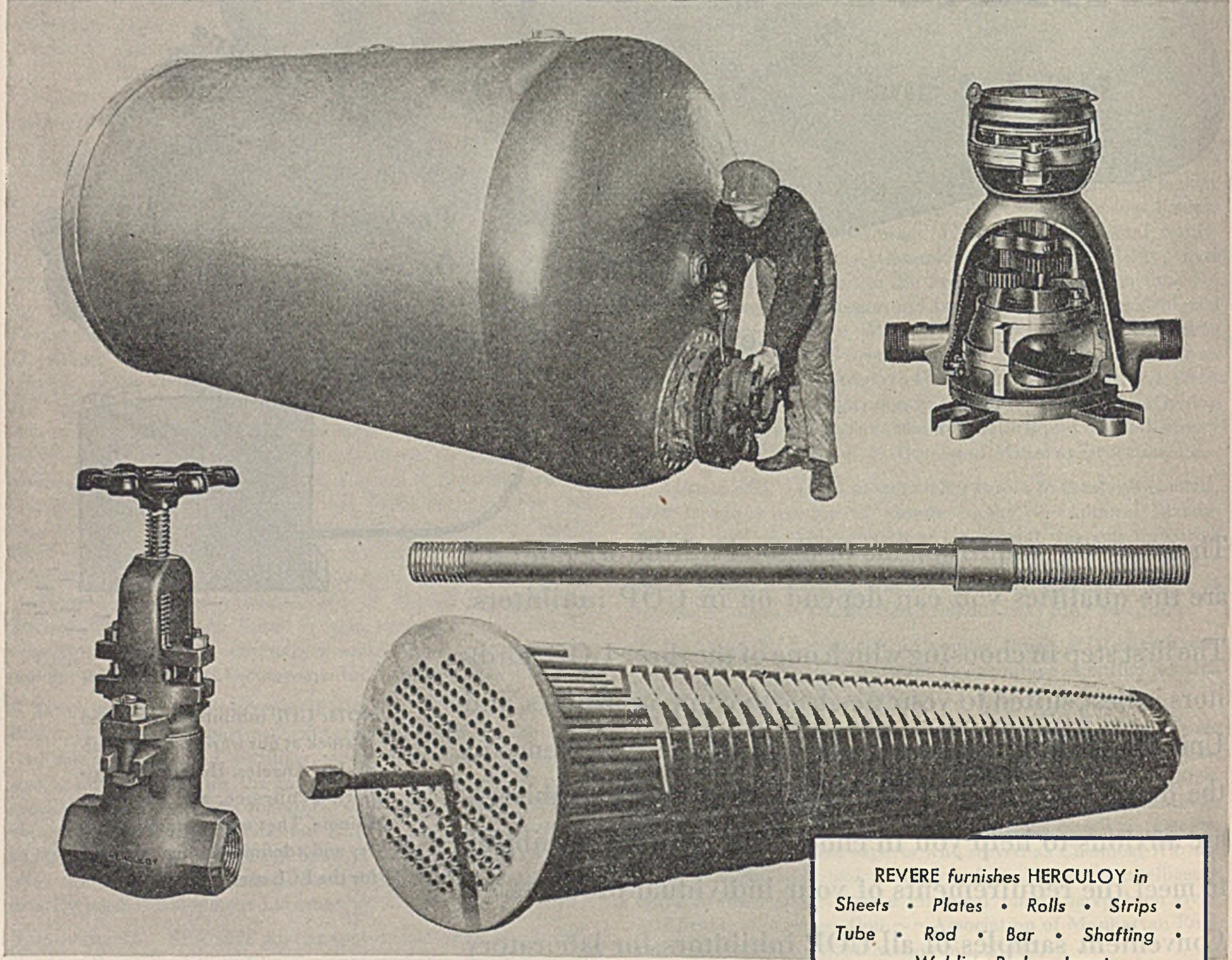
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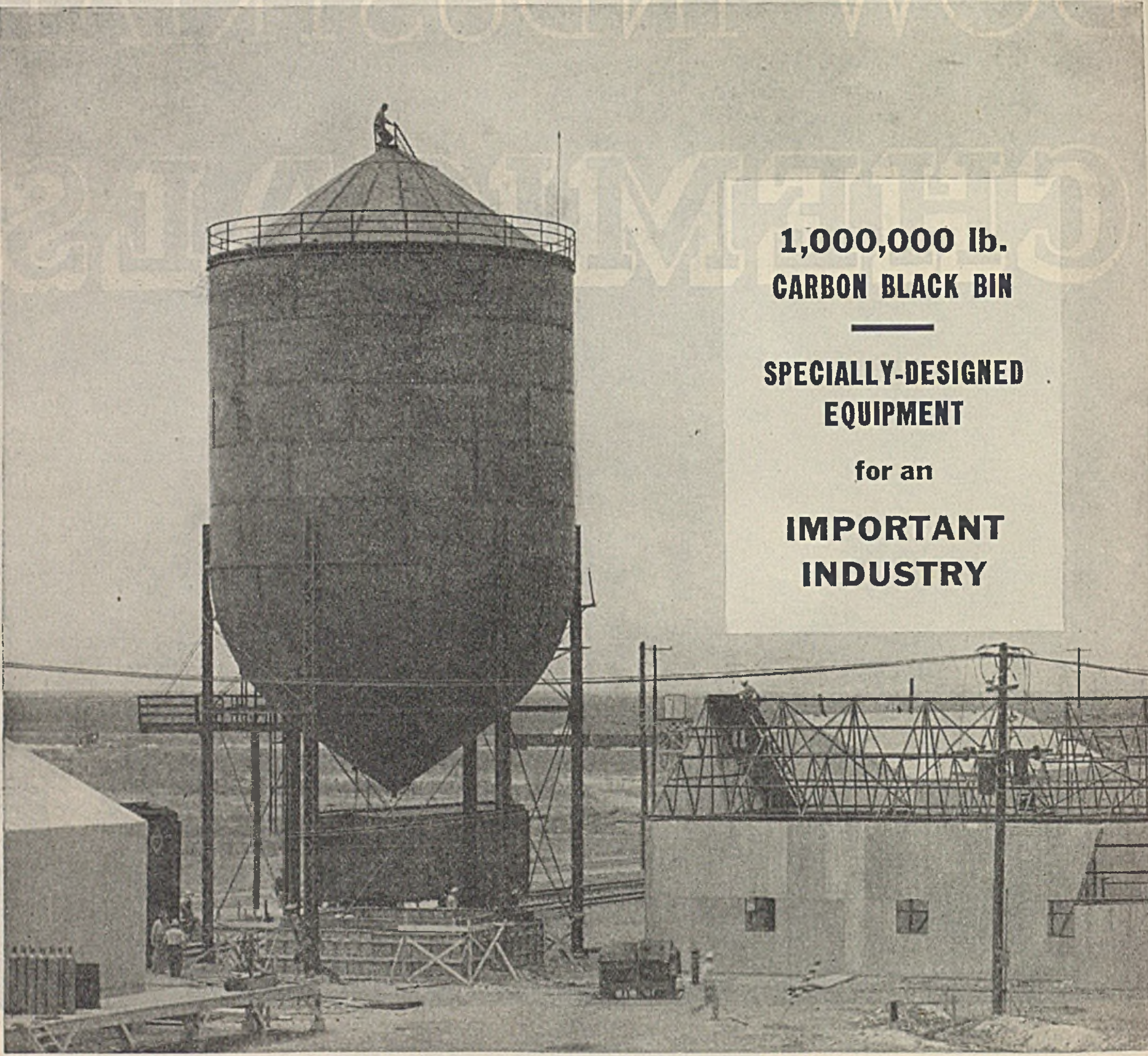

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Current Developments in
EQUIPMENT AND DESIGN

Advantages of two types of contract for use in construction of new plants.

Discussed by Charles Owen Brown

Two types of contract can be used to guide the construction of a new plant, especially one in the chemical field. In the first, an equipment manufacturer may be asked to design a plant, make the calculations and drawings, fabricate or purchase all the equipment, prepare a site, construct the plant, and finally test it and put it into operation. This method is sometimes called "a turnkey job". The second type of arrangement is for a company to use its own technical staff to investigate and specify process details and, possibly, use the services of a specialist to obtain the latest improvements. Design calculations and drawings are then made under the supervision of or by the company's technical staff, and purchasing is done on regular schedule by the company's agent. Plant construction is placed with an engineering firm or contractor on a competitive basis. Construction is supervised by the company's engineering staff, which follows through into testing and starting operations as the plant units are completed.

Turnkey Contract

Executives and directors are asking, What are the advantages of these two widely differing methods of construction? There are many considerations, for and against both plans. A brief analysis of the turnkey arrangement must first take into account the fact that relatively few processes are offered by equipment manufacturers on this basis. Although past experiences have not been too satisfactory, there is a strong tendency at present for equipment firms to extend this type of service to a larger number of processes. Plants producing products which require one or two unit operations or plants to perform a unit process are examples of the turnkey method. The production of caustic soda by the lime-soda process is among the most popular of the turnkey jobs. A complete blast furnace, which is often built on this type of contract, is not a good example because so much of the equipment is nonchemical, heavy, field construction. Complete plants for phosphoric acid, acid phosphate, and rubber compounding are better examples.

Many features must be considered before contracting for a turnkey job. "From raw material to plant in operation" includes a large number of major and minor studies. If a raw material problem is present, the skill, experience, and testing facilities of the equipment manufacturer will play a critical part in efficiency and production costs. If a special condition is involved in working up the raw material, it may be handled best by equipment designed around the problem, rather than by use of somewhat larger standard units. When plant design is reduced to a production basis, flexibility and efficiency in working up special raw materials are lost. Standardization reduces progress on improvements and is effective in reducing first costs only in cases where a large number of plants can be built at once. Individual pieces of equipment or machines built in large numbers profit most from standardization. In a complicated chemical process it may actually penalize the project.

Two plants for the production of fermentation products, one in the Gulf Coast area and one in New England, would operate in atmospheric temperatures varying, on a cumulative annual basis, from 8000° to 8500° F., with a corresponding acceleration for the southern plant. The average cooling water temperature is approximately 23–25° F. greater in the South, which increases the required cooling and condensing surfaces. Cold water is easily recovered in New England where humidity and dew points are more favorable throughout the year; but in many localities a cooling tower need not be included as the water from the tower is not so cold as new water. Operating labor conditions have an influence on plant design. Recently two similar plants making the same output of the same products were compared. One used 2.85 man-hours per ton, and the other, 3.64. The second plant should have been instrumented for efficient and automatic operation as far as possible. These important factors are strong considerations against too much standardization. There is little hope that turnkey jobs can become economical except where the processes are materially benefited by standardization of plants.

Testing-and-Starting Period

On completion of any plant, large or small, a chaotic but important testing-and-starting period follows. On a turnkey job this work would be done by the equipment manufacturer as prime contractor. Just how thoroughly the over-all performance can be proved is probably governed by the terms of a guarantee. If the client has a representative present from his own operating staff, it is a necessary duplication of personnel, mostly for educational purposes. The experience gained will probably be that definite knowledge needed to make a satisfactory product at guaranteed output. What the plant really can do and what the most desirable operating level is may not be known for a long time, because any organization will at first follow the operating practices recommended to it by the contractor. The most desirable methods of operation may not be known until they are revealed by experience.

It is impossible to predict just how much time and expense will be required to test and start a turnkey job. Some clients are anxious to get into production to meet contracts, some are very reasonable and make many allowances, but sometimes a client is exacting. These indefinite factors, or risk, must be estimated, and the lump sum loaded to take care of such contingencies. This is expensive for the real owner. Turnkey jobs are most useful to the client who does not have the personnel and staff to supervise this operation.

In any turnkey project the prime contractor or equipment manufacturer must handle all the auxiliary items connected with the job. For example, handling equipment for raw material, which is always highly specialized, may be quite foreign to the background talents of the

(Continued on page 72)

Equipment and Design

contracting organization. On a small job now under construction, it is necessary to handle and charge 500 tons of random wood logs per day. The cost of this equipment was of the order of 2.5% of the total plant equipment, but specifications and engineering of this one item were a much larger portion of total engineering costs. This equipment—the first to be required for operations—was actually the last to be purchased because of the many problems involved. On projects where ordinary buildings are required, someone must detail the building, the heating and plumbing, the ordinary power and lighting electrical work, and finishing, painting, and even furnishing of offices, laboratories, and special rooms.

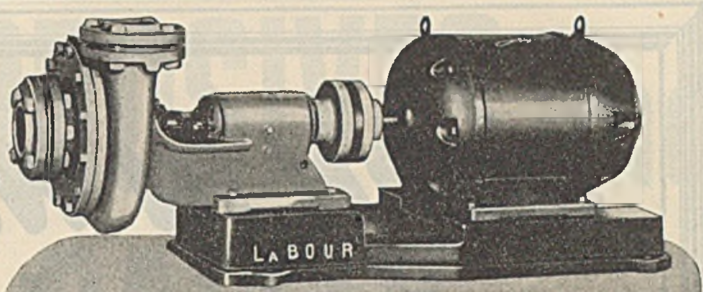
These trades and arts are quite different from the usual equipment fabrication and plant construction. It would be expensive, both in time and money, for an equipment manufacturer to maintain the talent qualified to handle these special features. The cost of their work, including overhead, would average more than the cost of the work done by the client directly with these specialists and perhaps would be less satisfactory. A firm offering turnkey jobs must be very large, with a number of jobs active all the time, in order to justify such a staff of specialists. It might be easy to make a profit on the manufacture of equipment and lose it all in overhead necessary to provide the "trades" and "special features" in a turnkey job. Designing and detailing of light steel walks, stairs, supports, and ladders are often let out to specialists in that line, even by the large engineering firms.

Staff Development Contract

What is the alternative to a turnkey job for the medium sized or small chemical company? Briefly, it is to do the development work with its own staff and sufficient consultants to cover the specialties. After satisfactory specifications are drawn, the entire construction may be let to an engineering firm on a competitive basis. There are some advantages to this program. Special raw material problems can be given intensive study before any commitment for a plant is required. Information acquired in this study can be protected and retained by the company proposing to build the plant, with less possibility that it may ever be used to assist a competitor to enter the same field. Plant designs can be made to fit exact specifications and basic requirements of the client.

Equipment is usually purchased from several manufacturers by a client or by a general engineering firm on a competitive basis, so that the most attractive design, lowest cost price, and best size or shape factor can be chosen. The latest available improvements in equipment, processes, and operating methods can usually be obtained from consultants. After quotations and performance data have been received for the major pieces of equipment, a preliminary estimate of operation costs can be made. This interim study is an important and helpful guide to proper plant design. It is a more logical basis for selecting the size and number of units and the amount of spares, than to take a so-called standard unit which is most conveniently made by the manufacturer. A rough estimate of operating costs may reveal that a major piece of equipment or unit operation can be modified and give better performance.

In the later stages of construction the client's operating staff takes over the testing and starting. This method usually results in better knowledge of possibilities. More data are collected without duplication. Actual knowledge of performance can be retained by the client.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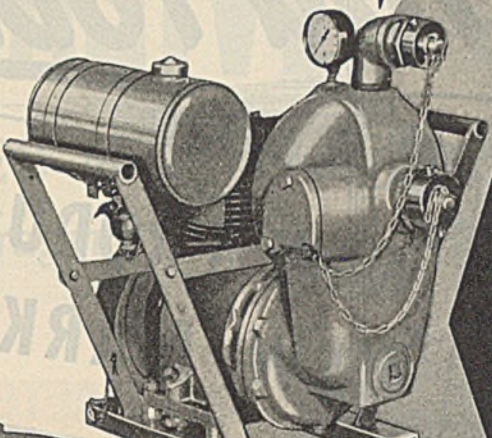

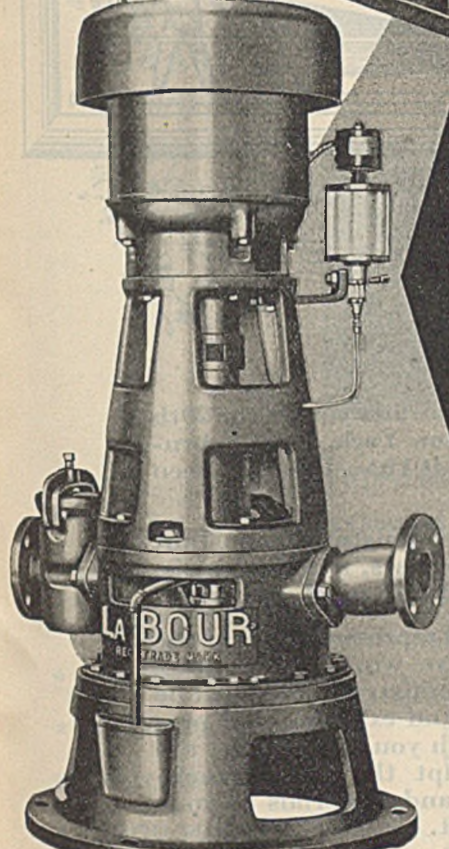
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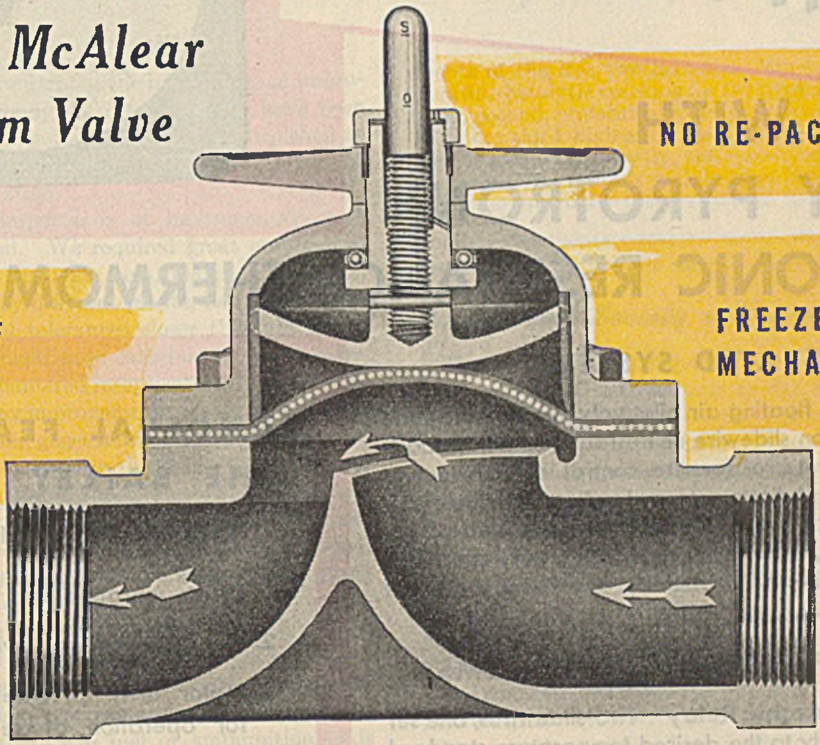
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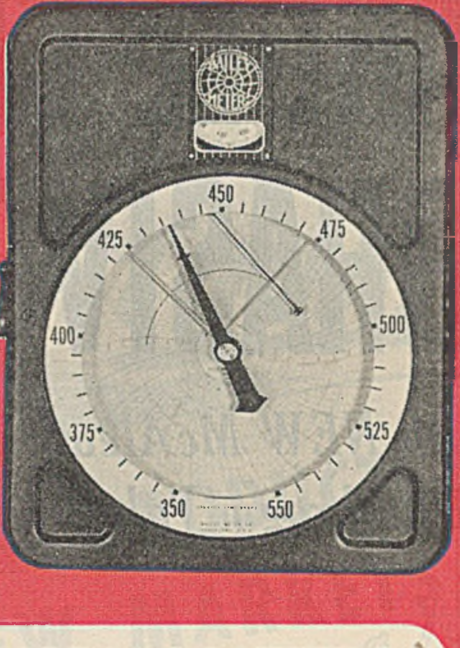

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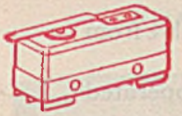

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Current Developments in INSTRUMENTATION

The Instrument Society of America sponsors education in the field of instrumentation.

Discussed by Ralph H. Munch

THE recent war effort demonstrated the importance of instrumentation more convincingly than it could ever have been done during peacetime. Tremendous impetus was furnished to the development of both the measurement and the automatic control aspects of instrumentation.

Many examples of the importance of instrumentation in winning the war can be cited. We required great numbers of complex mechanical devices such as guns, planes, and tanks. Parts for these, made in many different plants, had to be interchangeable, with dimensional tolerances closer than the metal working industries had previously been called on to meet—tolerances approaching those encountered in optical work. To check dimensions of such parts, many improvements in gaging technique were developed. Plug and ring gages made of synthetic sapphire are one of the interesting innovations in this field. They are said to have a useful life seven thousand times that of steel gages and twelve hundred times that of hard carbide gages. Electronic devices for measuring surface irregularities came to be essential tools in industries producing fine surface finishes. These measure irregularities as small as one micro inch.

In the design of such combat material, efficiency, ease of production, and low cost are of vital importance. A plane, gun or tank designed with too large or too small a safety factor, resulting from ignorance of true operating stresses in its parts, loses maneuverability or carries less fuel or ammunition or is less safe than one designed with the optimum safety factor. Therefore it is a less efficient weapon. The instruments used in experimental stress analysis have enabled our engineers to design the most efficient mechanisms possible with the materials at their disposal. The wire-type strain gage, one of the most important of these instruments, makes possible measurement of strains from a few micro inches per inch to 0.001 inch per inch. The photoelastic and brittle coating methods also proved of great value.

There has been, in addition, a great deal of instrumentation with direct military application such as radar, fire control equipment, bomb sights, automatic pilots, and navigating instruments. An interesting example is the fire control system of the B-29 superfortress. In this plane the gunners are stationed inside the pressurized cabin. Remote electric controls train the guns in the five turrets in the direction the gunners aim them. In addition, automatic computing equipment makes proper allowance for relative motion of plane and target and compensates for effect of wind and gravity on the bullet and for the difference in position of gunner and guns.

Increased use of instrumentation has enabled the process industries to meet the demands made on them during the war for increased production of more uniform materials in spite of less skilled labor and a minimum of equipment. Bradley Dewey, rubber director during the war, said in his speech accepting the Chemical Industry Medal:

> The synthetic rubber industry could not have been built without a tremendous utilization of our great technological developments of the last two decades. These were: First, high-temperature catalytic cracking for the production of monomeric materials; second, prefabricated welding of piping or steel, field welded in place; third, high-alloy steels for superheating hydrocarbons as well as steam; and lastly, the control of temperatures, pressures, and the flow of fluids within close limits by automatic control valves actuated by remote control instruments.

Similar statements could be made about the aviation gasoline program and the organic chemical industry in general.

Instrument Society of America

The increased importance of instrumentation has attracted a large number of new workers to the field. The examples just cited show that they came from many industries, each with its own specific type of instrumentation. These instrument engineers soon realized that they had much in common in spite of the apparent diversity of interests. In the past few years instrument societies were formed in most of the centers where there were enough interested workers to support them, about twenty in all. Efforts extending over the past year or so have recently culminated in the organization of these groups into the Instrument Society of America.

The objectives of the society are to advance the arts and sciences connected with the theory, design, manufacture, and use of instruments. Membership is open to any person interested. At present the membership is made up largely of those associated with instrument manufacturers, either as designers or as sales engineers, and of those who supervise installation and maintenance of instruments for large users of instruments, along with small groups from colleges and universities. The formation of this organization presents chemists and chemical engineers who have an interest in instrumentation with an opportunity to increase their knowledge of the subject. They would also be able to contribute to the effective use of instruments in the organizations to which they belong, because too frequently those in charge of instrument work in chemical companies have little knowledge of the chemistry involved in the plants they serve. What is needed is a mutual appreciation of the other group's problems by chemists and chemical engineers, on the one hand, and instrument engineers on the other. Only through such understanding and cooperation between these groups can the most benefit be gained from instrumentation.

Education in Instrumentation

One of the most important objectives of the society is to further education in the field of instrumentation. Its first major effort in this direction was to sponsor, in cooperation with the Carnegie Institute of Technology, a Conference on Instrumentation and the University, held in Pittsburgh from October 16 through 18, 1945. The objective of this meeting was to provide an opportunity for those who employ instrument engineers to meet with educators so that the two groups could exchange views on what an instrument engineer

(*Continued on page 78*)

Instrumentation

should learn in school and how the subject can best be taught to the student.

The general opinion of speakers representing employers of instrument engineers was that the graduate seeking a position as instrument engineer should have come in contact with and have some understanding of the more important types of instruments used in the industry he seeks to enter. For instance, in the process industries he should have some knowledge of flow measuring by means of differential pressure-orifice meters of the type commonly employed in plant practice. Actual experience in taking apart, reassembling, calibrating, and installing commercial instruments was advocated as the most effective means of acquiring a good understanding of these devices. Instruction of this nature was recommended, not because of a desire to make maintenance men of engineers, but to give a better understanding of the principles of the instruments and of the precautions necessary to make them function accurately in use.

Recommendations for Courses

Throughout this conference the overcrowded state of curricula of engineering schools was emphasized by representatives of both industry and education. Many suggestions were made as to means by which suitable instruction in instrumentation could be included without making this bad situation worse. One school which includes instrumentation in its mechanical engineering curriculum made room for it by dropping a highly specialized course of less general interest. This was done because it was recognized that instrumentation is a fundmental subject. Another possible method of approaching this problem is to choose subject matter for lecture and laboratory work in other scientific and engineering courses so that the principles of instrumentation are brought out, along with the primary objectives of the courses. Faculty members of another large university made a survey of their engineering curriculum and found that the only way they could include more "humanistic" courses and at the same time more courses in specialized engineering subjects such as instrumentation would be to omit some of the fundamentals or to increase the length of the course. They adopted the latter alternative, increasing the program to five years.

The Instrument Society of America is interested not only in the establishment of courses in instrument theory, design, application, and testing as parts of the curricula of technical schools but in providing educational opportunities for those already employed in the field. To serve this need, a number of short intensive courses covering the use and maintenance of particular types of instruments are visualized. Such a course would consist of four or five days of intensive practical instruction. It has been suggested that they might be given at one or more universities with the aid of the various instrument manufacturers. Another opportunity for the instrument man who is already employed could be provided through correspondence courses.

It is to be hoped that the many educators who attended this Conference on Instrumentation and the University will be able to find a place in their already crowded schedules for courses in instrumentation. It seems that all chemists and chemical engineers would find a survey course in instrumentation of great value. Those with a special interest in the field should be able to take more advanced work in instrumentation and automatic control. If, as a result of this conference, such courses become more available to chemists and chemical engineers, it will have done a great deal to advance the science of instrumentation.

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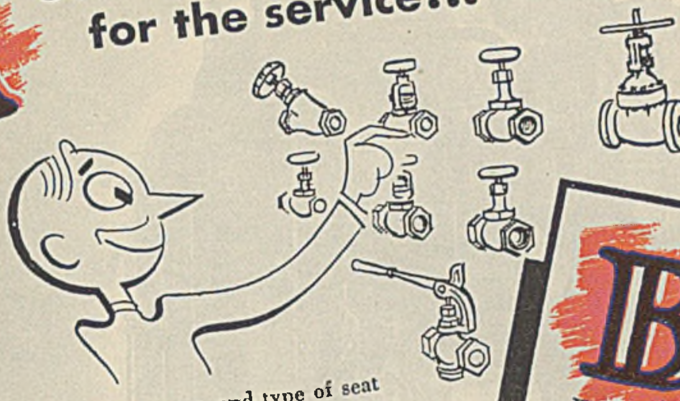

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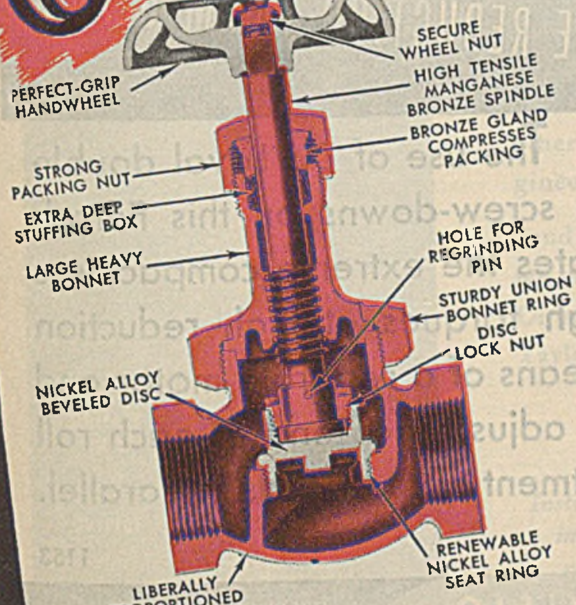

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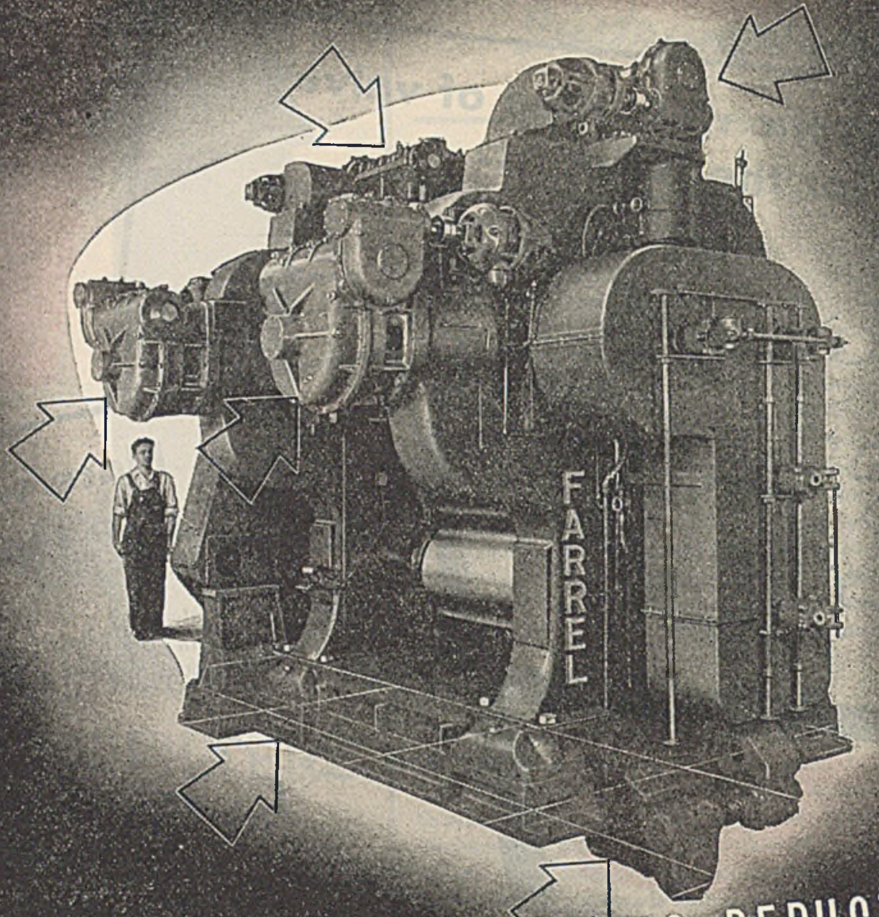

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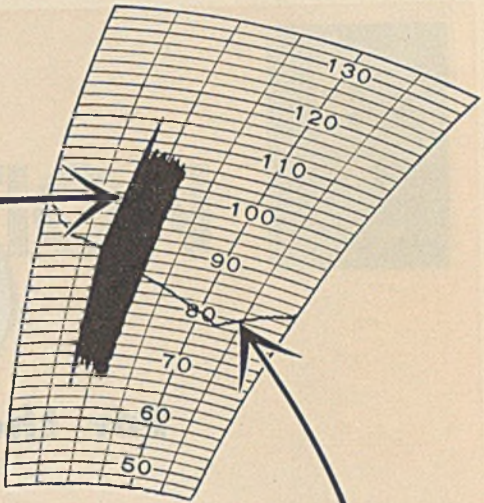
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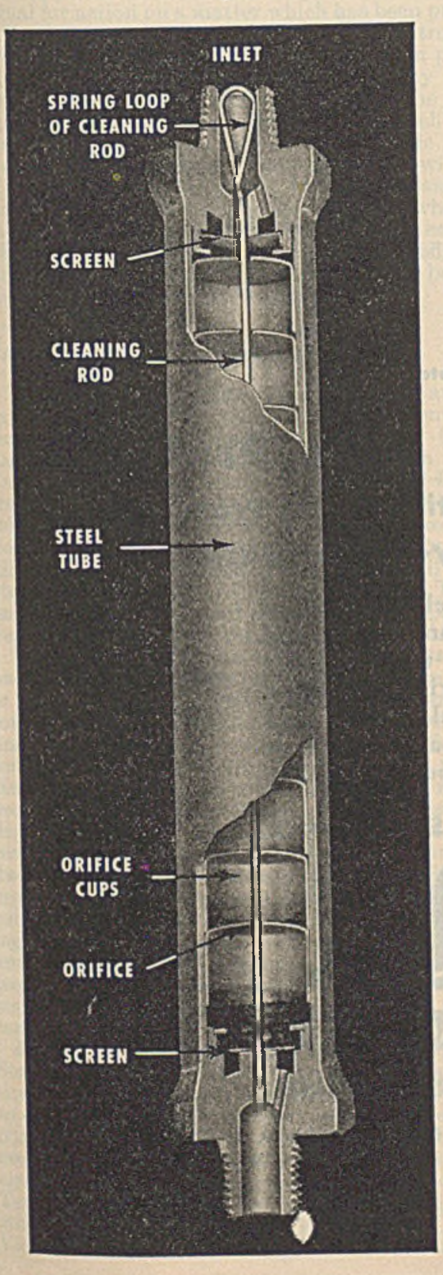
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Current Developments in
WASTE UTILIZATION

Cooperative study of inter- and intraindustry pollution problems yields far better results than independent efforts.

Discussed by Harold R. Murdock

Nothing is more fundamental than the right of the people to have the public streams from which they draw their water supply, free from pollution. That right is supreme, for the simple reason that health and life itself depend upon it. The people have the absolute right to have the 'ancient purity' of their streams preserved against all other considerations." This decision of the Court of Common Pleas of Philadelphia County, Pa., concerning the alleged pollution of the Schuylkill River is a frank and fearless statement which summarizes the general attitude of public authorities throughout the United States. It is a signal for action on a matter which has been put off too long.

Until recently most industrial plants troubled with waste products have attempted to solve pollution problems independently. They have been successful in many cases. But in the larger industries it is now realized that the fundamental principles are similar for all plants within each industry. Consequently various organizations, both public and private, have been created to study pollution difficulties with a national point of view. These groups have established basic principles necessary to a clear approach to the problem, which could not have been developed from an individual study of each plant operation. These efforts, which will be discussed briefly, are highly commendable. For the sake of clarity they can be divided into interindustry and intraindustry objectives.

Interindustry Activities

Technical societies have held symposia and many editorials have been written to point out the salient principles in the technology of utilization and disposal of trade wastes. The American Chemical Society, American Society of Civil Engineers, American Society of Mechanical Engineers, and Federation of Sewage Works Associations have been outstanding in this respect. Some universities have realized the serious situation which exists. For instance, in 1945 Purdue University initiated a two-day meeting of experts from all parts of the United States for discussion of industrial wastes. The meeting was so successful that the second Industrial Waste Conference at Purdue was held last month with a galaxy of experts in attendance.

Throughout the nation, state departments of health, sanitary water boards, and water control agencies are working vigorously to make sure that stream pollution abatement receives proper consideration in postwar planning. The State of Pennsylvania has been outstanding in such efforts. Earlier conceptions were confined to laws on purity of waters for the protection of Public Health. Now the point of view includes not merely public health protection but also the demand that streams "shall be free from discharges harmful to animal and aquatic life or to their use for recreational purposes". The Sanitary Water Board has conducted a series of ten hearings throughout the state, to afford an opportunity for interested parties to present their views on the subject. This board has reached a final decision, and "is preparing to issue orders to those responsible for the discharge of sewage and industrial wastes, informing them of the degree of treatment required before discharge into the waters of the state, and requiring the preparation and submission of plans for the treatment of same".

Illinois is proceeding along similar lines. In Michigan the State Department of Health and State Stream Control Commission are working closely with the State Postwar Planning Board to ensure inclusion of necessary pollution abatement projects for postwar. New York is carrying out similar programs with excellent results. Many states are handicapped because no agency is adequately empowered to control stream pollution. Tennessee recently enacted into law a plan based on thorough study which is basically the Pennsylvania method. Colorado, Virginia, Maryland, and many other states are collecting data for the drafting of effective legislation. Reluctant industries will eventually be forced to meet the requirements of the state.

Many state pollution control agencies are sponsoring or conducting valuable joint research on pollution of streams which run through more than one state. New York, New Jersey, and Connecticut have established an interstate commission which governs the pollution of New York Harbor and adjacent waters. Delaware, Pennsylvania, New Jersey, and New York have set up a similar commission to control the Delaware River. The watersheds of the Potomac, Ohio, and Red Rivers have been investigated by study groups empowered with interstate agreements. The Upper Mississippi Board of Engineers, comprising Minnesota, Wisconsin, Iowa, Illinois, and Indiana, are conducting joint scientific studies of industrial waste problems. Such governing bodies have capable scientists searching for ways and means of abating this national problem.

An excellent example of cooperation between state and industry is found within the beet sugar industry, which was born about 1900. Many complaints of the killing of fish in streams polluted by beet sugar wastes were registered as early as 1906. In 1910 studies resulted in the construction of pulp drying equipment at all beet sugar plants in Michigan. In some of the plants screening and sedimentation equipment were provided. In many cases these units were effective, but some fell into disuse because they were too small. When the Michigan State Planning Board was organized in 1929, surveys were made in cooperation with the Michigan State College Engineering Experiment Station, which resulted in the erection, in 1935, of a 100,000-gallon-per-day experimental unit at one of the sugar plants. Further studies were made in 1936 with a 1,000,000-gallon-per-day plant. On September 21, 1937, a general order was formulated by the commission which established standards of oxygen demand for such plant wastes. During the next three years various firms proceeded with the construction of waste disposal plants. These standards set by the commission for beet sugar plants waste have been substantially met, and the nuisance has been abated.

Intraindustry Activities

In passing from individualized and small group research on manufacturing wastes and stream pollution to an integrated national program, the pulp and paper industries have set the model for others. Earlier the American Iron and Steel Institute had made a concerted attack upon the single problem of waste pickle liquor disposal by establishing at Mellon Institute in 1938 a fellowship which was subscribed by the entire steel industry. Other industries have cooperated in the study of specific problems, but the pulp and paper industry appears to have been the first to establish an incorporated company entrusted with the general study of pollution problems within the industry.

The National Council for Stream Improvement Inc. (of the Pulp, Paper and Paperboard Industries) includes within its membership over 80% of the total pulp, paper, and paperboard production of the United States. Adequate financing is provided by an annual budget of $150,000 to which might be added an equivalent amount now expended on existing regional projects. These sums, according to information given out by this organization, are exclusive of expenditures for work carried on by individual mills concerning problems peculiar to their plants. The plan of action which is now being made effective appears to have been skillfully conceived in order to be acceptable to all responsible bodies concerned in the disposal or utilization of wastes from this industry. The pattern should be of definite help to other industries in coordinating their own disposal problems.

The first step was to bring together the technically qualified groups interested in stream pollution within each regional area for agreement on courses of action.

(*Continued on page 84*)

Waste Utilization

The following groups were considered interested agencies: pulp, paper, and paperboard industries; other industries; pollution control agencies; resource, conservation, and development agencies; research organizations; and water control bodies.

Seven regional committees have been created whose membership consists of representatives of executive and technical capacity empowered to speak for their companies. These men were selected to represent all products manufactured in the region, as well as each watershed area containing this industry. Through meetings of these committees, together with the council's staff and interested agencies just listed, a firm foundation for cooperation has been established in each region. The function of the regional committees is to assemble, with the aid of the council's technical staff, research and experience of individual companies relating to waste treatment, recovery, and utilization. These data will be helpful to some mills where immediate application of this information can be made. It will also be effective in preventing duplication of effort and investment in unsuccessful devices. The regional committee will also be responsible for the assembly of problems for the research fellowships established in various organizations selected by the council. It will also designate the priorities for these several problems within the region. When decisions are reached, it becomes the duty of the council's staff to provide ways and means for getting the work done.

The geographical distribution of the industry and the multiplicity of waste and stream problems required that research projects be spread throughout the country. However, a centralized research organization appeared essential for the study of those problems of wide interest to the industry and to serve as a contact group with other industries. Mellon Institute was selected to serve in this capacity. The first assignment of this group, according to information published by the council, was to review published literature and prior art on the treatment, recovery, and utilization of pulp, paper, and paperboard wastes with regard to modern technology, and to submit a series of reports containing summaries of such work for each class of wastes, including recommendations for lines of further study. The council believes such data will serve as a basis for decisions relating to other research projects.

The council has also entered into an agreement with The Institute of Paper Chemistry regarding maintenance of a complete bibliography on pulp and paper wastes. Such information is to be made available to all research groups within the council's membership. The council has taken over the activities of the Sulphite Pulp Manufacturers Committee on Waste Disposal of Wisconsin relative to waste disposal. The research activities of this Wisconsin group during the past six years have been conducted by The Institute of Paper Chemistry. Such studies will continue at this well-staffed organization but under the supervision of the National Council for Stream Improvement, Inc., which has agreed to finance the work. The utilization phase of the Wisconsin studies will continue at The Institute of Paper Chemistry under the supervision of the original Wisconsin group. Published data relative to this utilization study of waste sulfite liquor indicate an aggressive approach by scientific investigation toward utilization of this specific waste by unique processes.

An important phase of the council's activities is the study of streams and determination of the relative responsibility for pollution of the pulp and paper industry, municipalities, and other industries on the watersheds concerned. It must be determined what degree of abatement shall be provided by each mill in order to place the receiving waters in satisfactory condition for the uses required of each stream. The Council has established a project at Manhattan College, under supervision of the Civil Engineering Department, to make such studies of individual stream conditions under consideration by the regional committees.

The priority of regional projects supported by the Council is based on consideration of the following four factors: concentration of particular product production, severity of the stream problems, facilities of research organizations in the region, and facilities of the regional mills for assisting in the work. In some cases regional projects have been placed at university and research laboratories outside of the industry. In other cases projects have been set up at regional mills which were staffed and equipped to carry on adequately the studies required. The National Council has demonstrated unusual skill in coordinating the many factors which enter into the problem. Success in their activities is apparent already in many quarters. The procedures used will become models for other industries.

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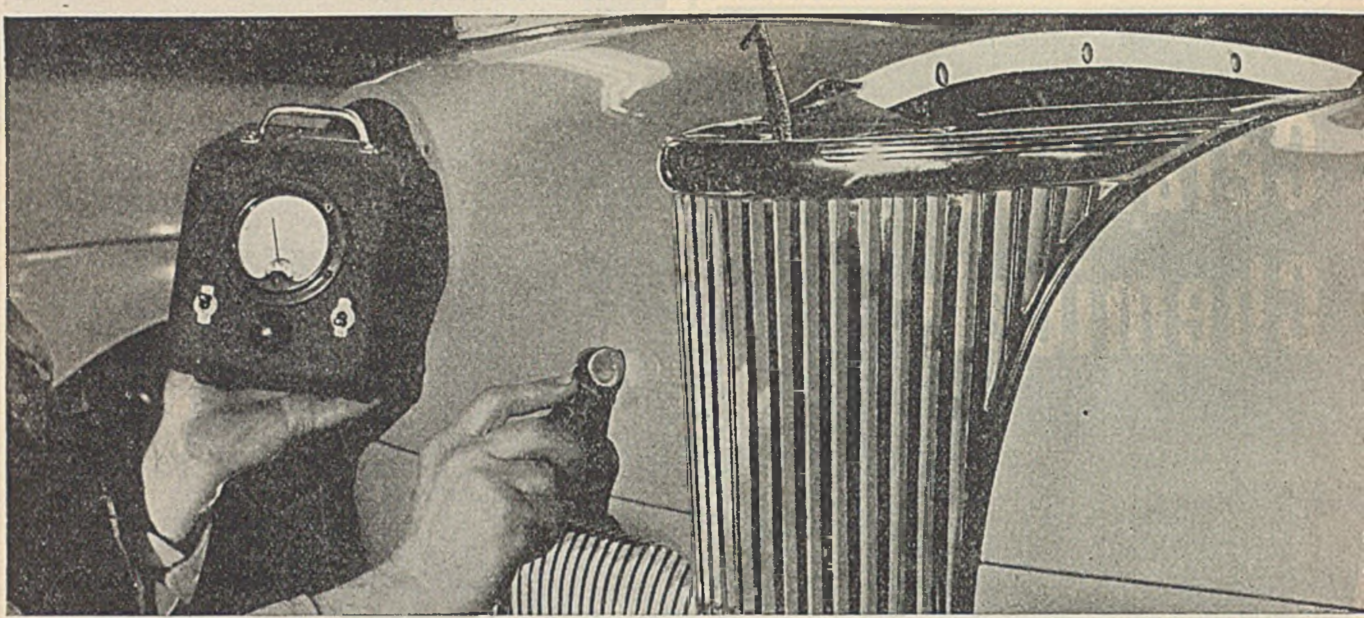

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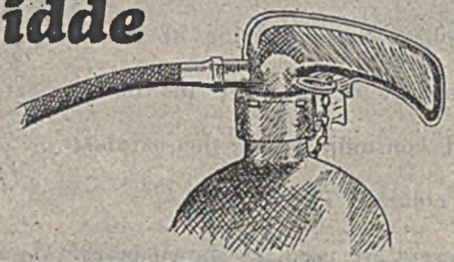

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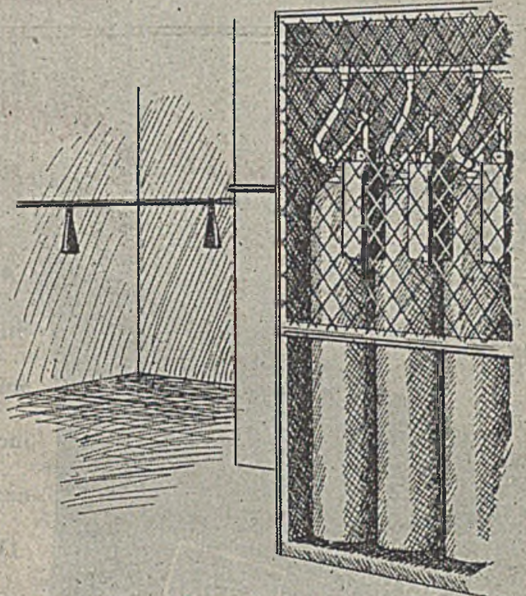

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Current Developments in
PLANT MANAGEMENT

Taking physical inventories in chemical industry entails special problems.

Discussed by Walter von Pechmann

Discrepancies between book records and physical quantities on hand cannot be avoided. However, they must be confined to a practical minimum. For this purpose physical inventories are taken. Friction sometimes develops between production and accounting departments because the fundamental reason for taking physical inventories is not properly understood. If members of the accounting department, for instance, show the attitude of auditors who can demand a detailed explanation from production for errors detected, they cannot expect a cordial welcome when they enter a department to take a count. Production executives, on the other hand, should not blame the accounting department for the interruption of departmental routine if they comply only halfheartedly with prevailing inventory regulations. It is management's responsibility to outline clearly the work for the accounting department and for the production department when inventory instructions are developed. It is recommended that such instructions be issued over the signature of a person who is not directly connected with either accounting or production in order that there be no suggestion of favoritism. Attention is called to the fact that for production departments to take their own physical inventories is contrary to sound accounting practice. For the consumer to check his own inventories is like having a cashier verify his own books; it may lead sooner or later to intentional or unintentional falsification of records. The importance of close cooperation between production and accounting cannot be stressed too much, especially in the chemical industry where physical inventories can generally not be taken without the help of technically trained personnel or laboratory analysis.

Continuous or Periodic Inventory

Physical inventories are conducted on either a continuous or periodic basis. Under the continuous method perpetual inventory records are checked against the physical inventory at least once a year. Counts are taken when the balance on hand falls to the ordering point or before newly arrived material is put away. If the periodic method is used, the entire perpetual inventory is verified at a given date. Opinions vary considerably as to which of the two methods is best suited to the chemical industry. Checking on the periodic basis has the advantage that inventory records for the entire plant can be brought up to date at one time. When the physical inventory is timed with the end of the fiscal period, management is assured that the recorded material assets check with the actual amount of material on hand. However, the periodic inventory method often requires suspension of operations and, sometimes, a shutdown of the entire plant. It is argued that the continuous method of taking inventories seldom works out satisfactorily since the count is made when the plant is in full operation. It is often impossible to hold up production until a count is made, and therefore procedures can seldom be complied with. This method provides employees held responsible for physical counts with a legitimate excuse for not fulfilling their duties; they may simply state that a physical count cannot be made without impairing operations. Even the most accounting-conscious production executive is likely to weaken when confronted with such an argument.

Some manufacturers find it advantageous to assign to a group of employees the task of checking inventories any day of the year at the convenience of the production departments. This method usually works out to the satisfaction of all concerned but unfortunately can be used only by large concerns.

The following discussion deals with inventories taken at the end of the fiscal year since this is the procedure most commonly employed in our industry. Many inventories are extended over too long a period because of such difficulties as identification of material, insufficient personnel, or inadequate instructions. It is important that the period of the physical count does not exceed a few days if operations continue during the time of inventory. Any experienced accountant will verify that most of the difficulties experienced in the pricing of inventories originates in the receiving department which cannot be shut down when the physical count is taken. Materials received but not invoiced and materials delivered to production departments during the period of the inventory are likely to cause confusion if the count is unnecessarily prolonged. Storekeepers, therefore, should be advised to prepare the stock for inventory by grouping it as nearly as possible according to kind and size. Bin tags should be carefully examined and, if necessary, altered or replaced. Where there is no numerical identification of material, the name on the bin tag should be identical with the name used in the accounting department. It is advisable to check bin tags against accounting records before the count is taken and to reorganize the raw material records at this time so that they comply with the various systems used.

Care should be taken that the order in which materials are identified follows one pattern. If this is not done, one material is likely to be classified under two or more names—for example "one half-inch gummed tape" and "tape one half inch, gummed". Materials should be put where they can be counted with little effort and without undue risk to personnel. To save time when the physical count is taken, some concerns instruct their storekeepers to write inventory tags a day or two beforehand. This method usually works out satisfactorily if instructions are given not to inscribe on the ticket the amount on hand. It is not uncommon to find that the balance on hand has been entered several days before the official date of the inventory, with adjustments made by either predetermining the amount which will be needed or correcting the tags on the date of the inventory. Such systems, which usually originate with employees who want to cooperate with the official counter, violate the very principle of taking physical inventories and should not be allowed.

Where it is necessary to make an analysis of the materials contained in chemical mixtures, laboratory procedures should be worked out in advance. Attention is called to the fact that occasionally analyses are made unnecessarily because production refuses to supply the accounting departments with formulas or because the accounting department does not accept the official formulas in computing the chemicals contained in a solution. Such practices cost money and often prolong the inventory time without due cause.

To speed up counting, many concerns find it practical to have inventory counters precede the inventory checker. The inventory counters write the description of the stock on an inventory tag, count the stock, write the quantity and unit of measure on the ticket, and attach it to the material. The inventory checker, who follows the counter and who should be under the direction of the cost department, then checks the description of the stock, recounts the stock, and checks the quantity and unit of measure recorded on the ticket. It is good practice for the storekeeper to make a visual check of the stock room to make certain that all the material has been counted.

Inventory tags should contain the following information: consecutive number, material, location, quantity, unit of measure, and space for signature. The tag should contain this information twice and should be perforated in the center so that one part of the tag can remain with the stock and the other be sent to the office for comparison with the book inventory. It is recommended that only a certain amount

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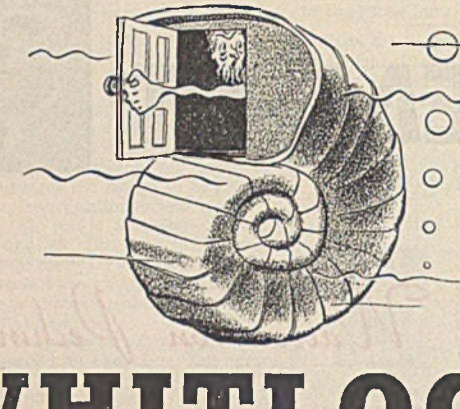
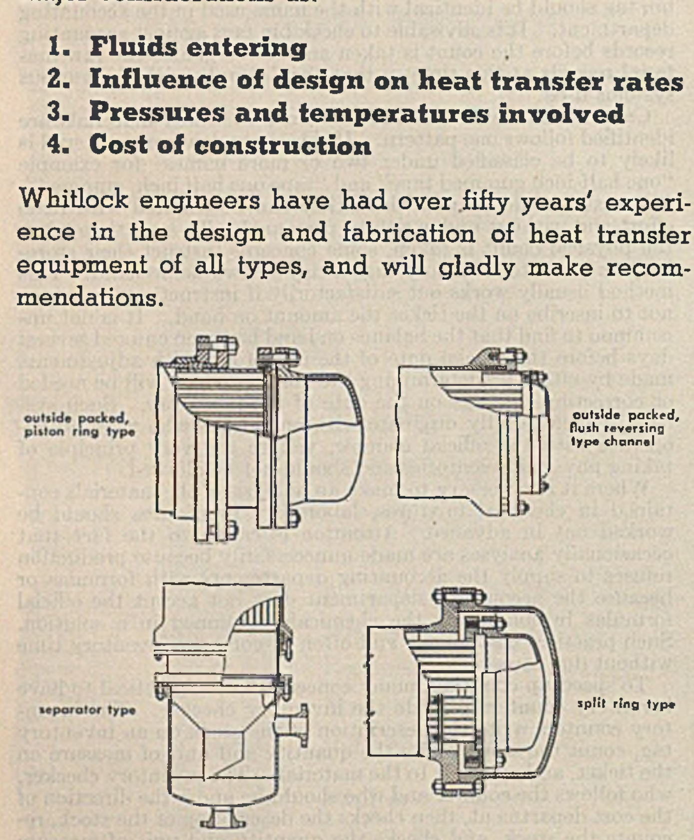




Plant Management

of prenumbered tags be issued to each department, and that each department be required to return all of its tags to the accounting department. To facilitate the pricing of physical inventories for balance sheet and income tax purposes, it is common practice to segregate inventories into raw materials, work in process, finished goods, and scrap materials. Many concerns use colored tags to facilitate identification.

The accounts-payable section of the accounting department should furnish to the cost department a list of all material received, but not invoiced, before the inventory is taken. Inventory sheets are used for computing inventory tags and for accounting. It is not wise for production to enter item and quantity prior to extension and pricing by the accounting department. It is most practical to submit the stubs of the inventory tags to the accounting department and to have all further recording made there.

Inventory Pricing

The following methods are used for the pricing of inventories first in and first out, moving average, average price at close of preceding month, market price or price of last purchase, and standard price. Although the pricing of inventories is purely an accounting function, each method will be described briefly.

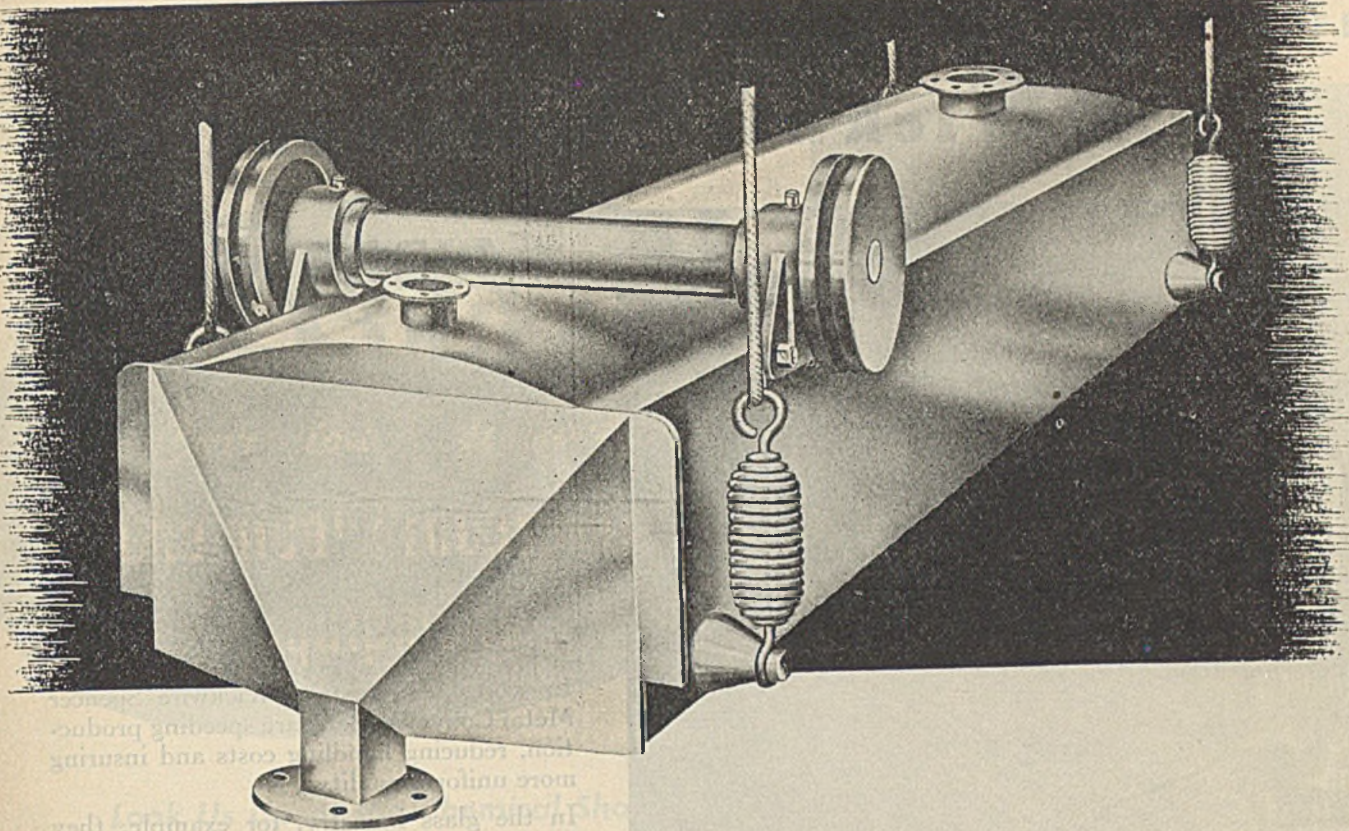
The first-in and first-out method is based upon the reasoning that materials should be issued in the order of and at the price of their original purchase. It is claimed that this method is theoretically accurate because the materials are charged into working process at actual cost. However it is impossible always to use the materials in the order in which they are received. Furthermore, the procedure of record keeping, if many purchases are made at different prices, is cumbersome. It might be of interest to the reader that the first-in and first-out method is favored by the United States Bureau of Internal Revenue.

The moving average method of inventory pricing is used by companies which desire the average cost of material rather than the actual cost. The method works as follows: Upon receipt or issue of material, entries are made in the same manner as in the first-in and first-out method. However, the quantities are added to the amount in the balance column. The cost of the material is also added. The total secured is divided by the total quantity, resulting in the new average price. Some concerns average the price of each kind of material on hand at the close of each month and use this price in costing all requisitions for the following month. This system should be used only where the price of material does not fluctuate too much from month to month and where a concern purchases its material near the end of each month for the following month's operations.

The method of market price or price of last purchase is often referred to as the last-in first-out method. The storekeeper keeps only a quantitative inventory. Requisitions are priced by the cost accounting department at market. This method should be employed only if the market price for materials purchased is steady; it should be eliminated at a time of rising prices because then the earnings will be understated. It might be advisable to mention in this connection that the switching from one method to another without due cause is unlawful; the Bureau of Internal Revenue stipulates that the pricing method of inventories must be used consistently from year to year.

The pricing of inventories according to an established standard is very simple. The purchasing department and the accounting department agree upon a price which they believe represents an average for a certain period. Variations found at the end of the predetermined period are charged to an adjustment account. The writer, however, cautions against too free use of the standard price method, especially if the standards cannot be based on reliable cost records. Furthermore, provision must be made that the total variation to be charged to the adjustment account can be broken down in such a manner that discrepancies may be traced without too great an effort. Provision must also be made that standards be revised quickly if prices for materials go up or down to an unusual extent.

These opinions are the writer's personal ideas for taking physical inventories in a practical manner. They are intended to be a general guide, since the various types of chemical industry are confronted with special problems which have to be solved individually.



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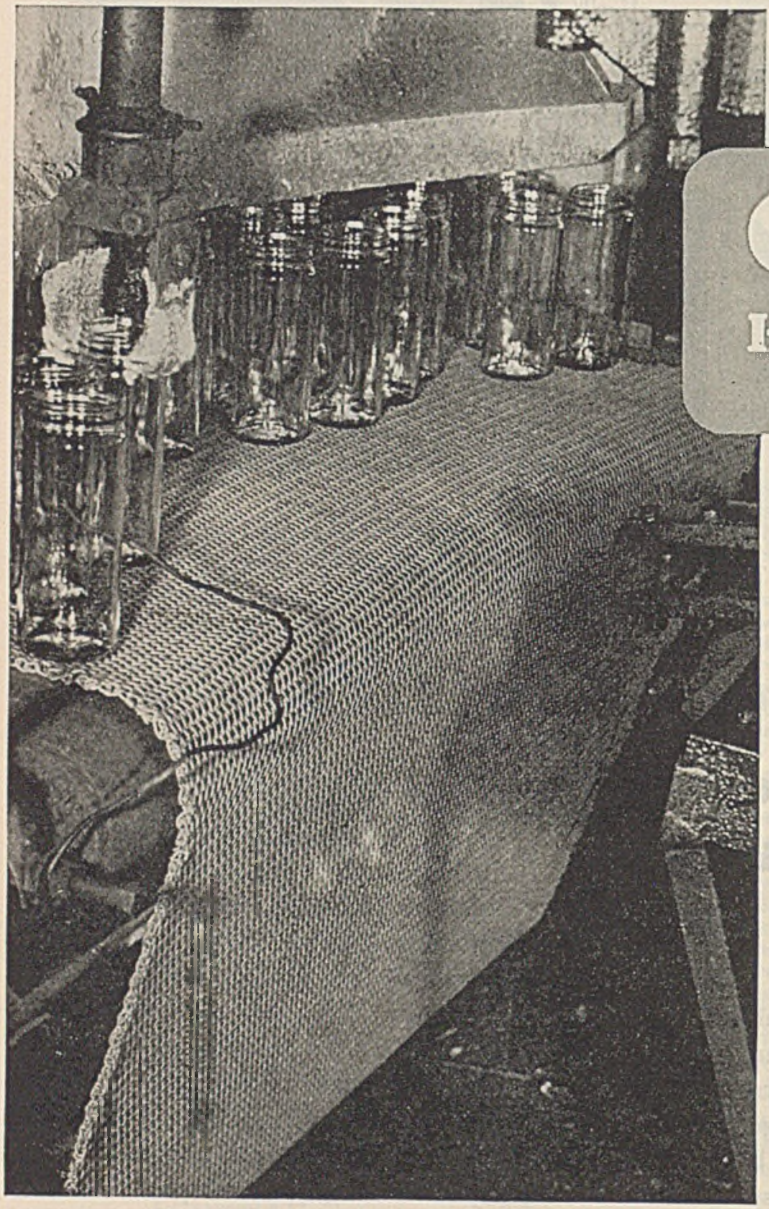

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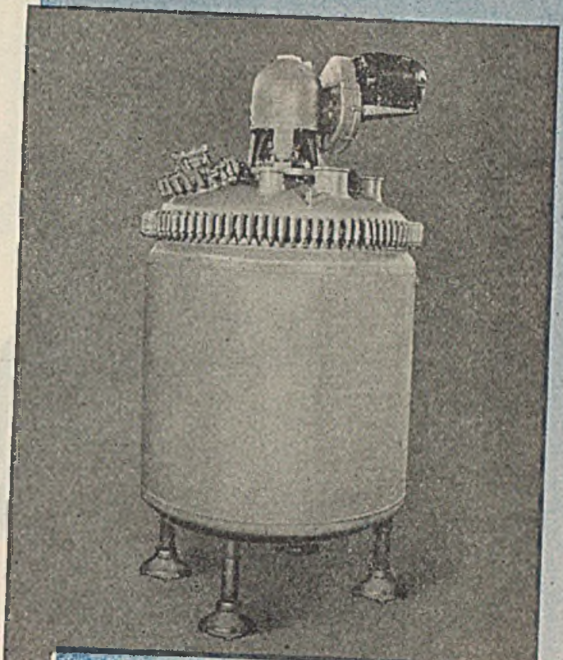

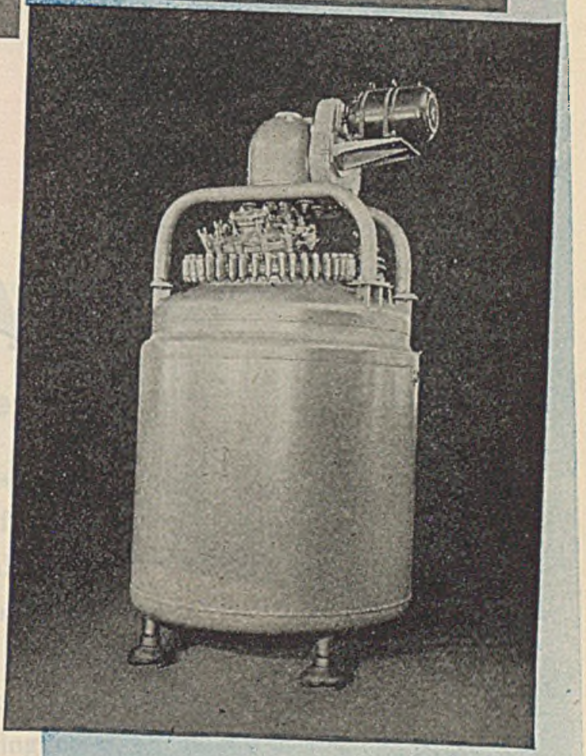

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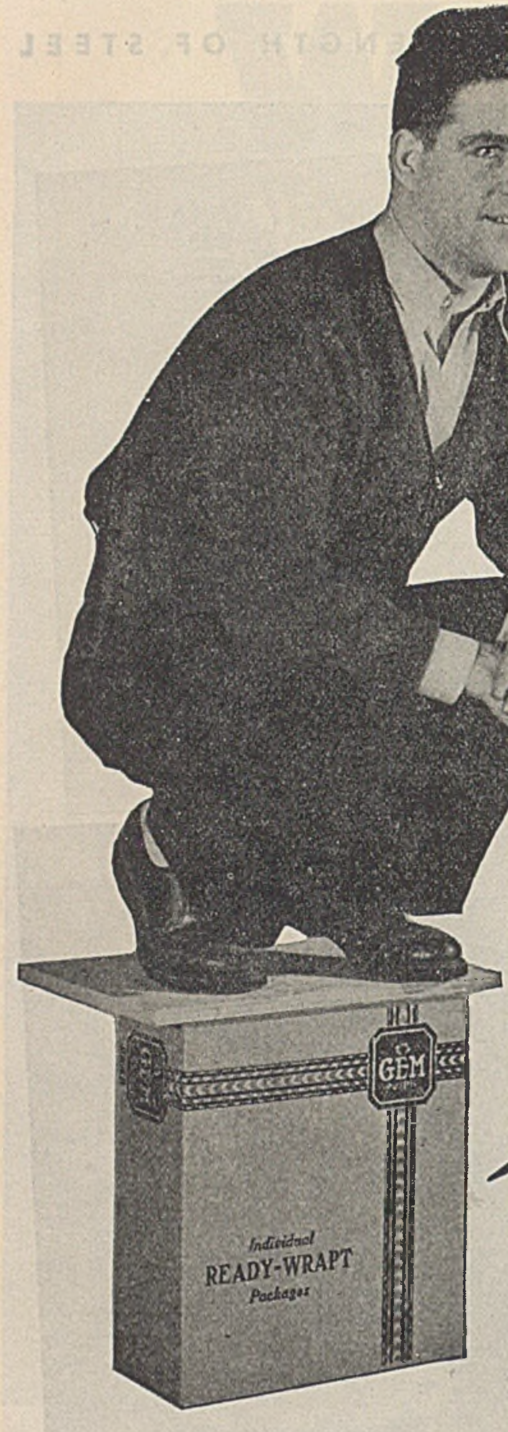
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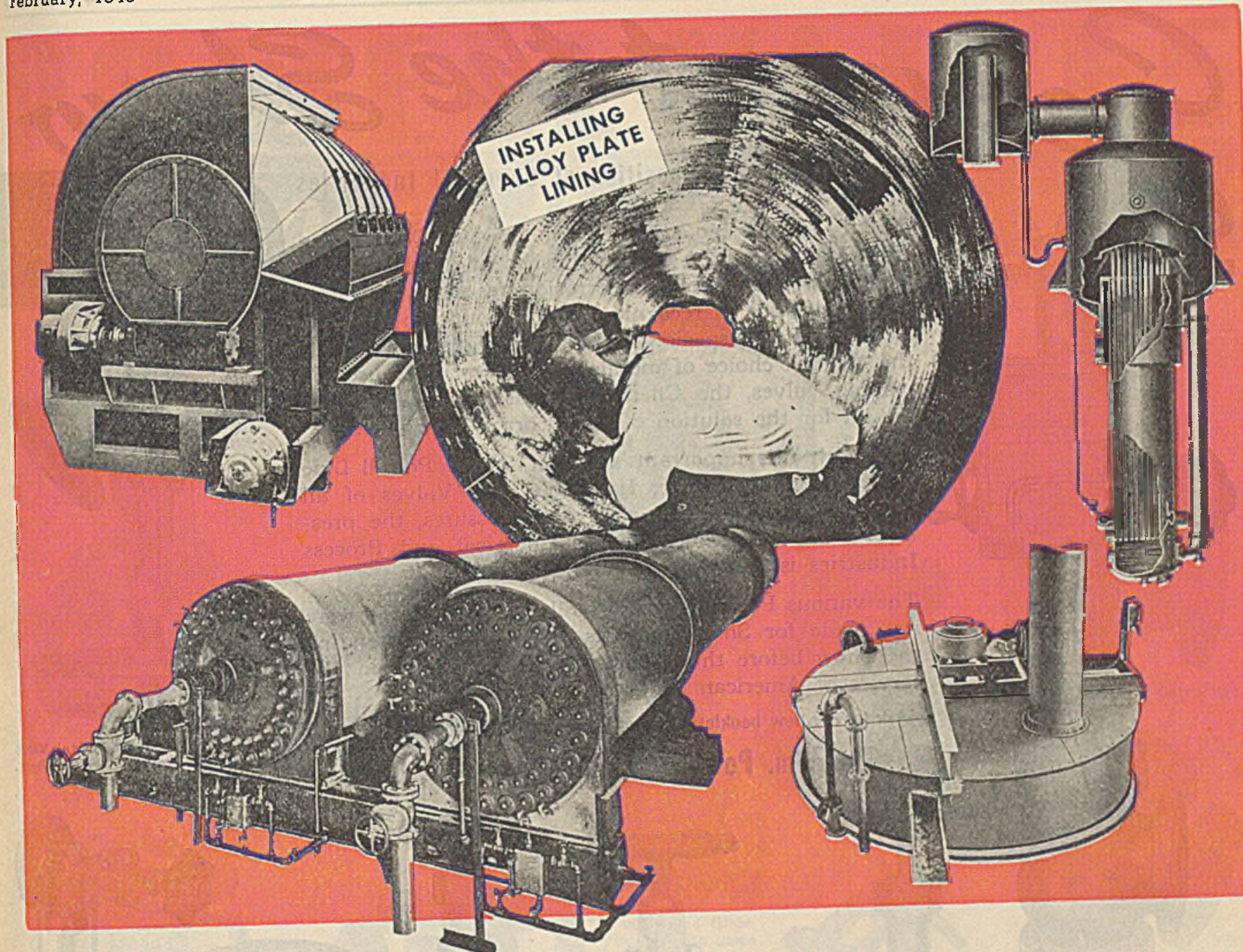
READY-WRAPT
Packages



DESIGNS and FABRICATES

Processing Equipment that Performs as Specified

General American uses the coordinated efforts of its research laboratories, pilot plants, chemical engineers and fabrication experts to build equipment that will perform according to specifications.

Experienced process engineers design the equipment to meet precise product requirements. Metallurgists select the materials, carbon steels, stainless steels, clad steels, silicon bronze, Monel, alloys, aluminum, Hastelloy, etc.

Units are precision built in the Sharon Shops from the materials selected to suit the particular process requirements, resist corrosion or prevent product contamination. The result is more efficient equipment for producing higher quality products with lower operating costs.

You are invited to visit our booths 326-331 at the 20th Exposition of Chemical Industries, New York City and talk with our engineers.

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

SALES OFFICE:
513a Graybar Bldg., New York 17, N. Y.
WORKS: Sharon, Pa.; East Chicago, Ind.

OFFICES: Chicago, Louisville, Cleveland, Sharon, Orlando, St. Louis, Salt Lake City, Pittsburgh, San Francisco, Washington, D. C.

See us at the Show

Booth 54—20th Exposition of Chemical Industries

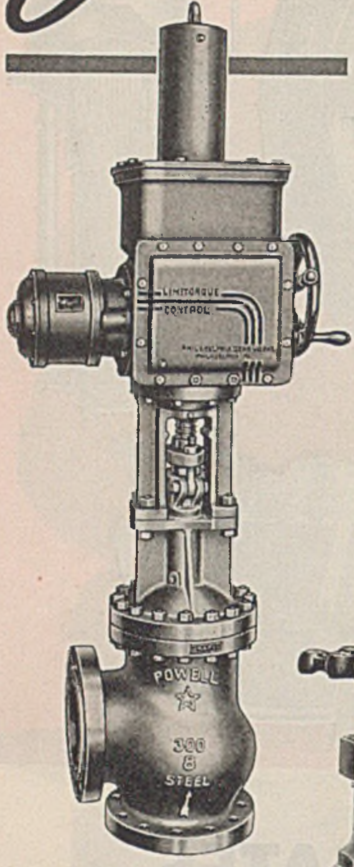
Twenty years ago, the Powell Special Design and Alloy Valve Division was established and today Powell leadership in the field of corrosion resistant flow control equipment is recognized throughout the country. Because of our specially adapted designs and by far the greatest choice of metals and alloys* ever used in making valves, the Chemical Industries now look to Powell for the solution of their corrosion problems.

And with this important addition to the Powell Line which includes Bronze, Iron and Steel Valves of all required types, designs, sizes and pressures, the prestige of Powell Valves in the Chemical and Process Industries is easily understood.

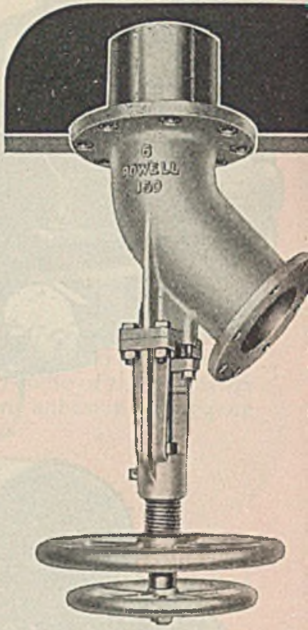
The various Powell Valves you'll see in Booth 54 were not made for Show purposes—they're just attending the Show before they start their long careers in the service of American Industry.

Ask for our new booklet "Powell Valves for Corrosion Resistance"

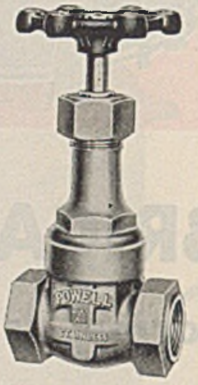
The Wm. Powell Co., Cincinnati 22, Ohio



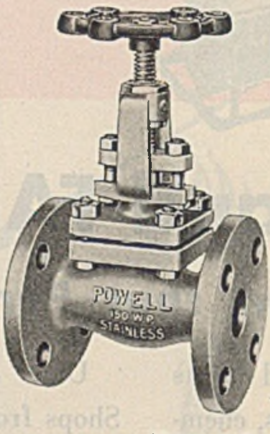
300-pound Angle Valve with top-mounted Limitorque Motor Operator.



150-pound Flush Bottom Tank Valv with Powell Patented Seat Wipe Disc rises into tank to open.

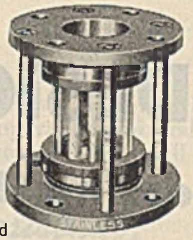


200-pound Gate Valve with screwed-in bonnet.

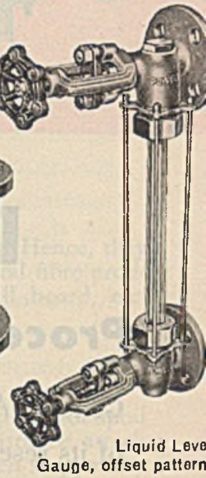


150-pound O. S. & Y. Globe Valve.

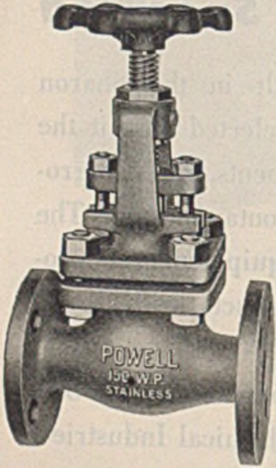
Needle Globe Valve.



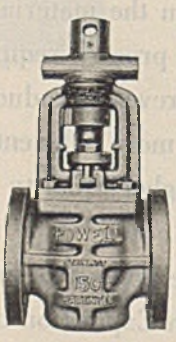
Glass Sight Feed



Liquid Leve Gauge, offset pattern

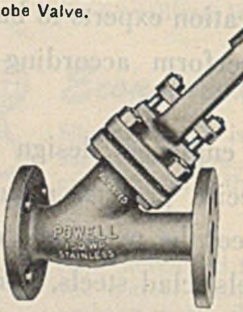


150-pound O. S. & Y. Gate Valve.

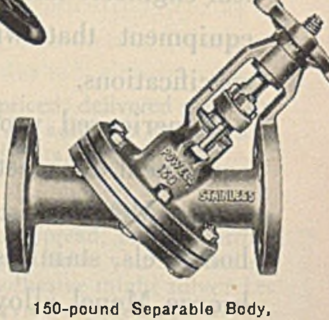


150-pound Straight-way Mechanical Lift Plug Cock.

Angle Relief Valve.



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

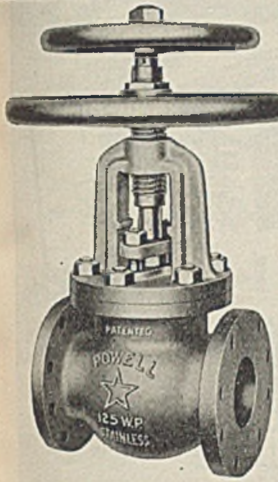


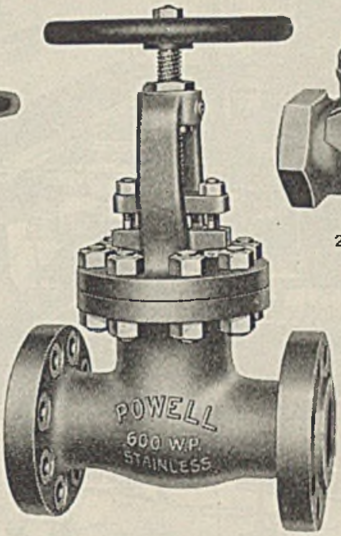
150-pound Separable Body, Reversible Seat, "Y" Valve.

POWELL

POWELL VALVES

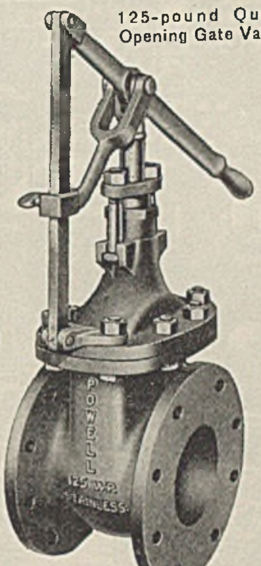
for Corrosion Resistance

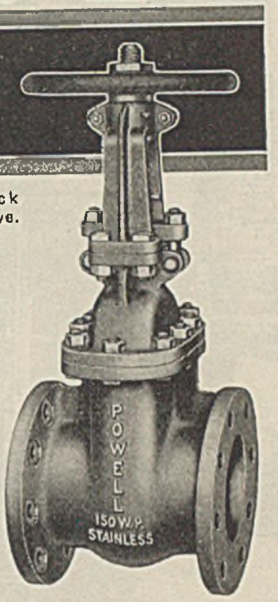

125-pound O. S. & Y. Globe Valve with Powell Patented Seat Wiper.



600-pound O. S. & Y. Gate Valve.

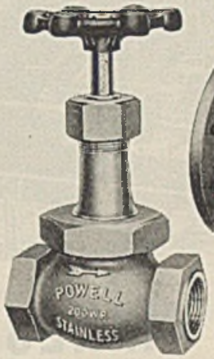

200-pound Swing Check Valve.


125-pound Quick Opening Gate Valve.

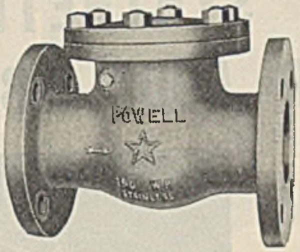


150-pound O. S. & Y. Gate Valve.

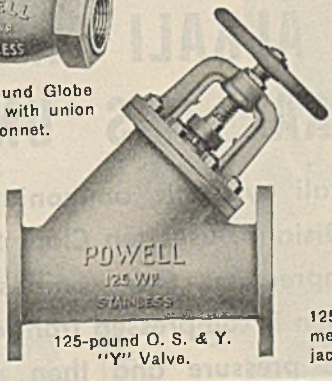
150-pound Horizontal Lift Check Valve.



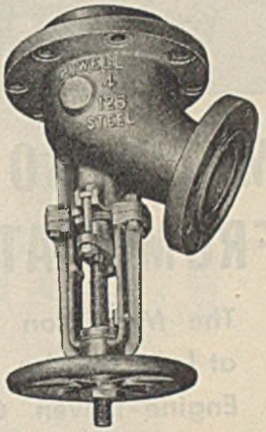
200-pound Globe Valve with union bonnet.



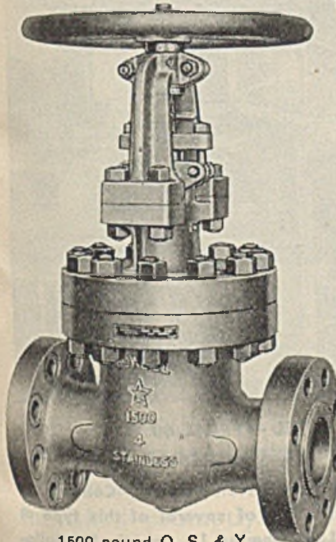
150-pound Swing Check Valve



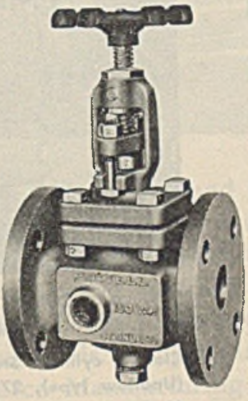
125-pound O. S. & Y. "Y" Valve.



125-pound Flush Bottom Tank Valve for metal tanks and autoclaves with steam jackets. Disc lowers into valve to open.



1500-pound O. S. & Y. Gate Valve.

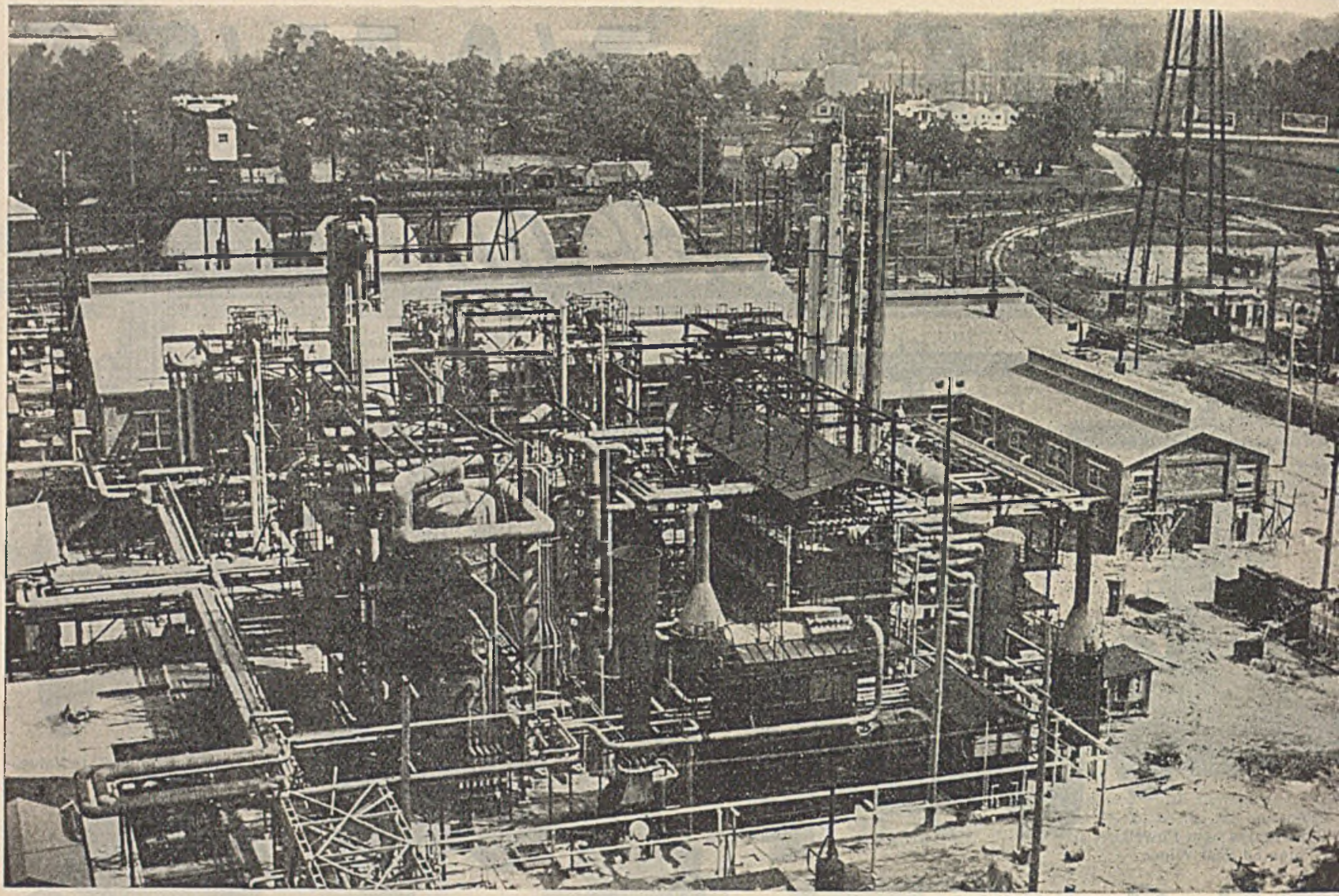

150-pound Steam Jacketed Globe Valve.

***Powell Valves for Corrosion Resistance are available in the following Pure Metals and Special Alloys.**

- Acid Bronzes
- All Iron
- Aluminum
- Aluminum Bronze
- Ampco Metal
- Carbon Steel
- Durimet "T", "20"
- D-10
- Everdur
- Hard Lead
- Hastelloy Alloys "A", "B", "C" and "D"
- Herculoy
- Inconel*
- Illium
- Misco "C"
- Monel Metal*
- Nickel (Pure)
- Nickel Iron
- Ni-resist*
- Silver (Pure)
- 4-6% Ch. .5 Mo. Steel
- 18-8S
- 18-8S Mo.
- 11.5-13.5% Ch. Iron
- 18% Ch. Iron
- 28% Ch. Iron
- 25% Ch. 12% Ni. Alloy Steel

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

VALVES



MATHIESON ALKALI MAKES SYNTHETIC AMMONI FROM NATURAL GAS UNDER 5000 LBS. PRESSUR

The Mathieson Alkali synthetic ammonia plant at Lake Charles, Louisiana, uses ten Clark Steam-Engine-Driven Compressors. Gas composed of hydrogen and nitrogen is compressed from atmospheric to 5000 lbs. pressure and then passed through a catalytic process which converts it into ammonia.

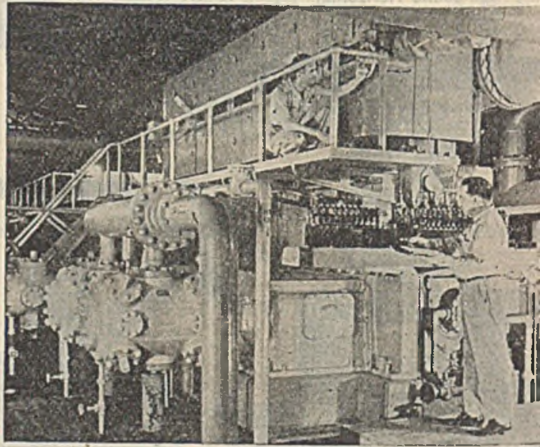
This type of compressor unit can be built and installed faster and more economically than other types, an important factor in peacetime as it was in the war emergency.

Write, phone or wire for full information.

CLARK BROS. CO., INC., OLEAN, N. Y.

One of the Dresser Industries

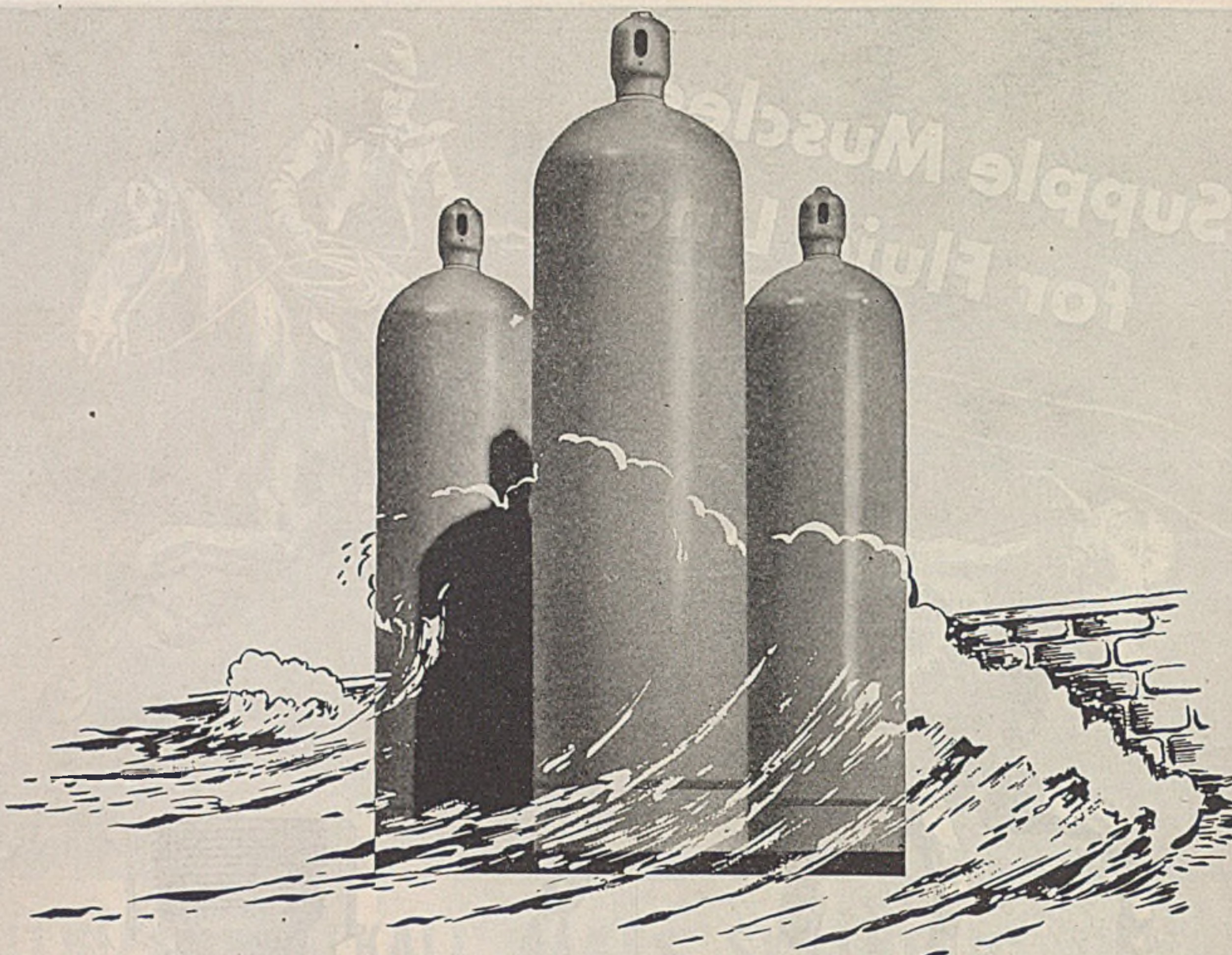
New York • Tulsa • Houston • Chicago • Boston
Los Angeles • London • Buenos Aires



CONTROLLED SPEED — FROM 60 TO 300 RPM — UNDER FULL LOAD

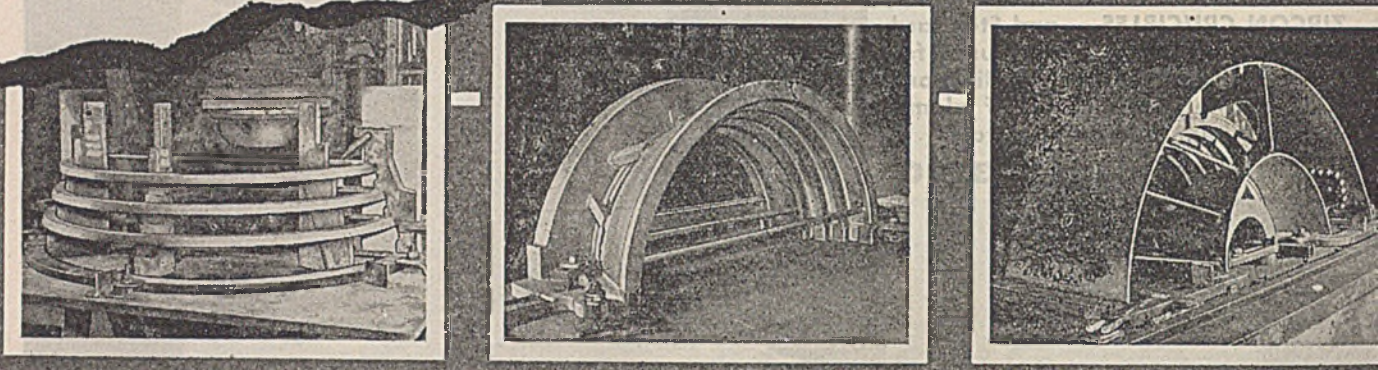
Clark 8 cylinder Steam-Engine-Driven "Angle" Compress
(Unaflow type), 2735 BHP, one of several of this type
Mathieson Alkali Works, Lake Charles, La. Speed of install
tion and low plant cost are important advantages of th
type of engine, as well as the ability to operate at full loa
with speeds varying from 60 to 300 RPM.

CLARK STEAM-ENGINE-DRIVEN "ANGLE" COMPRESSORS

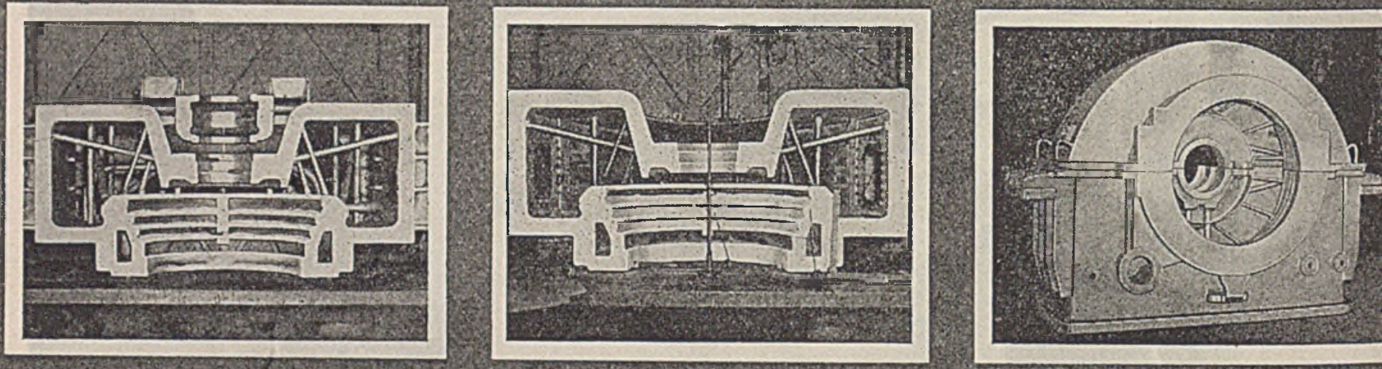


Why worry?

..USE ALCO WELDMENTS



Building a Turbine Casing with ALCO Weldments fabricated in ALCO'S Dunkirk, New York, plant.



Here's why:

Weldments are becoming increasingly popular as a superior, more economical method of fabricating metal parts and products.

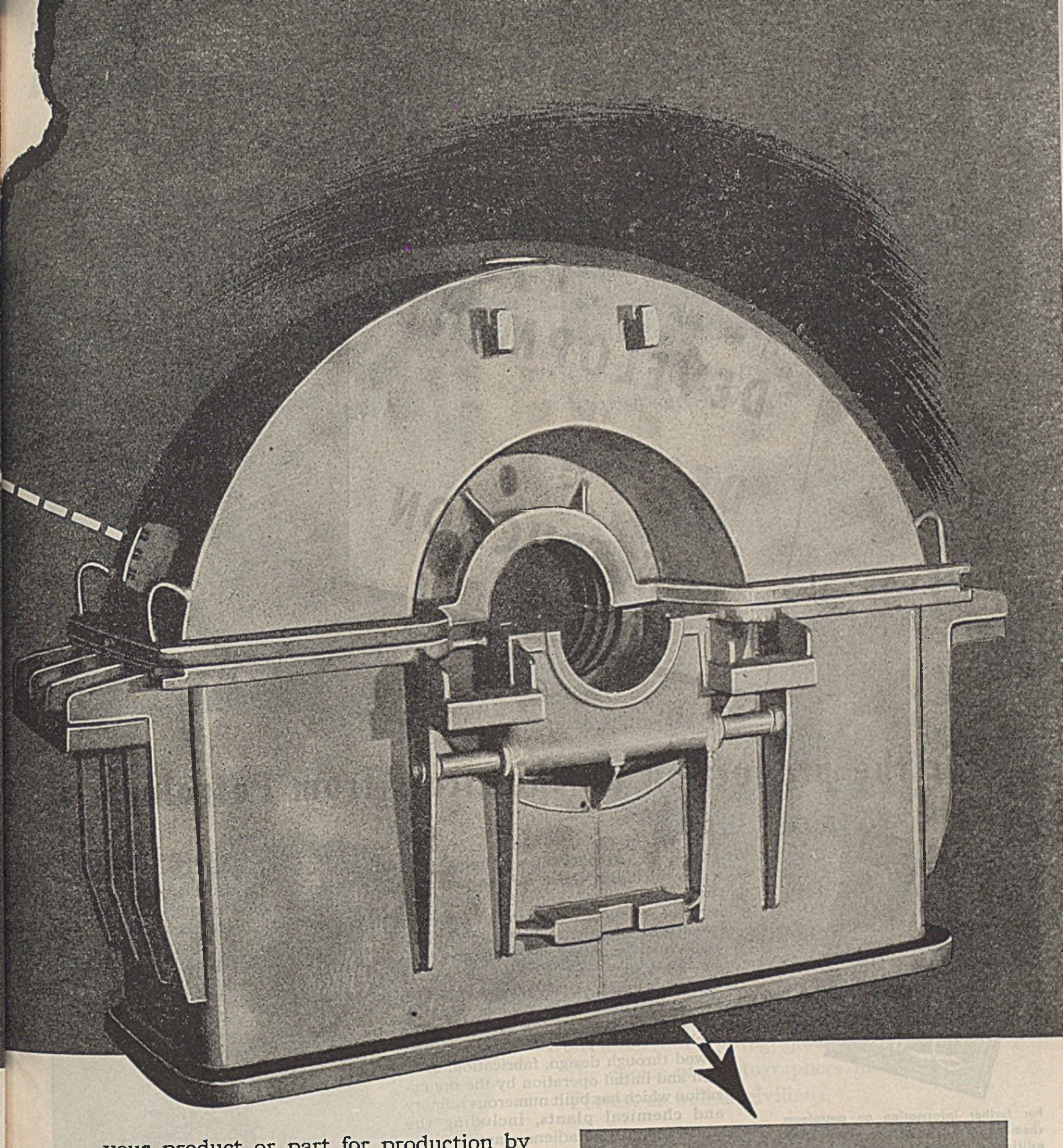
Of course. For one thing, rejects do not occur with weldments after machining starts. That means weldments *save worry and waste.*

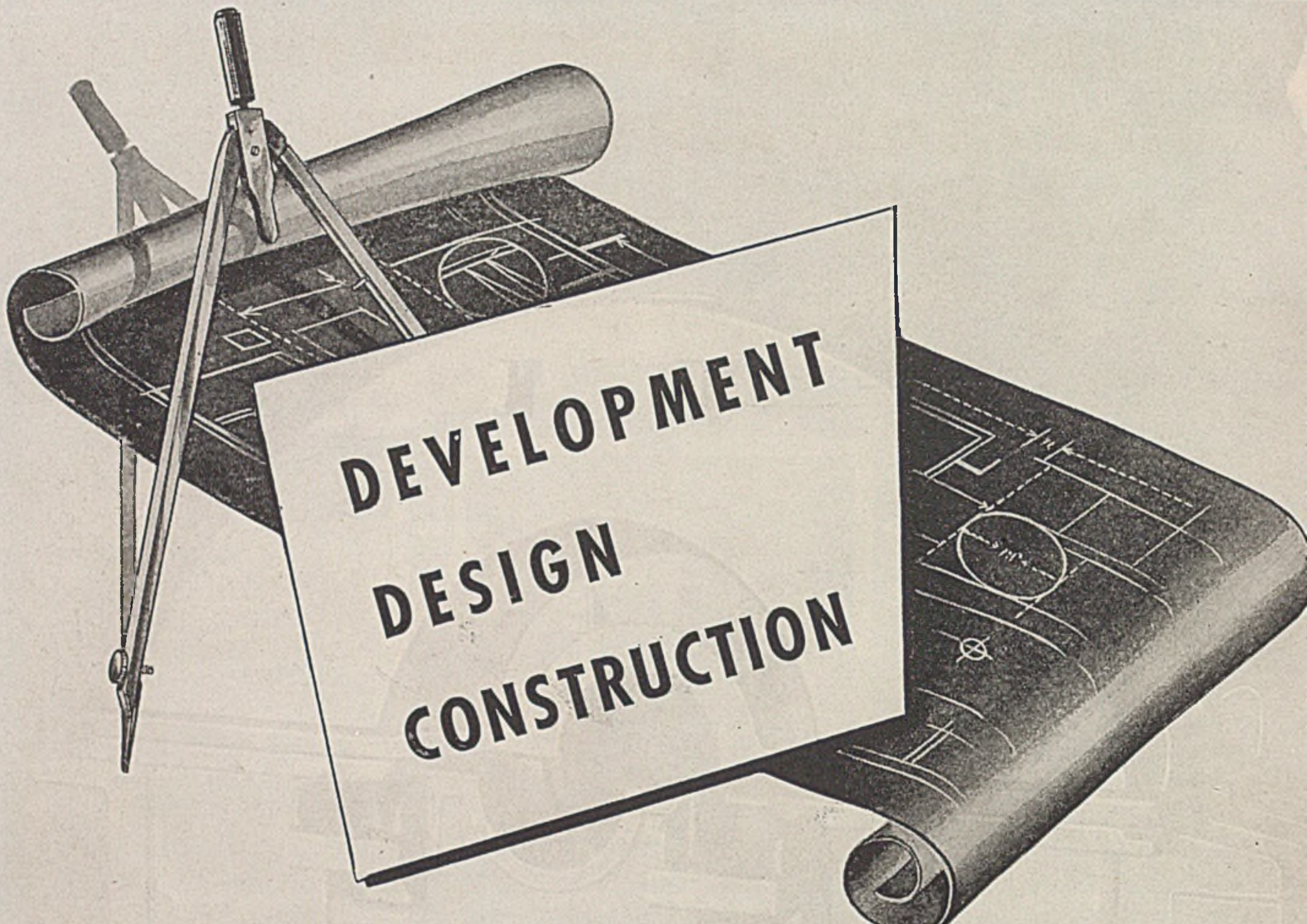
For this reason, and other reasons stated below, weldments often *cost less* than any alternative available for the same service.

Another important angle is that there is a large body of skilled welders. Hence, schedules are less likely to be interrupted because of possible skilled-labor shortage.

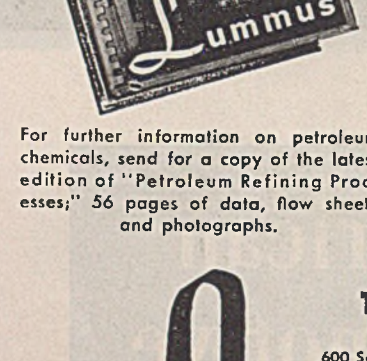
ALCO guarantees

to furnish engineering talent to design





for the production of Chemicals from Petroleum

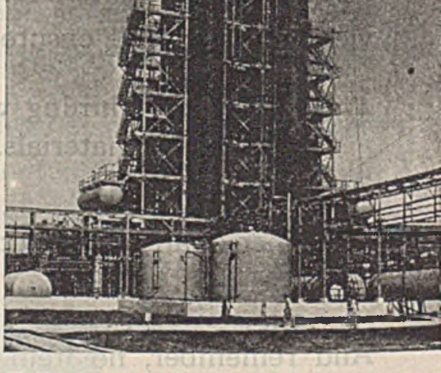


For further information on petroleum chemicals, send for a copy of the latest edition of "Petroleum Refining Processes;" 56 pages of data, flow sheets and photographs.

Pioneer in the development of many chemical and petroleum refining processes, including those for the manufacture of ethylene, propylene, butadiene, styrene, phenol, etc., Lummus offers its wealth of experience to the petroleum and chemical industries. Lummus engineers will be glad to make individual studies of products and selection of processes, and operating costs can be determined in a study of the economics for each individual project. Projects are followed through design, fabrication, erection and initial operation by the organization which has built numerous refinery and chemical plants, including the world's largest butadiene plant.

The development of large scale, commercial operation from pilot plant operation has long been a specialty of The Lummus Company. Among chemica processes projected to commercial op eration by Lummus are those for th production of ethylene, styrene, propy lene, phenol, alcohol, and butanol.

If you are interested in the economi cal – profitable – production of petro leum chemicals, put your problem up t Lummus.



50,000 ton per year styrene and ethylene plant, designed and built by Lummus.

THE LUMMUS COMPANY

420 Lexington Avenue, New York 17, N. Y.

600 South Michigan Avenue
Chicago 5, Ill.

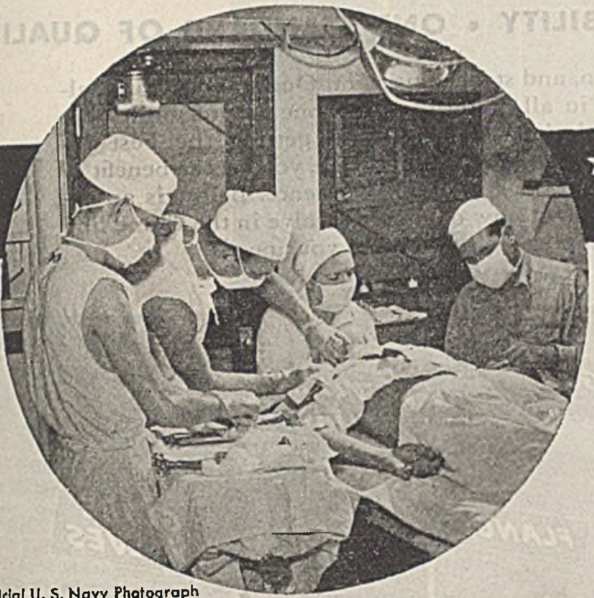
Mellie Esperson Bldg.
Houston 2, Texas

634 South Spring Street
Los Angeles 14, Calif.

78 Mount Street
London, W. 1. England

Lummus

PETROLEUM REFINING PLANTS



Official U. S. Navy Photograph

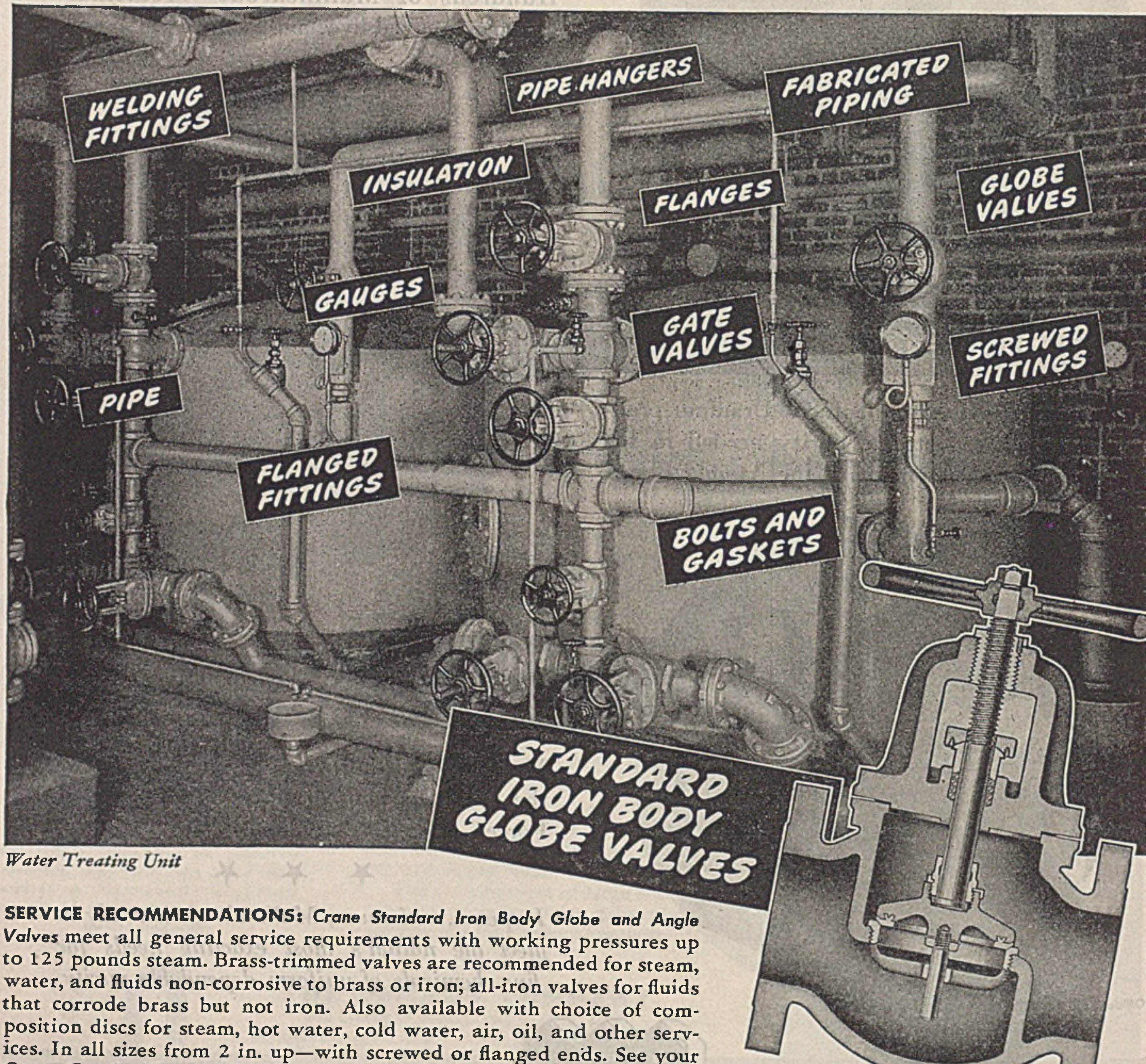
Official Photo, U. S. A. A. F.

Official U. S. Navy Photograph

For Piping Equipment . . . Any Kind . . . it Pays to Rely on CRANE

ONE SOURCE OF SUPPLY • ONE RESPONSIBILITY • ONE STANDARD OF QUALITY

Rebuilding piping systems . . . and keeping them at peak efficiency . . . is made a lot easier by using Crane *complete* piping materials service. One order—to your Crane Branch or Wholesaler—can cover *all* your valves, fittings, pipe, piping accessories and fabricated assemblies. You can choose from the world's greatest line of brass, iron, and steel equipment. One standard of quality in all materials—and one responsibility behind them—helps insure getting the best installation. At the same time, you get the benefit of Crane Co.'s 90-year experience. Below is an example of how one typical valve in the Crane line is applicable to many of your needs.



Water Treating Unit

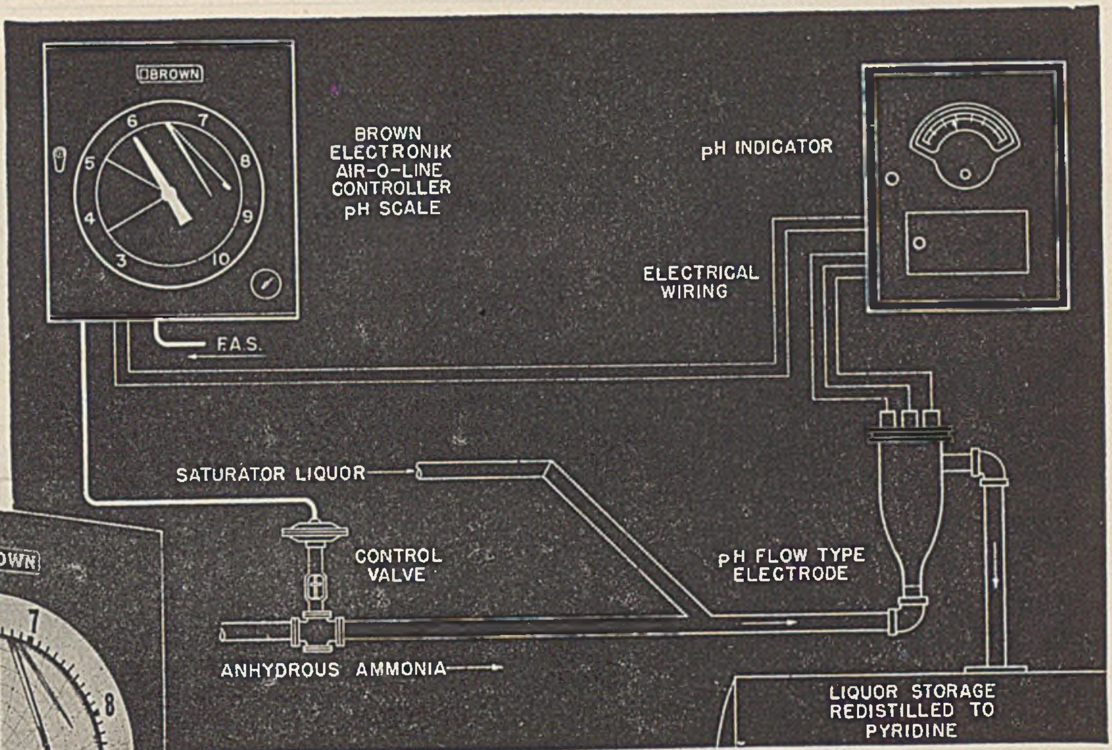
SERVICE RECOMMENDATIONS: *Crane Standard Iron Body Globe and Angle Valves* meet all general service requirements with working pressures up to 125 pounds steam. Brass-trimmed valves are recommended for steam, water, and fluids non-corrosive to brass or iron; all-iron valves for fluids that corrode brass but not iron. Also available with choice of composition discs for steam, hot water, cold water, air, oil, and other services. In all sizes from 2 in. up—with screwed or flanged ends. See your Crane Catalog for specifications.

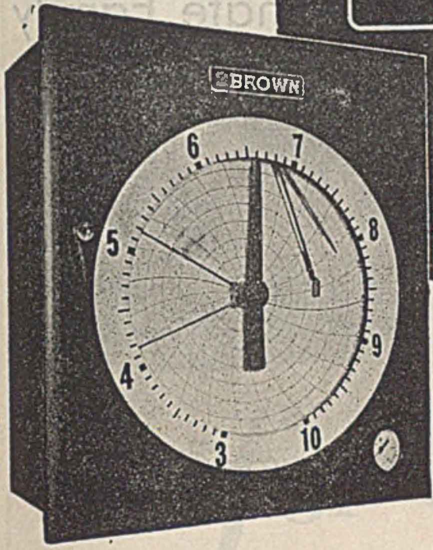
CRANE CO., General Offices: 836 S. Michigan Ave., Chicago 5, Ill. *Branches and Wholesalers Serving All Industrial Areas*

CRANE

VALVES • FITTINGS • PIPE
PLUMBING • HEATING • PUMPS

Visit with Crane at the 20th Chemical Exposition—Booths 312 and 313, Grand Central Palace, New York—Feb. 25 to Mar. 2





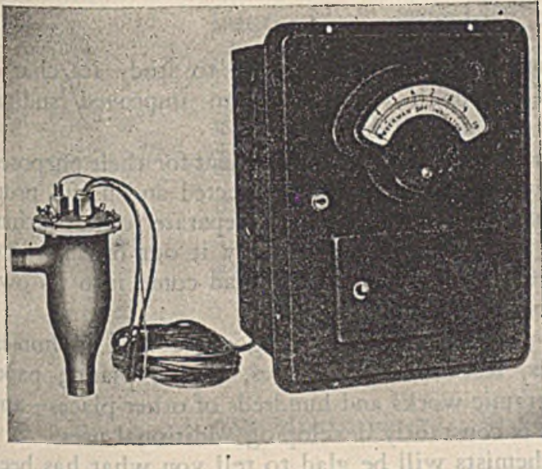
Brown ElectroniK Air-o-Line Controller, pH Scale

pH Continuously Controlled

pH measurement and control is widely recognized as an economic factor throughout the chemical, petroleum, and other process industries. It ranks in importance with the measurement and control of pressure, temperature, and flow. Modern industry is continually discovering new benefits and new economies through utilization of proper pH measurement and control.

The Brown ElectroniK Potentiometer Air-o-Line Controller and the Beckman Primary Unit affords a system unexcelled for continuous precision measurement and control of pH. Accurate and instant response to pH changes with this equipment safeguards plant efficiency and assures uniform process operation. The system shown above, used in producing Pyridine is typical of the many applications of the ElectroniK Air-o-Line Controller and the Beckman pH Indicator.

Available in several ranges, this system may be used for measurement and control where solution temperatures do not exceed 212° F.



pH Flow Type Electrode Assembly

pH Indicating Amplifier

For complete information on measurement and control of pH, call a Brown engineer — he is as near as your telephone — or write THE BROWN INSTRUMENT COMPANY, a division of Minneapolis-Honeywell Regulator Company, 4480 Wayne Avenue, Philadelphia 44, Pa. Branch offices in all principal cities. Toronto, Canada; London, England; Stockholm, Sweden; Amsterdam, Holland.

BROWN ElectroniK POTENTIOMETERS

the "ugly duckling"

of the Phosphate Family

Chemical Families, too sometimes have members whose ways don't quite conform to the expected patterns. These deviations are often irritating, so there is always a tendency to ignore these members of the family and concentrate on the ones which fit into the orderly pigeonholes worked out for them.

Then someone comes along and takes the time to study these ornery individualists—and often the "ugly duckling" turns out to be the swan of the family.

That is the way it worked out with the sodium phosphate glass called "sodium hexametaphosphate." This substance was observed as early as 1820, studied in some detail in 1833, given its complicated chemical name in 1849.

Throughout this whole period, and up until 1930, it was merely a laboratory curiosity. Then Hall Laboratories, searching for the most suitable phosphate for boiler water conditioning, began to study its charac teristics. Through their work an improved sodiu phosphate glass was developed.

This not only proved to be excellent for their purpose but demonstrated so many unexpected and useful prop erties in other fields that a separate organizatio Calgon, Inc., was formed to carry it out broadly int industry. The "ugly duckling" had come into its ow as Calgon*.

Today, various forms of Calgon are used in home laundries, restaurants, tanneries, textile plants, pap mills, ceramic works and hundreds of other places—an research is constantly developing additional uses.

Our chemists will be glad to tell you what has bee done in the particular application in which you a interested, and to cooperate with you in the study possible new applications.

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

HAGAN
HALL
BUROMIN
CALGON

calgon, inc.

A SUBSIDIARY OF
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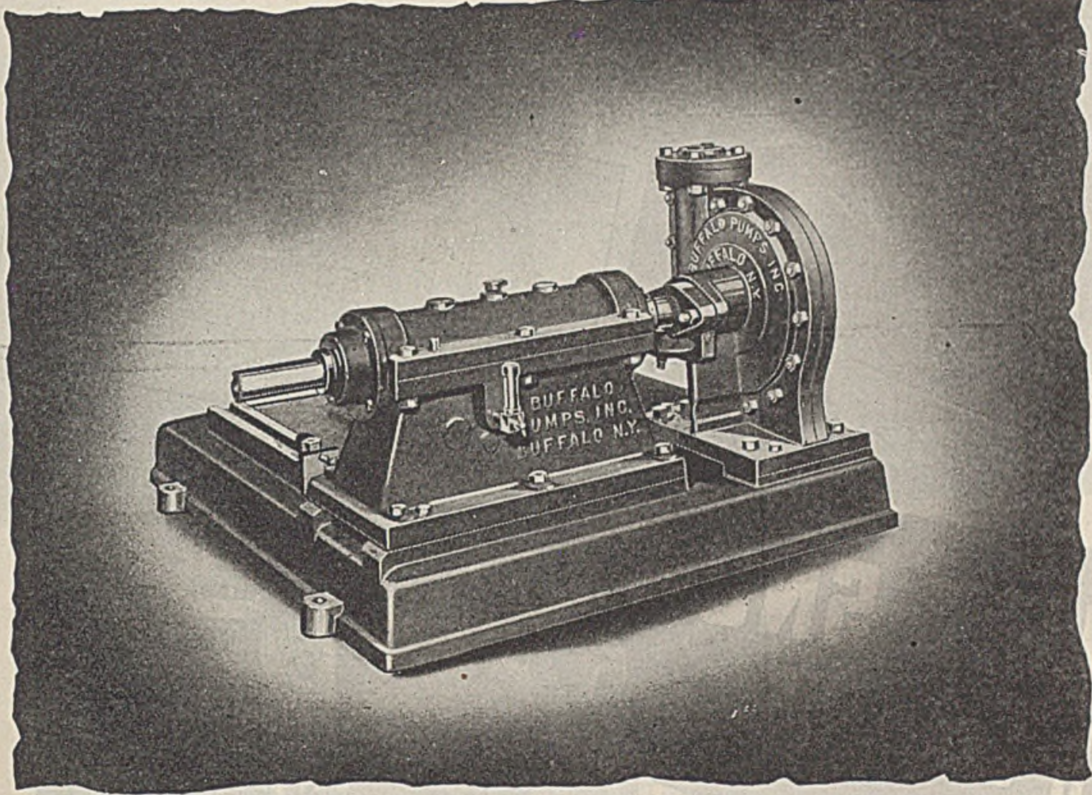
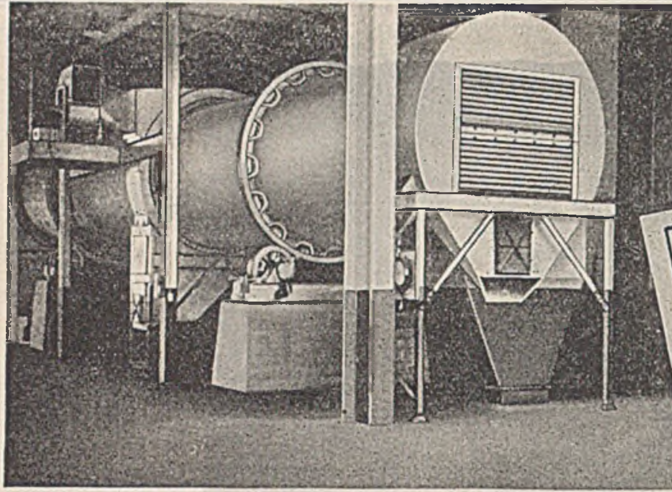
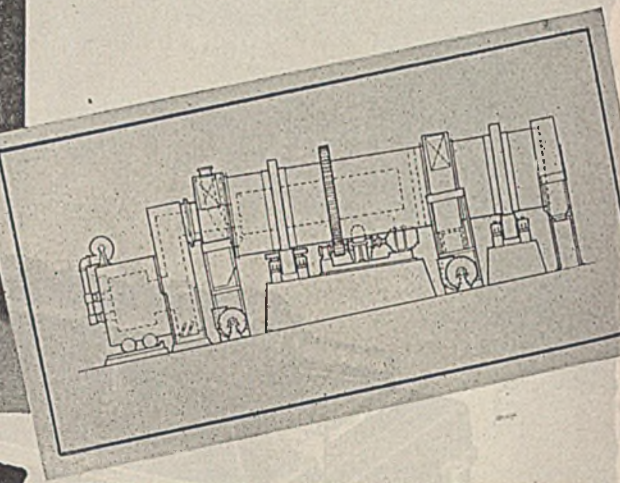
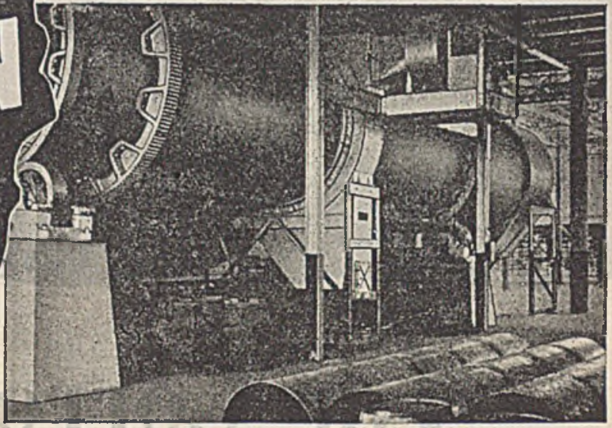
HAGAN BUILDING
PITTSBURGH 30, PA.


BUFFALO PUMPS INC.
BUFFALO N.Y.
BUFFALO PUMPS INC.
BUFFALO N.Y.







BARTLETT-SNOW DRYER-COOLERS

..2 processing operations in a single cylinder

● Bartlett-Snow dryer-coolers consist of a Bartlett-Snow Style "H" indirect-direct heat dryer, and a Bartlett-Snow rotary air cooler combined into a single shell. Material is introduced into the feed end of the dryer,— and gives up all but a very small amount of its moisture. The material then passes through a specially designed lock—which—without involving any moving or complicated parts—permits the material but not the hot air and flue gases to pass into the "cooler" end. Here, in the cooling section, the material loses the balance of its moisture, and also enough sensible heat to bring the temperature down to 110°F. or less, at the point of discharge.

Two fans, of exceedingly low horsepower requirement, are employed, both discharging to a single dust collector. A minimum of fuel is required,— and because the drying and cooling sections are built integrally the power requirement is only slightly more than would be needed for either the dryer or cooler used singly. 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.

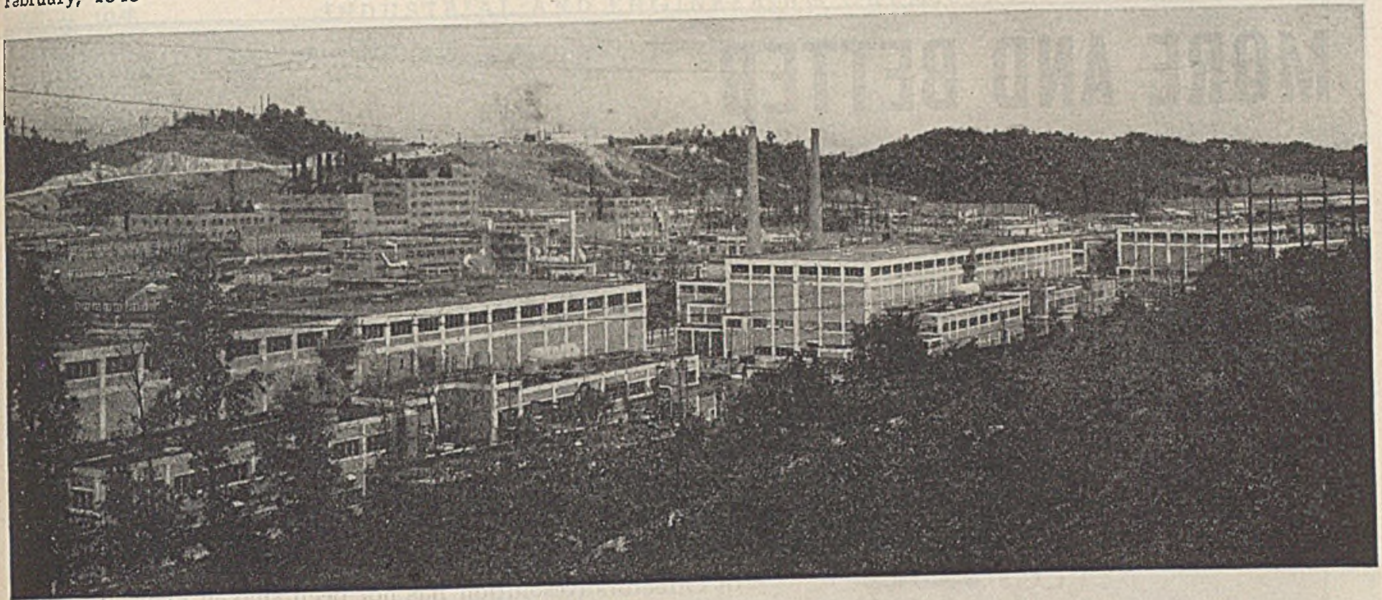
THE C. O. BARTLETT & SNOW CO.

6207 HARVARD AVENUE • CLEVELAND 5, OHIO

Engineering and Sales Representatives in Principal Cities

DRYERS • CALCINERS • KILNS • PRESSURE VESSELS

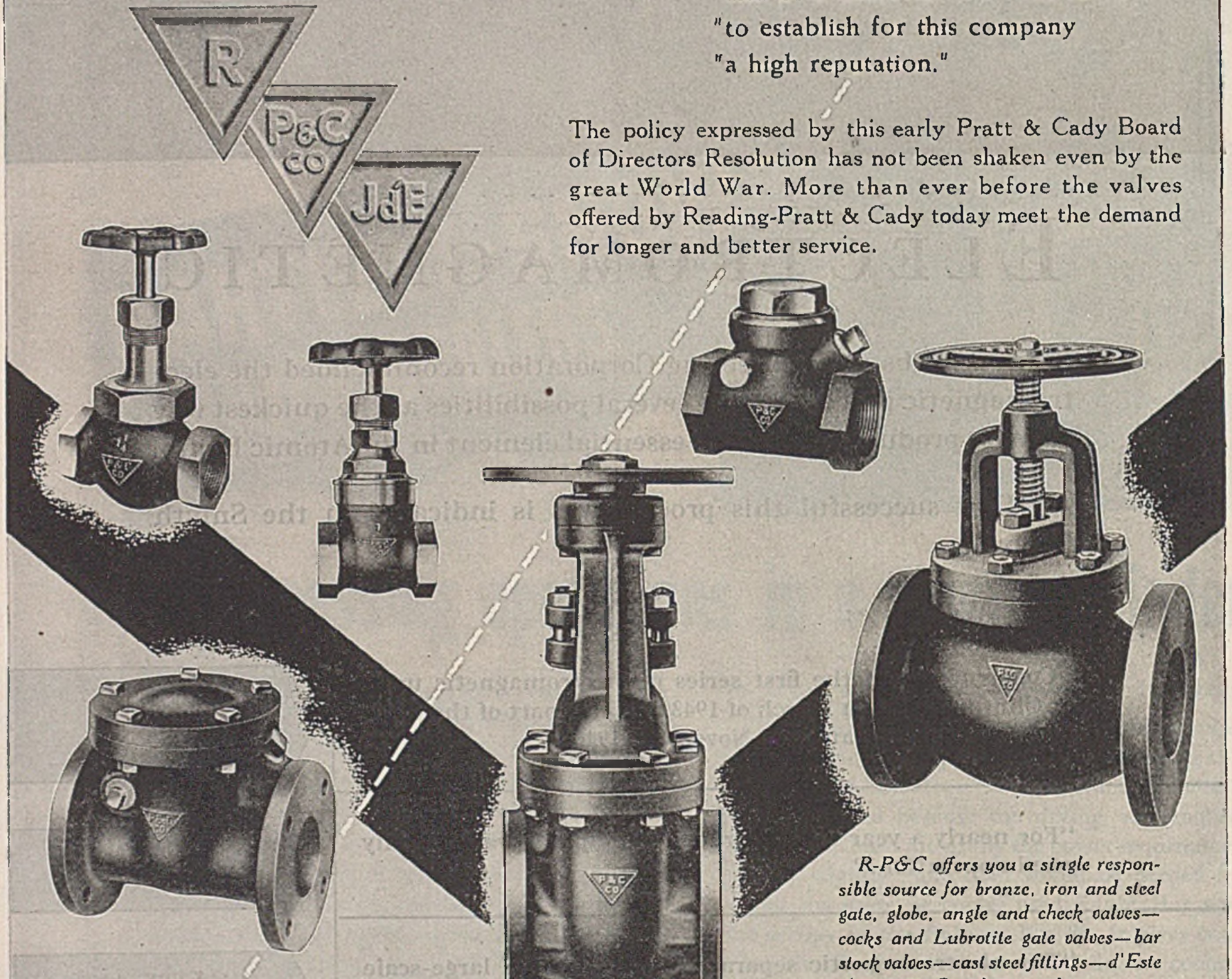
• • COMPLETE MATERIAL HANDLING FACILITIES TO MEET ANY REQUIREMENT • •
ONE CONTRACT • ONE GUARANTEE OF SATISFACTORY PERFORMANCE • UNIT RESPONSIBILITY



MORE AND BETTER *Service* FROM TODAY'S VALVES

"RESOLVED:
"That the superintendent
"shall be held responsible
"for the production of goods
"as near perfect in design,
"material and workmanship
"as shall make them merchantable
"and of a character that will serve
"to establish for this company
"a high reputation."

The policy expressed by this early Pratt & Cady Board of Directors Resolution has not been shaken even by the great World War. More than ever before the valves offered by Reading-Pratt & Cady today meet the demand for longer and better service.



R-P&C offers you a single responsible source for bronze, iron and steel gate, globe, angle and check valves—cocks and Lubrotite gate valves—bar stock valves—cast steel fittings—d'Este Automatic Regulating valves.

READING-PRATT & CADY

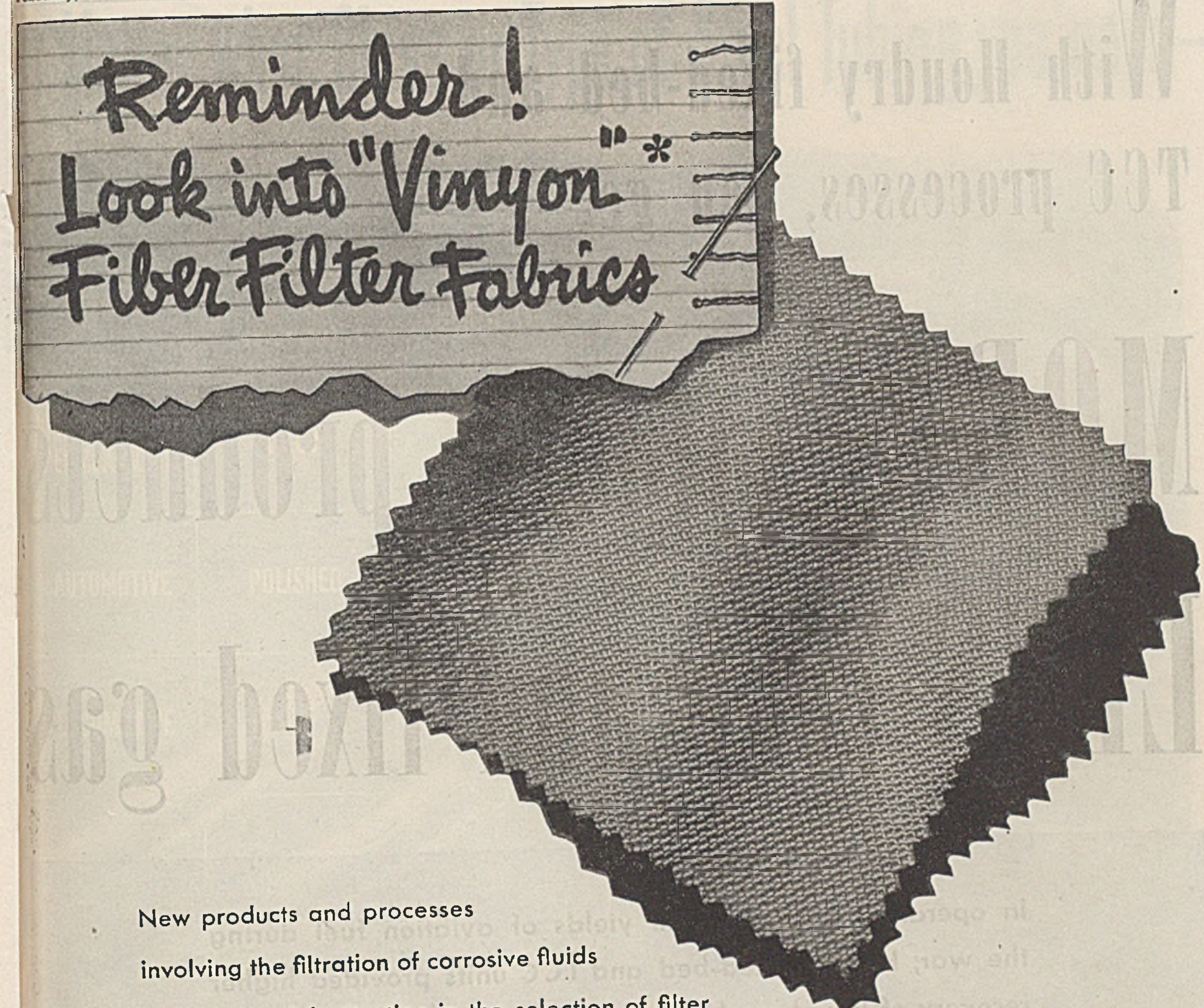
MANUFACTURERS OF
READING CAST STEEL VALVES AND FITTINGS • PRATT & CADY BRASS AND IRON VALVES
D'ESTE AUTOMATIC REGULATING VALVES

Reading, Pa. • Atlanta • Chicago • Denver • Houston • Los Angeles • New York • Philadelphia • Pittsburgh • San Francisco • Bridgeport, Conn.

ACCO

READING-PRATT & CADY DIVISION
AMERICAN CHAIN & CABLE

ACCO
TRADE MARK


Reminder!
Look into "Vinyon"*
Fiber Filter Fabrics

No Matter what Class or Type of Steel Tubing you need--

CARBON	STAINLESS WELDED (Gloweld)	HIGH DUCTILITY	HIGH TEMPERATURE SERVICE	CORROSION RESISTANT	AIRCRAFT
HIGH MAGNETIC PERMEABILITY	ALLOY	HIGH PURITY IRON (Globeiron)	STRUCTURAL	PRESSURE	SPECIAL ANALYSES
AUTOMOTIVE	POLISHED	STAINLESS SEAMLESS	COLD DRAWN	CONDENSER AND HEAT EXCHANGER	SPECIAL SHAPES AND FORMS
LOCOMOTIVE			TOUGH	ANNEALED	MECHANICAL
			RECTANGULAR	ROUND	SQUARE

*You can be sure of Uniformity and Quality when you Specify *Globe*

5018

GLOBE TUBES

Globe Steel Tubes Co. specializes in the manufacture of steel tubes — pressure — mechanical — stainless. Advanced machinery and methods characterize all mill operations.

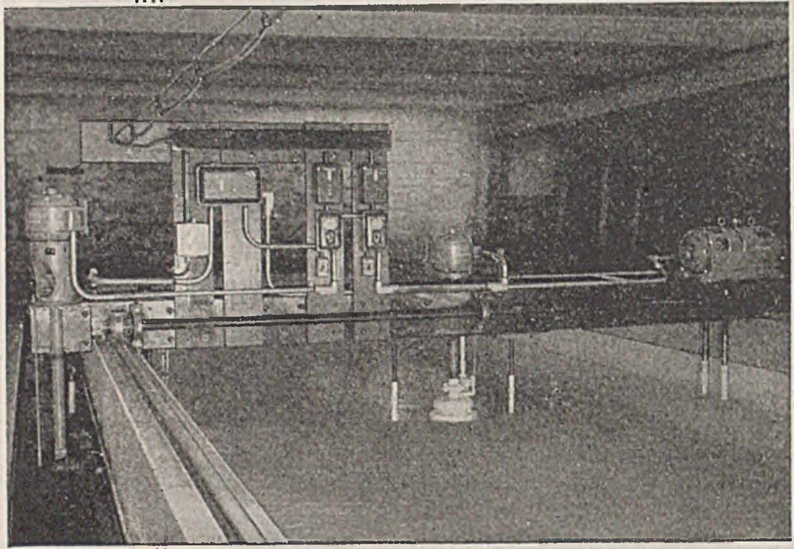
The uniformity and quality of Globe Steel Tubes is controlled by constant checks and tests in the Globe Laboratories, equipped with complete facilities for chemical, physical and microscopic analyses.

Globe engineers gladly give you the benefit of specialized knowledge and experience gained from countless laboratory and field tests of tubing in a wide-range of services and applications.

GLOBE STEEL TUBES CO. MILWAUKEE 4, WISCONSIN, U.S.A.

Hardinge will see you at the Chem. Show...

EXHIBITING 2 GREAT NEW HARDINGE PRODUCTS*
OF REAL INTEREST TO THE CHEMICAL INDUSTRY

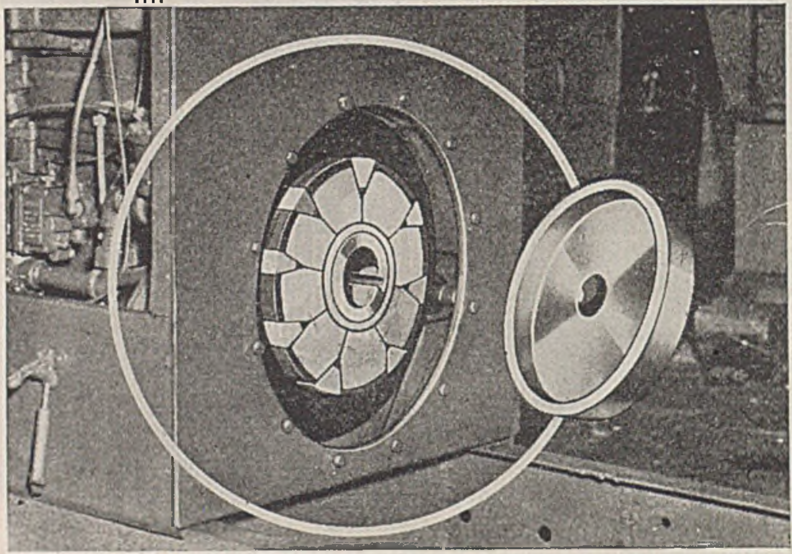


Hardinge Automatic Backwash Sand Filter operating in a paper mill.

Booth 60

THE A.B.W. RAPID SAND FILTER

An effluent filter for removal of suspended solids from liquid wastes, not readily removed by sedimentation methods. Unit consists of a specially compartmented sand bed with underdrains, and an *automatic backwash* cleaning mechanism traveling on tracks along the sidewalls of the filter tank. *Drawings on exhibition.*



Type SRC-50 B.L.M. Clutch installed directly on flywheel of power unit. Note simplicity of construction.

Booth 60

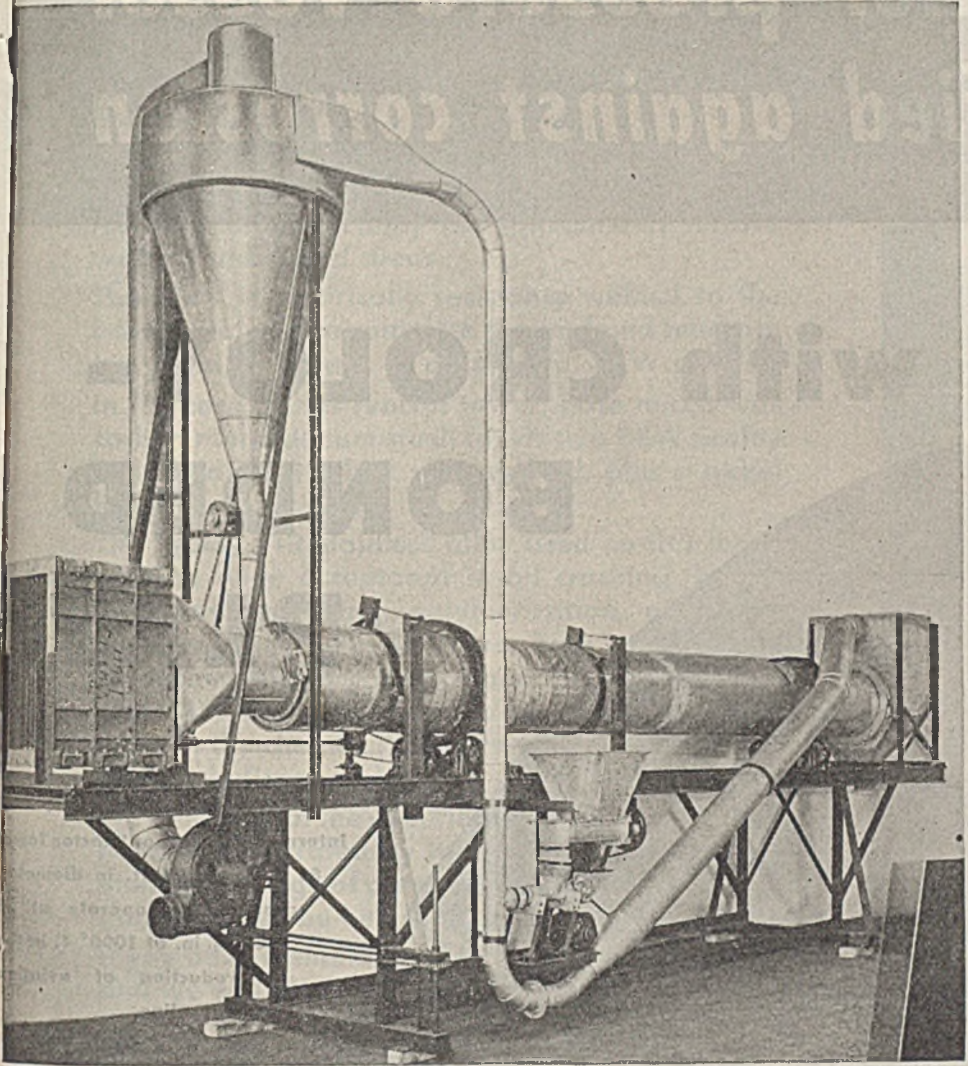
THE B.L.M. CENTRIFUGAL CLUTCH

Simple, positive-acting, and trouble-free, the Hardinge B.L.M. Automatic Centrifugal Clutch can be applied to all kinds of transmission drives. With only three main parts, it will outlast the power unit that drives it. No metal-to-metal surfaces to wear, no oiling necessary. *Working unit exhibited.*

* **Plus up-to-date information on a host of Hardinge "old reliables" . . .** including Ruggles-Coles Dryers, Hardinge Thermomills, Air Classifiers, Constant Weight Feeders, Thickeners and Clarifiers. You are invited to call at Booth 60, our headquarters at the 1946 Exposition of the Chemical Industries, Grand Central Palace, New York, February 25 – March 2. *Write nearest Hardinge Office for guest tickets.*

HARDINGE COMPANY INCORPORATED • YORK, PENN.
NEW YORK 17—120 E. 42nd St. • 205 W. Wacker Drive—CHICAGO 6
SAN FRANCISCO 5—501 Howard St. • 200 Bay St.—TORONTO 1

The Hersey INTERMEDIATE FEED SYSTEM



for DRYING

- Root Starches
- Vegetable and Fruit Waste
- Sweet Potato Meal
- Bagasse
- Saw Dust

and

Similiar 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.

Typical of the many alloy-clad pressure vessels fabricated by Babcock & Wilcox is a huge Reactor Tower—85 ft. high, 27 ft. diameter and weighing 360,000 lb.—recently completed for a refinery producing aviation gasoline. For long life and high resistance to corrosion at 30 lb. per square inch and 1000° F., it was fabricated from B&W Croloy-Bonded Plate.

Developed and used exclusively by B&W, this plate consists of a base metal clad with a corrosion-resisting chromium alloy over *the complete surface without unbonded areas.*

The alloy is electrically resistance-welded to the base metal with a complete thermal and mechanical bond by means of an original B&W process.

In the case of this reactor tower, base metal was carbon molybdenum steel, to which a B&W Croloy #13 Bond 7/64" thick was applied, plus a nickel insert layer.

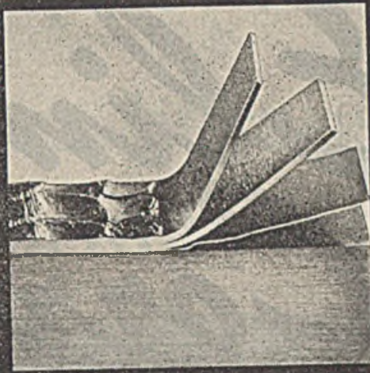
The Croloy #13 stainless alloy used on this job is gaining wide acceptance in oil cracking, hydrogenation, reforming, polymerization, alkylation and gas cracking or wherever high strength and corrosion resistance are factors. This is one of several B&W Croloy alloys used for types of process work in the chemical industry where their properties are indispensable.

We believe that the experience and skill, which we have demonstrated by many "firsts" in development and design of pressure vessels for the process industry, may be helpful to you.

If you have a similar problem now, drop us a line and we will gladly offer advice and provide data.

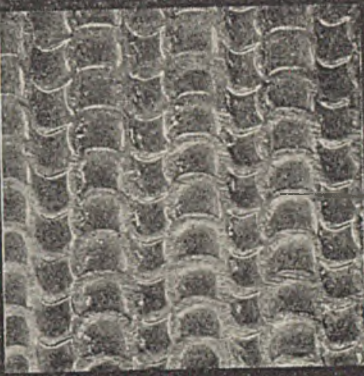
BABCOCK & WILCOX

THE BABCOCK & WILCOX CO.
85 LIBERTY STREET NEW YORK 6, N. Y.



LAYER CONSTRUCTION

Layer construction makes possible the bonding process by increasing the resistance to the flow of welding current, and by reducing the required pressure on the sheets to complete the bond.

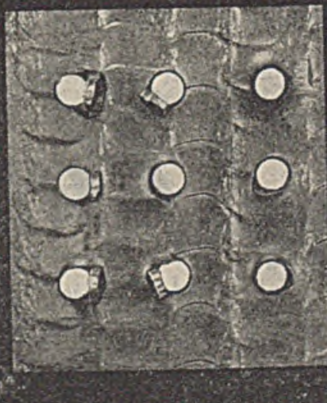


COMPLETE BOND OVER ENTIRE SURFACE

High thermal-conduction efficiency, with the complete over-all bond, minimizes temperature differentials between alloy and base metal that might cause bulging of the lining and its consequent failure. The complete bond also has high resistance to failure that might otherwise result from repeated heating and cooling — and eliminates the possibility of liquid flow between base metal and alloy.

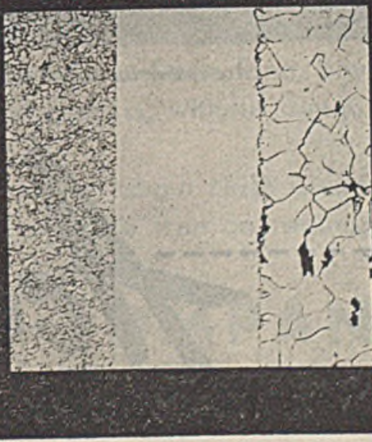
PUNCH TEST SHOWS STRENGTH OF BOND

Holes were drilled with a flat-bottom drill through the base metal of a bonded plate to, but not beyond, the junction line between the alloy layers and the steel plate. The bonded alloy was punched with a square-nose punch slightly smaller than the holes in the plate. With only ½-inch and ¼-inch ligaments between holes, the alloy did not pull away from the plate, but broke clean around the holes.



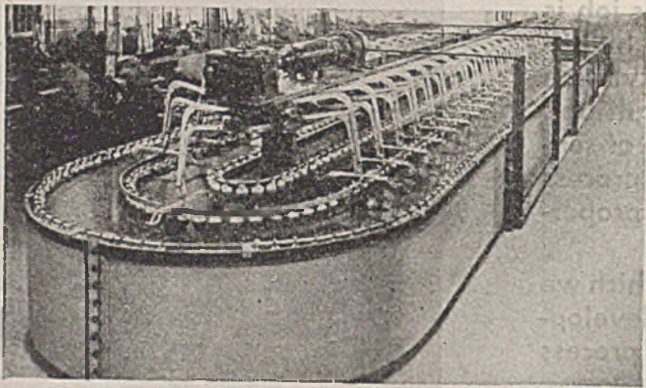
NICKEL SHEET STOPS CARBON MIGRATION

The importance of the nickel sheet between the base metal and the Croloy lining is illustrated by this micrograph. Note the absence of carbon migration from the base metal to the alloy, due to the lack of affinity of nickel for carbon. Thus, interface precipitation of carbon is prevented when the materials are subjected to high temperatures during bonding.

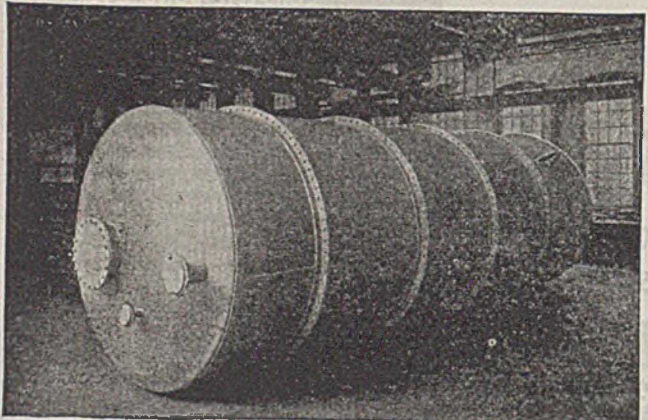


Eliminate Corrosion

ON 3 FRONTS



Ace rubber lined sectional tank for paper processing



Ace rubber lined return-type plating tank

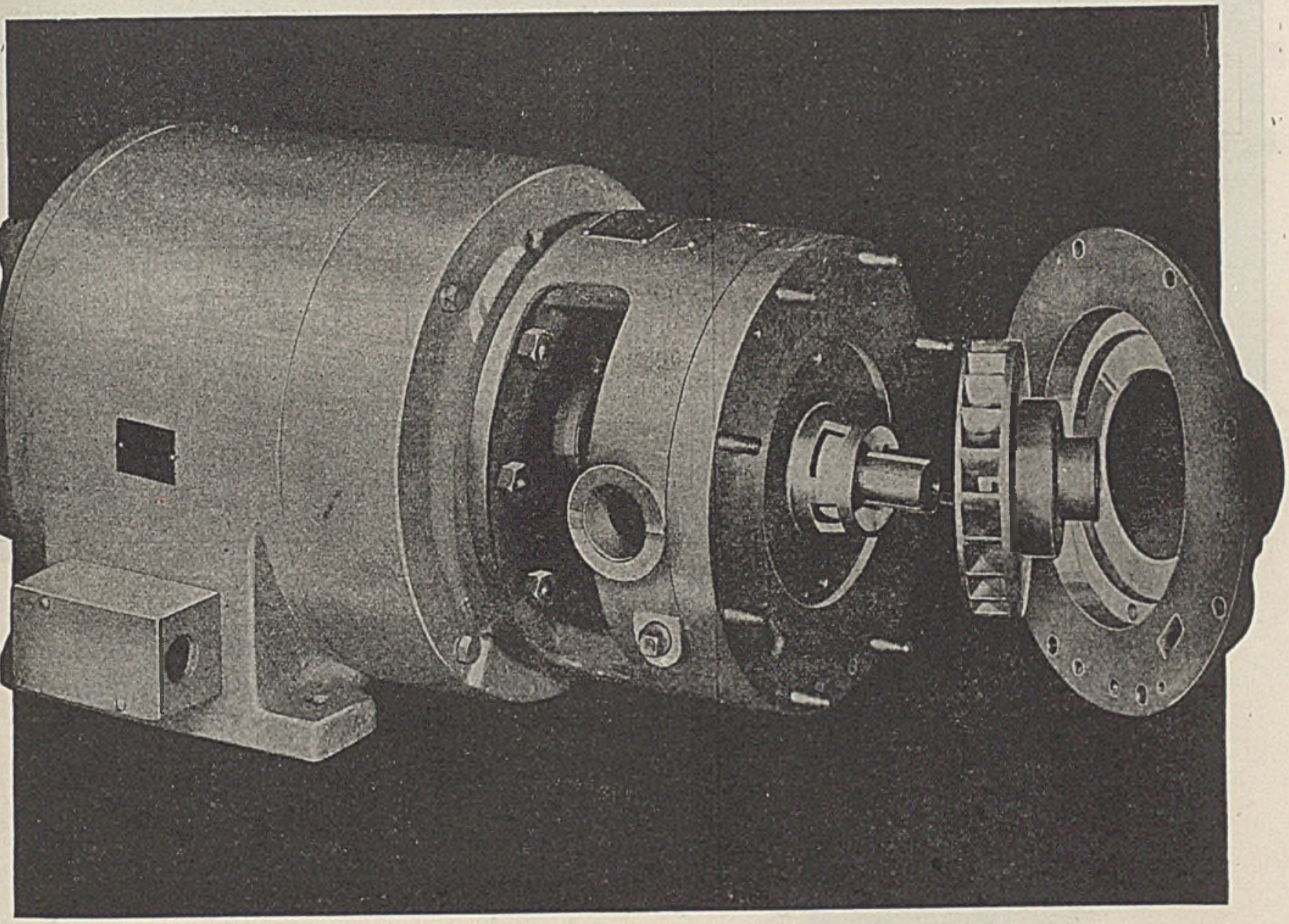
1. *Prevent damage to finished product.*
2. *End contamination of valuable chemical solutions.*
3. *Avoid deterioration of equipment.*

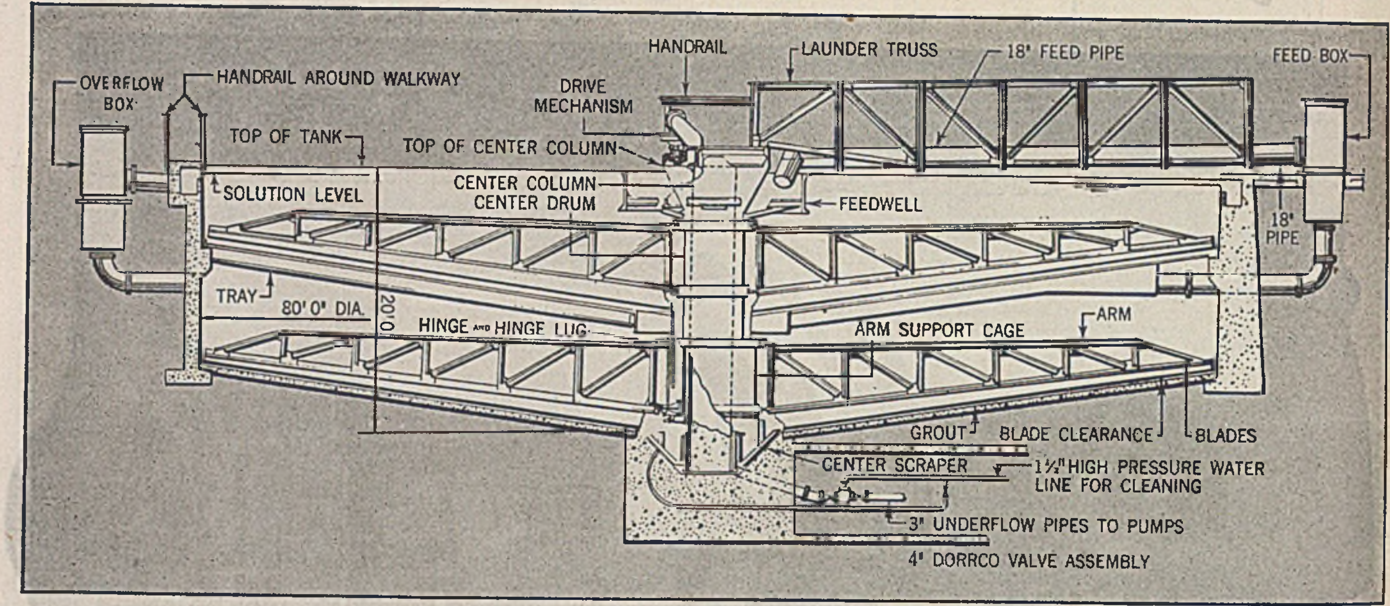
Draft Ace Hard Rubber in your war on corrosion affecting circulating, storage and processing operations. Ace Hard Rubber has been employed in leading industrial plants for corrosion-resistant services for nearly 75 years... with significant and substantial economies. Put Ace Hard Rubber to work in your plant—write for "ACE RUBBER PROTECTION", 64 page catalog containing important information for plant executives.

American Hard Rubber Company
11 Mercer Street, New York 13, N. Y.

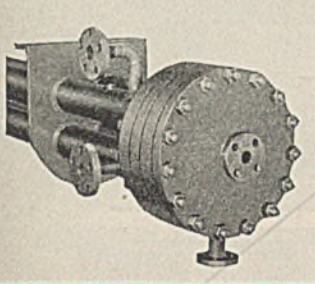
Ace Hard Rubber

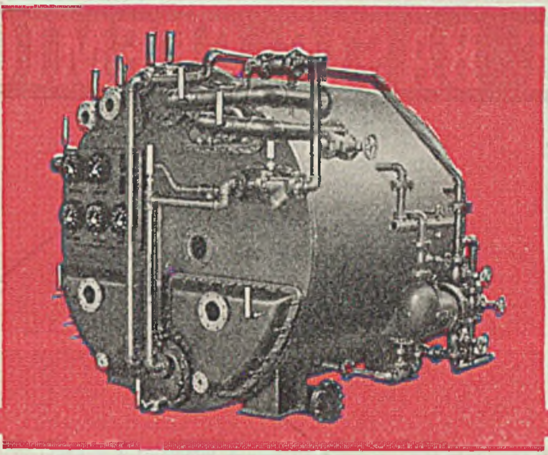
Hard and Soft Rubber Lined Tanks, Pipe and Fittings
All-Hard Rubber Pipe, Fittings and Utensils
Hard Rubber Pumps in a Wide Range of Sizes and Capacities
Made-to-Specification Equipment—Hard Rubber and Hard Rubber Lined

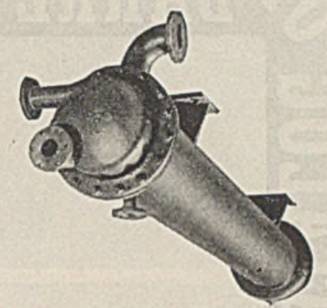



HANDRAIL
LAUNDER TRUSS
18" FEED PIPE
FEED BOX
OVERFLOW BOX
HANDRAIL AROUND WALKWAY
DRIVE MECHANISM
TOP OF TANK
TOP OF CENTER COLUMN
SOLUTION LEVEL
CENTER COLUMN
CENTER DRUM
FEEDWELL
18" PIPE
TRAY
80' 0" DIA.
20' 0"
HINGE AND HINGE LUG
ARM SUPPORT CAGE
ARM
GROUT
BLADE CLEARANCE
BLADES
CENTER SCRAPER
1½" HIGH PRESSURE WATER LINE FOR CLEANING
3" UNDERFLOW PIPES TO PUMPS
4" DORRCO VALVE ASSEMBLY

Left to right, a Fuel Oil Heater, Evaporator-Distiller, Feed Water Heater manufactured by B & G for the U. S. Coast Guard.





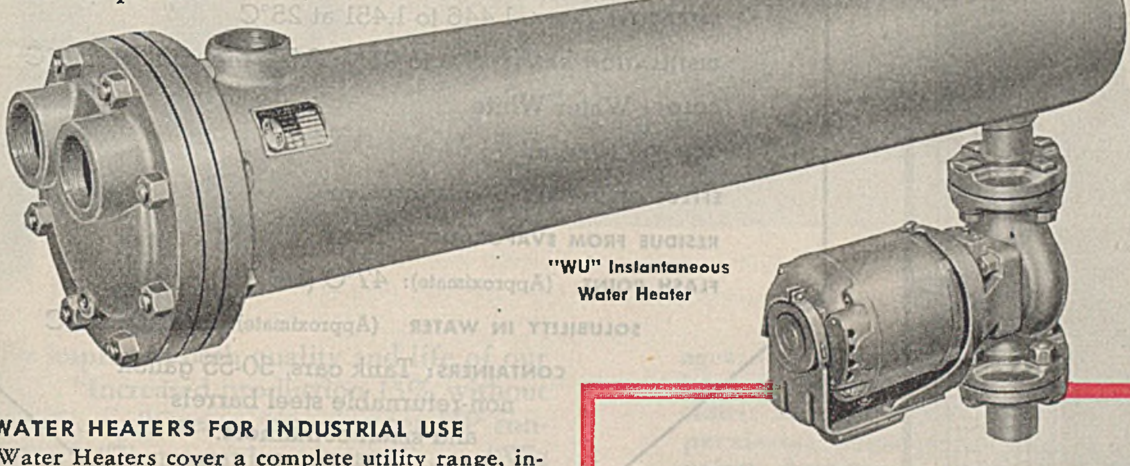


THE "KNOW-HOW" THAT WON THIS AWARD

IS BACK AT ITS OLD JOB OF BUILDING ADVANCED DESIGN HEAT TRANSFER EQUIPMENT

The art of building good heat transfer equipment is based not only on sound theoretical engineering, but also on practical experience which can anticipate and compensate for the difficulties sometimes encountered in actual operation. Bell & Gossett offers this kind of engineering *plus* modern manufacturing methods capable of translating good design into fine product.

Whether you are planning modernization of present equipment or are experimenting with new ideas for faster production and better quality, there is no obligation involved by a consultation with B & G engineers.



"WU" Instantaneous Water Heater

WATER HEATERS FOR INDUSTRIAL USE

B & G Water Heaters cover a complete utility range, including tank and tankless models for either water-to-water or steam-to-water heat transfer. Whatever your requirements, you'll find the proper type and capacity in the B & G line.

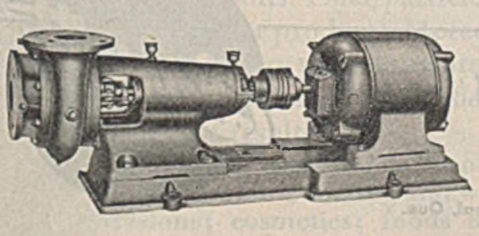
CENTRIFUGAL PUMPS

Rugged compact units, with all parts machined to rigid specifications and carefully assembled. Positive uniformity throughout assures quick and easy replacement in the field.

B & G Centrifugal Pumps are available in either flexible-coupled, base mounted models or with motor and pump integrally mounted. Open or semi-enclosed impellers.

For cash savings plus positive temperature control

The "WU" Instantaneous Water Heater is equipped with a B & G Booster, which pumps boiler water through the shell, thereby greatly increasing heater capacity. Whenever service water temperature drops below the desired degree, the Booster automatically pumps boiler water through the shell until service water is again at the correct temperature. Pumped circulation permits smaller pipes and fittings—hence material cost is cut to the bone and cutting and threading can be done on the job.



B & G

HEAT TRANSFER EQUIPMENT

BELL & GOSSETT COMPANY, DEPT. K-15 MORTON GROVE, ILLINOIS

FROM THE CATALOG OF BARRETT BASIC CHEMICALS...

CYCLOHEXANONE

A water-white ketone with exceptional solvent power. The industrial application of cyclohexanone is based largely on its powerful solvent action for a wide variety of materials including crude rubber, some of the synthetic elastomers, natural and synthetic resins and gums, cellulose ethers and esters, and especially for many vinyl chloride polymers and copolymers.

SPECIFIC GRAVITY: 0.941 to 0.945 at 25°C/15.5°C

REFRACTIVE INDEX: 1.446 to 1.451 at 25°C

DISTILLATION RANGE: 5% to 95%; 2.5°, including 155.6°C

COLOR: Water White

ACIDITY: Neutral

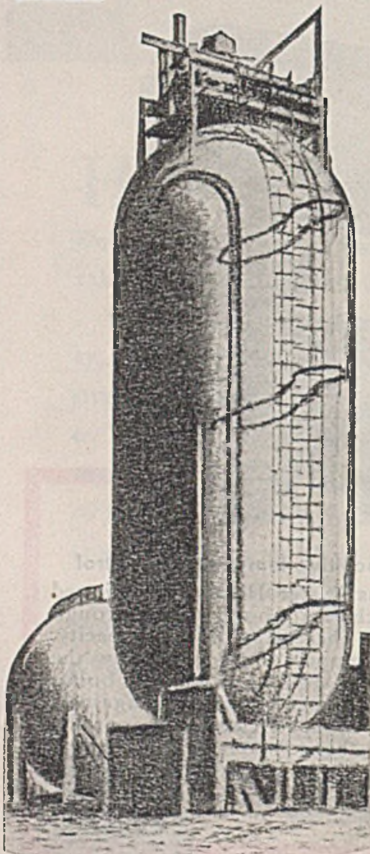
EFFECT ON METALS: Non-corrosive

RESIDUE FROM EVAPORATION: None

FLASH POINT (Approximate): 47°C (116.6°F)

SOLUBILITY IN WATER (Approximate): 8-9% at 20°C

CONTAINERS: Tank cars, 50-55 gallon
non-returnable steel barrels
and small containers.



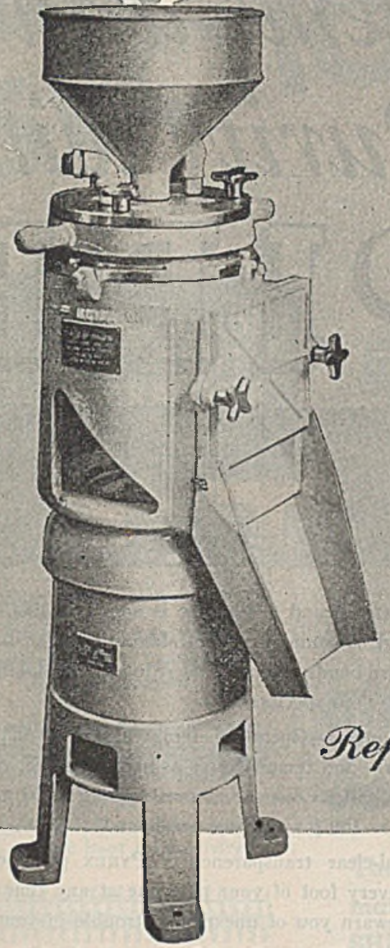
THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

In Canada: The Barrett Company, Ltd., 5551 St. Hubert Street, Montreal, Que.

Barrett

ONE MOVING PART . . . SIMPLE IN DESIGN . . . SANITARY IN CONSTRUCTION

THE DOOR TO EFFICIENCY



SANITARY
HOMOGENIZING
EMULSIFYING
DISPERSING
GRINDING

Increased Production at Lower Costs
Definite Product Improvements are
Reported by **PREMIER COLLOID MILL** *users*

"Definitely improved both quality and life of our product" . . . "Increased production 15% without added labor" . . . "Greater capacity per HP consumption" . . . "Test samples superior" . . . "We no longer have packing-gland trouble or product contamination" . . . "No internal corrugations to cause unsanitary conditions". These actual quotations are typical of performance reports from users of Premier Colloid Mills.

Whether the work to be done is emulsifying, dispersing or disintegrating . . . whether the material to be processed is liquid, paste or solid, every Premier installation proves itself by giving consistently successful results. Finer particle size is an important factor in finer products. Moreover, compulsory treatment of every particle assures uniform standards of quality. A partial list of fields which benefited from these results:—

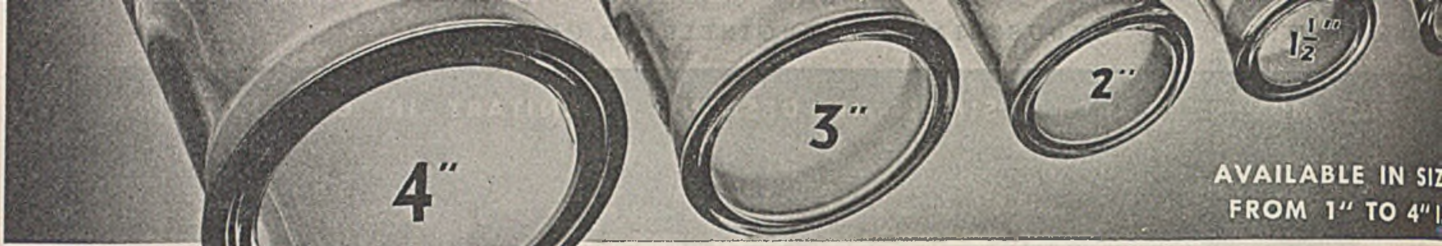
Adhesives, sealing compounds; asphalt emulsions; ceramic colors; coating and waterproofing emulsions; cosmetics; foods and beverages; oil emulsions; inks; leather finishes; latex (synthetic and natural); lacquer emulsions; lubricating oils, greases; pigment dispersions; organic chemical dispersions; paints, lacquers, varnishes; paper coatings, fillers, waterproofing; pharmaceuticals; plastics, resins; polishes, waxes; rubber compounds; textile finishes. (Special laboratory models are available for research work.)

Where a new process is involved and performance data desired, a test run may be arranged. Premier Mill Corporation, Factory and Laboratory, Geneva, N. Y.; General Sales Offices, 110 East 42nd Street, New York 17, N. Y.

Descriptive Literature on Request

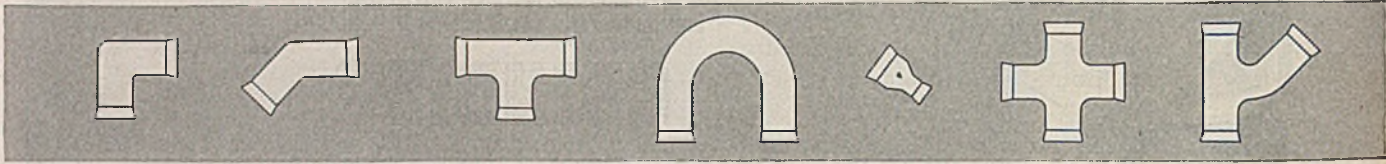
THE PREMIER MILL

Better products more profitably processed



Lick your Corrosion Problems and Maintain Product Purity with

GLASS PIPE



You can install Pyrex brand Glass Pipe Lines with complete confidence that they will stand up under actual plant operating conditions. Their sturdiness and serviceability have been proved by installations that have been in operation in process industry plants for many years. If your present pipe lines need frequent replacement because of chemical attack, if product purity is a factor, if visual inspection of your pipe lines and their contents would be helpful, you can profit materially by installing Pyrex Pipe.

PYREX PIPE & FITTINGS

Ease of Installation—Your own men can install a Pyrex brand Glass Pipe Line. No special tools or special training are required. The pipe, the fittings and the hardware come to your installation point ready for assembly. There's no cutting to lengths, no threading necessary on the job. Stock adaptor flanges are available to connect Pyrex Pipe to metal pipe and other plant equipment.

Sizes and Fittings—Pyrex Brand Glass Pipe is now available in 1", 1½", 2", 3" and 4" i.d. A complete line of standard Pyrex fittings includes ells, tees, return bends, laterals, and reducers. Special fittings can be readily made to your specifications.

Pressures and Temperatures—Operating temperatures as high as 250°F. are not unusual—and temperatures as high as 400°F. can be considered. Most installations operate at pressures up to 50 p.s.i.—but pressures as high as 100 p.s.i. can be considered.

Visibility—The crystal-clear transparency of Pyrex pipe permits visual inspection of every foot of your pipe line at any time. This feature serves to forewarn you of unexpected trouble in your pipe lines.

Low Cost—Whether you figure costs of new equipment in terms of initial outlay or in terms of over-all costs—spread over the length of service it will give you—Pyrex Pipe is your best bet.

Maintaining Product Purity—Pyrex Pipe is resistant to all acids (except HF) and moderate alkalis. There is no heavy metal pick-up or danger of metallic contamination.

Corning Engineers will gladly co-operate in applying it to your particular requirements. Write to the Industrial Sales Dept IE-2 Corning Glass Works, Corning, N. Y.

Pyrex BRAND GLASS PIPE

IS A REGISTERED TRADE-MARK AND INDICATES MANUFACTURE BY CORNING GLASS WORKS, CORNING, NEW YORK

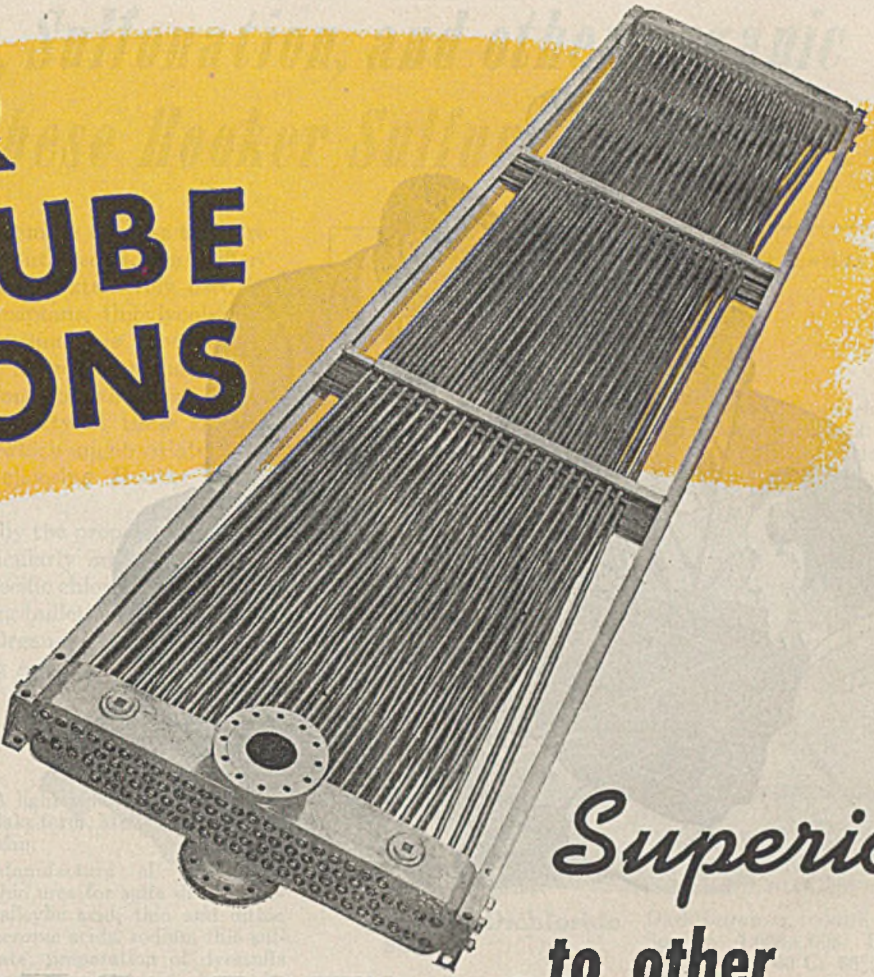
INDUSTRIAL SALES DEPT., IE-2
Corning Glass Works, Corning, New York

Please send me IA-1 "Pyrex Pipe" for the Process Industry

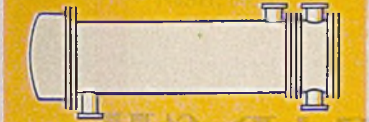
Name..Title..................

Firm..

G-R BENTUBE SECTIONS



ONLY G-R BUILDS THIS WIDE VARIETY OF HEAT TRANSFER APPARATUS



SHELL and BARE TUBE
Heaters, Coolers, Condensers, Heat Exchangers

G-FIN
Longitudinal-finned elements for greater heat conductivity

K-FIN
Helical-finned elements for vapors and gases

BENTUBE SECTIONS
with scale-shedding elements for hard or salt water

TUBEFLO SECTIONS
Non-clogging design for residuum and other dirty fluids

Superior to other atmospheric condensers and coolers *because . . .*

Their greater compactness . . . sturdiness . . . ease of installation . . . low maintenance expense . . . high salvage value . . . and their exclusive SCALE-SHEDDING feature which maintains rated heat transfer rates without requiring manual de-scaling of tubes . . . these features have made G-R Bentube Sections by far the most widely used atmospheric condensers and coolers for hydrocarbon vapors and petroleum derivatives.

These units have replaced pipe coils, cast iron sections, straight tube sections, shell-and-tube units, and other types of heat transfer apparatus in installation after installation; and today, more than 10,000 Bentube Sections are in service.

For complete description of these units, write for our Bulletin 1601.

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

GRISCOM-RUSSELL
Pioneers in Heat Transfer Apparatus

PROCTOR RESEARCH

eliminates guesswork in selecting drying equipment

Because of the accurate work done by Proctor research engineers, it is possible for Proctor & Schwartz to guarantee the performance of every drying system installed. Every single phase of the dryer's performance is clearly established by Proctor engineers before the sales contract is signed. You can see the effect of this on your production and costs. It, once and for all, eliminates any element of guesswork in selecting your equipment . . . often saving many production hours and considerable money. Not only this, but so thorough is the work of Proctor research, that it has frequently eliminated the necessity for a pilot plant. The data assembled by Proctor engineers over the years, the up-to-date testing equipment at their finger tips, plus their long experience in dealing with drying problems—makes it possible for them to interpret their laboratory findings in the light of commercial practice. The Proctor drying system recommended to you, after a thorough study of your drying problem, will be one suited in every detail to your individual needs. If you are considering any process that includes drying—it will be to your own selfish advantage to consult Proctor & Schwartz first.

PROCTOR & SCHWARTZ • INC •

PHILADELPHIA 20 • PA •

For Chlorination, Sulfonation, and other organic syntheses, use these Hooker Sulfur Products...

Hooker sulfur products are valuable to chemists because they are all extremely reactive and capable of being utilized in many different reactions. For example, the sulfides are extensively used in the preparation of organic sulfides, mercaptans, thioglycols and thio acids. All of the sulfur-chlorine compounds are important as chlorinating agents. Sulfuryl chloride, in addition, has great potentialities in organic synthesis for sulfonation, and as an acylating and condensing agent. The high quality of these Hooker chemicals, their freedom from impurities which might vitiate these reactions, are important reasons for choosing Hooker sulfur products.

Technical data sheets describing more fully the properties of these products are available. If you are particularly interested in the reactions of Sulfuryl Chloride or other specific chlorinating agents, you may also want copies of the following bulletins:

Bulletin No. 330—Sulfuryl Chloride in Organic Chemistry.
Bulletin No. 328A—Hooker Chlorinating Agents.

PRODUCT *Chemical Formula* *Molecular Weight*	**DESCRIPTION & USES**
Sodium Sulfhydrate $NaSH$; 56.1	A light lemon colored solid in flake form. Melting point 55°C Min. Manufacture of thiosulfate, thio urea for sulfa drugs, thiosalicylic acid, thio and dithio benzoic acids, sodium thio sulfate; preparation of dyestuffs and other organic chemicals; catalyze formation of thioamides; unhairing hides; desulfurizing viscose rayon and in ore flotation agents.
Sodium Sulfide Na_2S; 78.1	A light salmon colored solid in flake form. Melting point 100°C Min. Manufacture of dyestuffs, intermediates, organic sulfides, insecticides, paper pulp, special glass, soap and rubber; as an ingredient of dye liquor; engraving, lithography, and printing; ore flotation and refining metals, dissolving cresol from coal tar oils; unhairing hides; desulfurizing viscose rayon.
Sodium Tetrasulfide Na_2S_4; 174.23	Aqueous solution containing 40% by weight of compound. Clear, dark red liquid. Reducing organic nitro bodies; manufacture of sulfur dyes; insecticides and fungicides; ore flotation reagent; soaking hides and skins; preparation of metal sulfide finishes.

HOOKER RESEARCH *Presents*

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A new hydrogenation product of Hooker Research is offered for your consideration. An examination of its physical properties may suggest interesting applications. Dimethyl Cyclohexane is a hydrogenated xylene, but in its chemical behavior it resembles the aliphatic hydrocarbons more than the aromatic. It can be oxidized or reacted with halogens to yield products of potential value in organic synthesis.

Briefly, Dimethyl Cyclohexane is a water white liquid of mild odor. It consists of a mixture of meta-, para-, and ortho- isomers. Its freezing point is below -65°C, its boiling point is 120°C, its specific gravity at 15.5°/15.5°C is 0.776. Its water solubility is extremely low and it is completely miscible with most common solvents.

Technical Data Sheet No. 360 describing the chemical more completely, and experimental samples are available when requested on your business letterhead.

PRODUCT *Chemical Formula* *Molecular Weight*	**DESCRIPTION & USES**
Sulfur Dichloride SCl_2; 103	Dark brown or reddish liquid. Sp. Gr. 1.638±.005. Decomposes above 40°C. 66% Min. Cl_2 content. Chlorinating agent, in manufacture of organic acid anhydrides and in organic synthesis.
Sulfur Monochloride S_2Cl_2; 135	Yellow to slightly reddish liquid. Sp. Gr. 1.690±.005. B. P. 138°C. 50% Min. Cl_2 content. Manufacture of insecticides, linseed oil substitutes, dye intermediates, pharmaceuticals, organic acid chlorides.
Thionyl Chloride Refined and Technical $SOCl_2$; 119	Colorless to yellow or pale red liquid. Sp. Gr. 1.644. B. R. Tech. 72° to 79°C. B. R. Refined 75° to 78°C. Chlorinating agent. Forms organic acid chlorides and anhydrides, alkyl chlorides from corresponding alcohols.
Sulfuryl Chloride SO_2Cl_2; 135.0	Light yellow liquid. Sp. Gr. 1.680. B. R. 2° including 69.1°C. Chlorinating agent to produce chlorphenol and other chlorination reactions in organic synthesis. Forms chlorides and anhydrides of organic acids.

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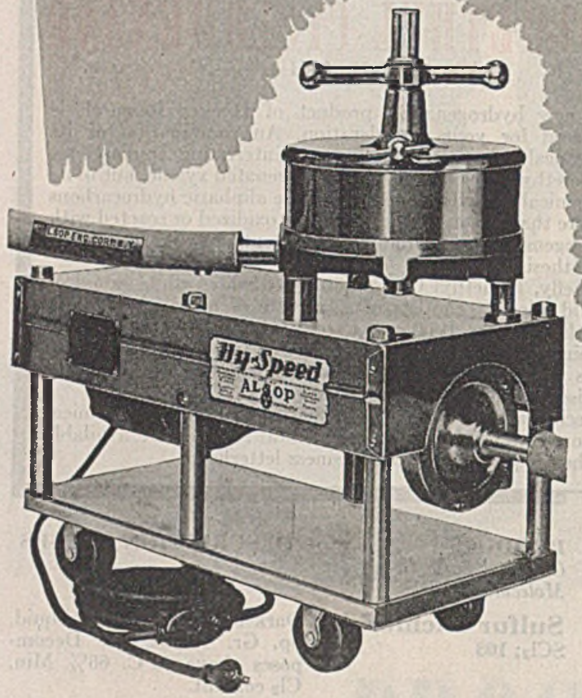

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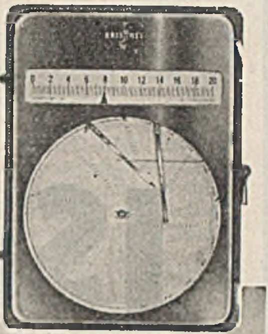

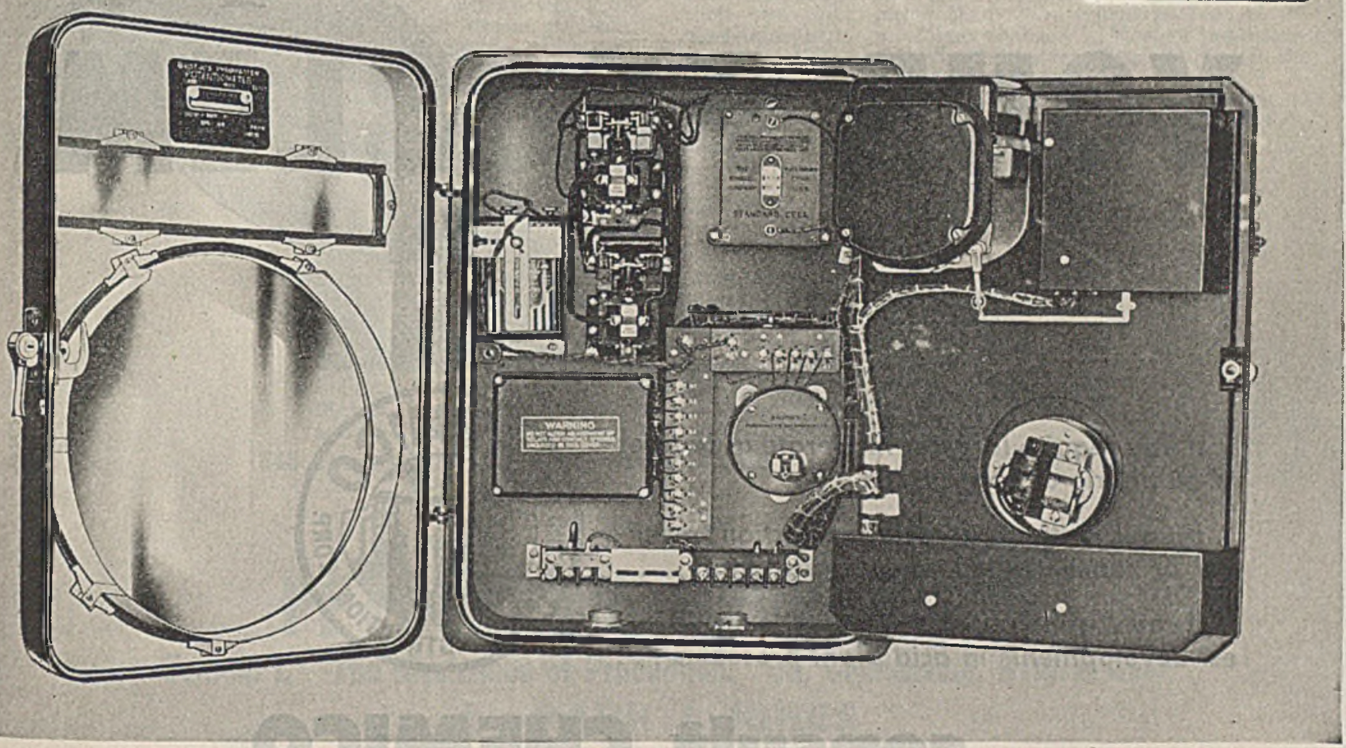

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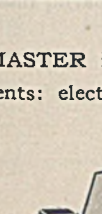

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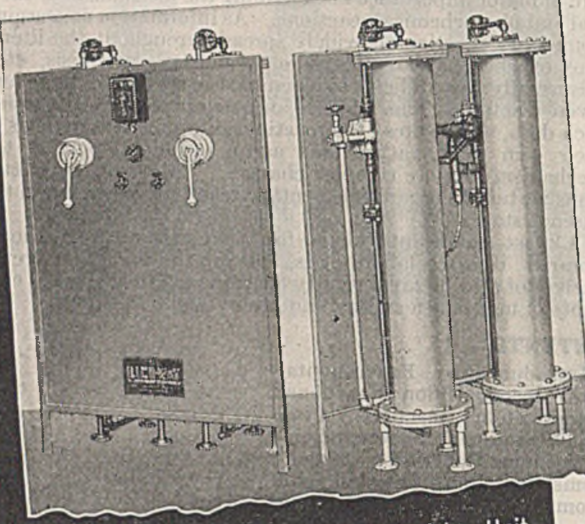

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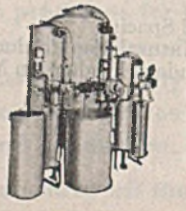

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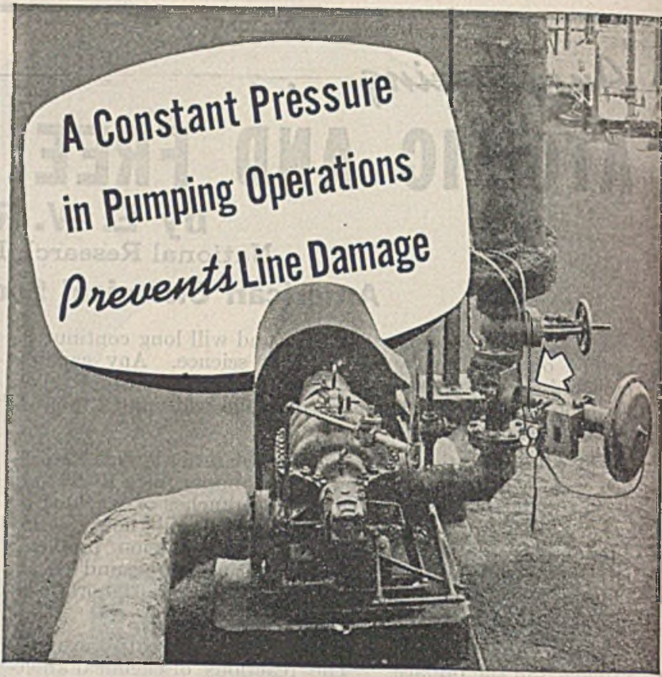

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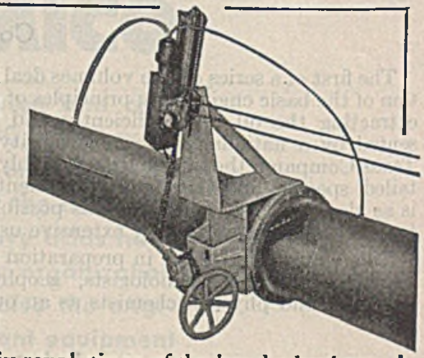

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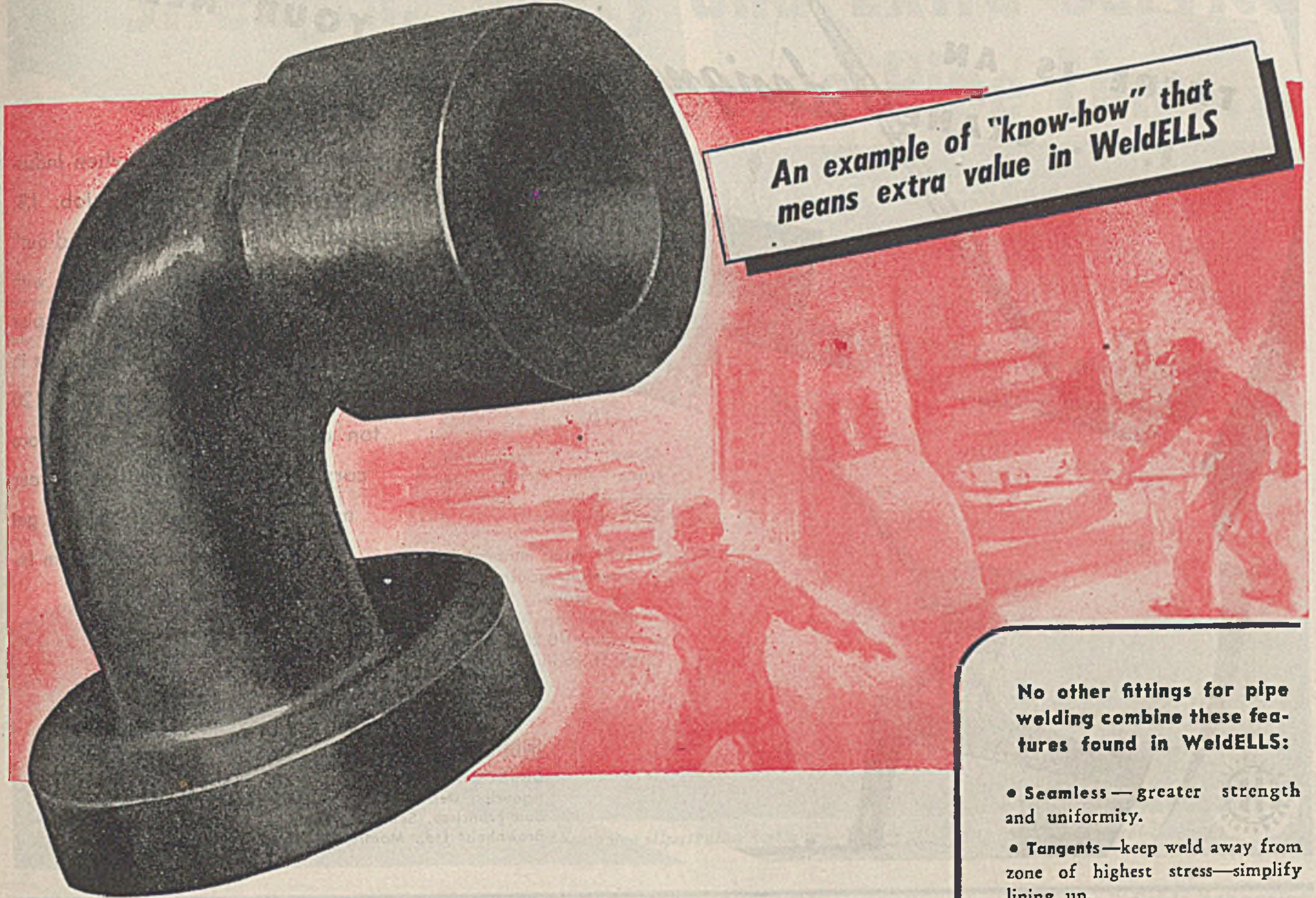

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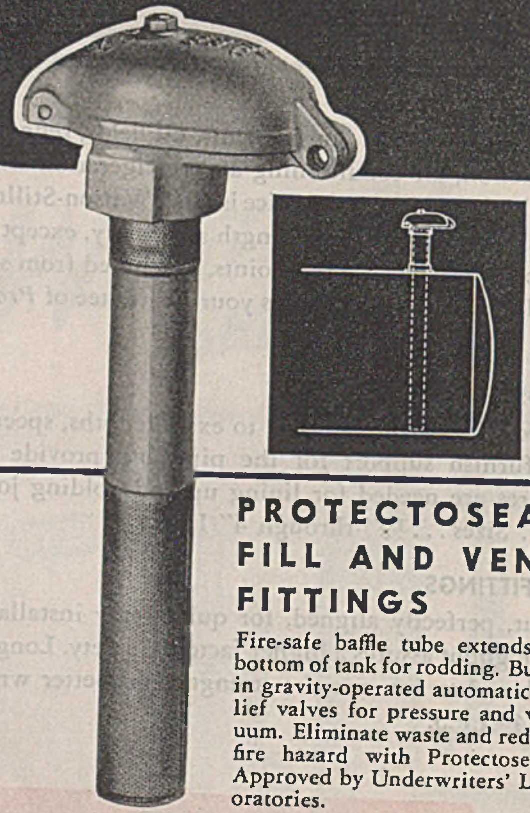

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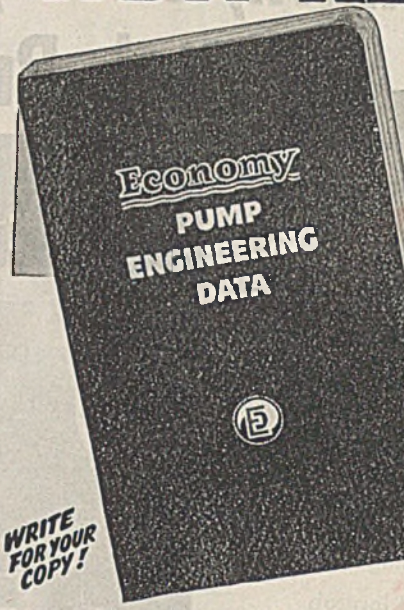

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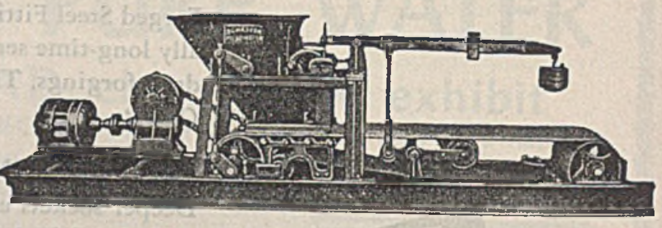

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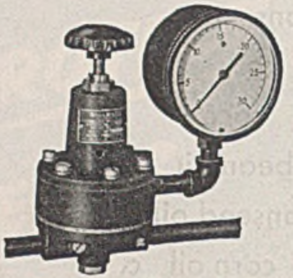

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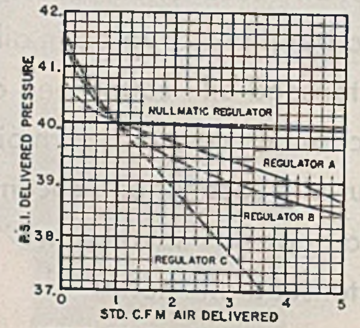

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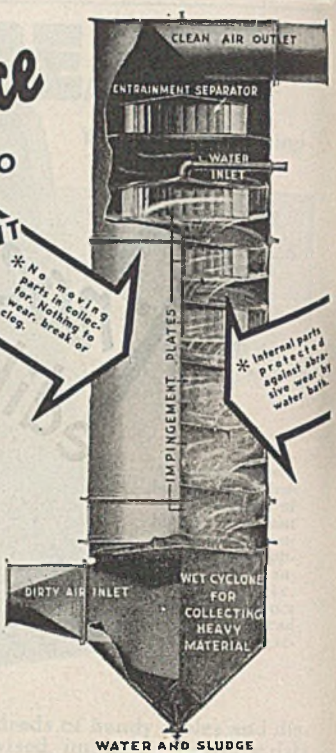

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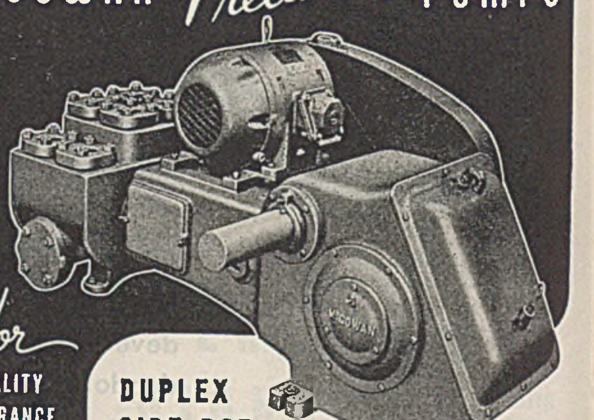

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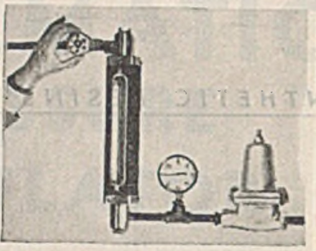

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Boiling point	14.0° F. (−10.0° C.)
Density of liquid at 80° F.	(85.03 lbs. per cu. ft.)
Specific gravity at 80° F.	1.363
Density of gas at 0° C. and 760 mm:	2.9267 grams per liter (0.1827 lb. per cu. ft.)
Critical temperature	314.82° F. (157.12° C.)
Critical pressure	1141.5 lbs. per sq. in. abs.
Solubility	Soluble in water
Purity	99.9+% (by wt.) SO_2 (H_2O less than 0.01%)

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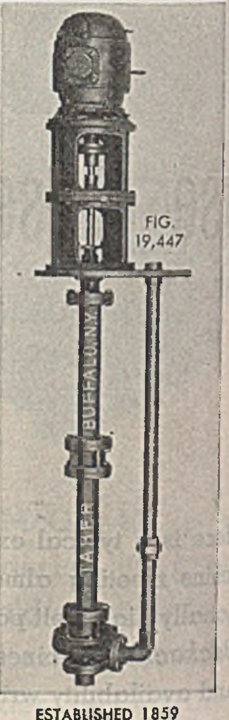

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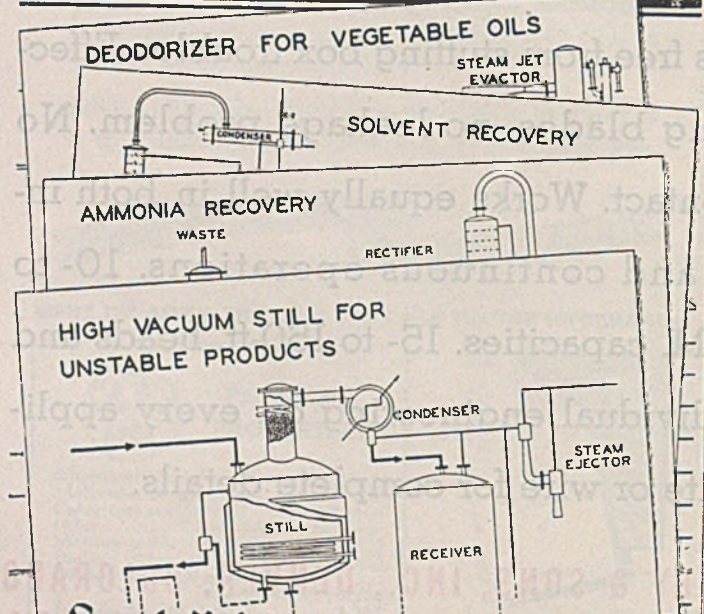
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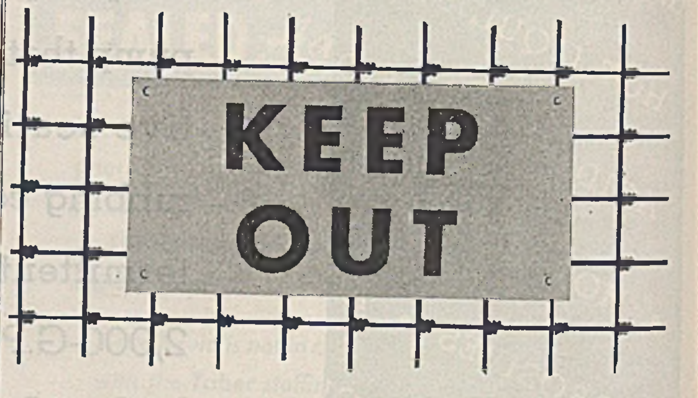
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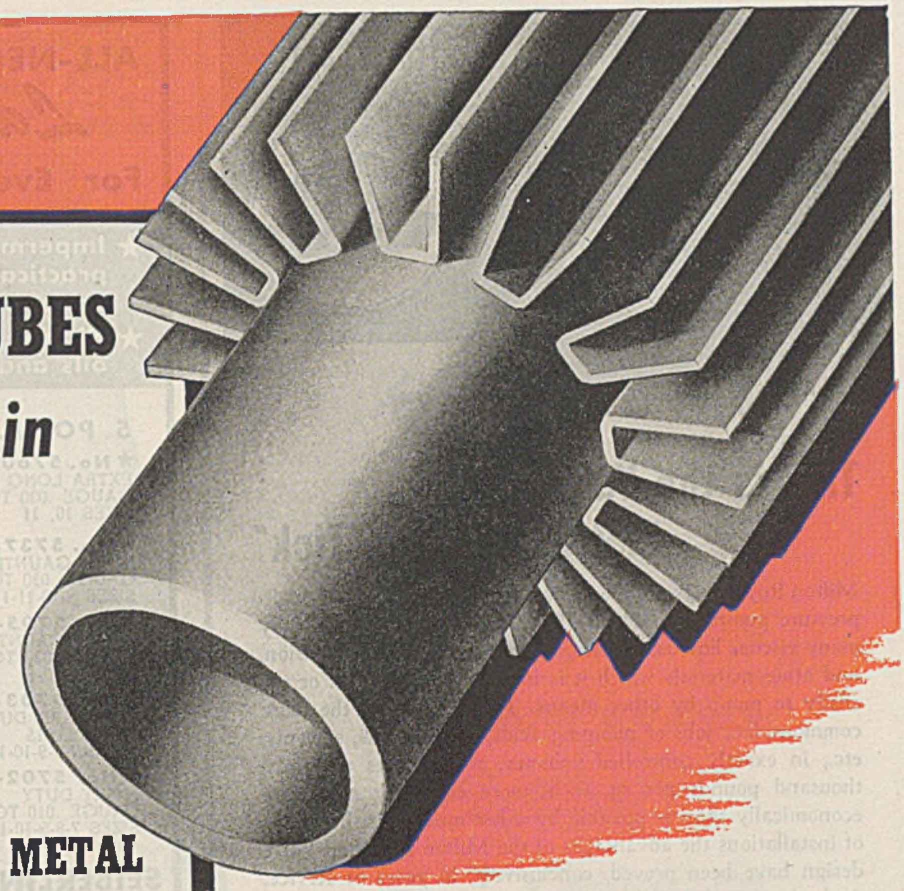


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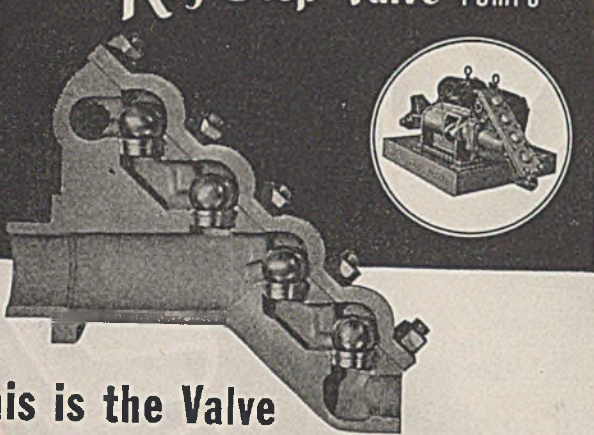

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- **Streamline flow of liquid through valve with resulting *self-cleaning action* and *minimum slippage*.**
- **Double-ball checks . . . positive in action, even when working with liquids containing high percentages of solids in suspension. If one ball is held off its seat the second ball-check holds . . . thus eliminating "orifice action" under a partially closed valve and effectively *eliminating wire-drawing of the valve seat*.**
- **Complete and immediate discharge of air or gas from the valve chamber . . . impossible to "pocket" air. With the Step-Valve pump, therefore, high and reproducible volumetric efficiencies are assured . . . *exactly the same volume of material is delivered* at a given stroke setting with every stroke of the pump.**
- **The Milton Roy Step-Valve with single cover plate (illustrated) is particularly well adapted for handling VISCOUS MATERIALS, CRYSTALS IN SUSPENSION, FIBRES IN SUSPENSION, SLURRIES, FOOD PRODUCTS.**
- **Flow resistance in this type Step-Valve is at a minimum because the ball-checks *lift completely out* of the stream of flow . . . the flow passes *under the ball-checks,* not around them.**
- **Removal of the single cover plate provides complete and quick accessibility . . . ball-checks and pump chamber may be thoroughly cleaned whenever required, as in handling foods for example.**

These are only a few of the principal advantages of Step-Valve design. Write for Bulletin 426 with the complete story. Ask also for the Milton Roy Pump Catalog if you do not have one in your files.

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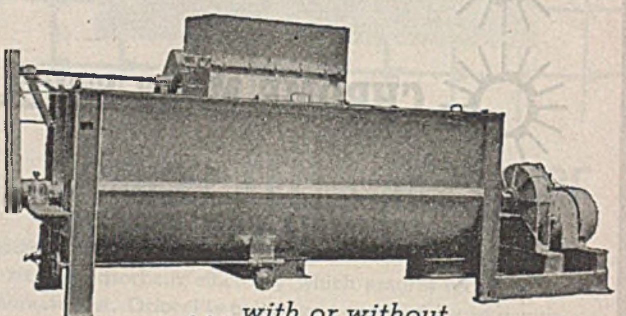

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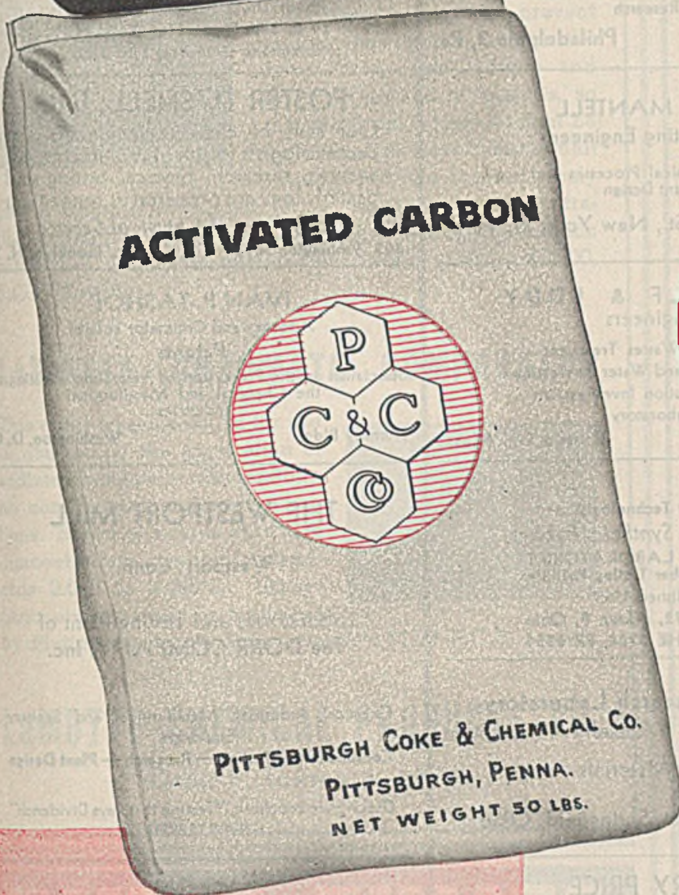
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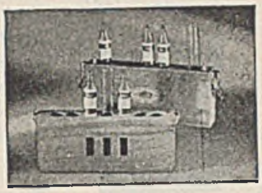

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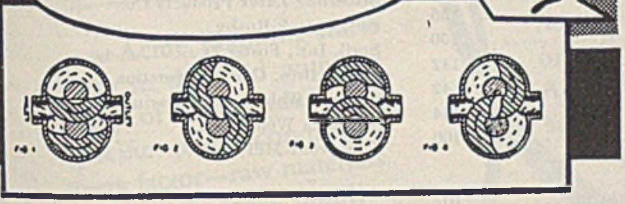

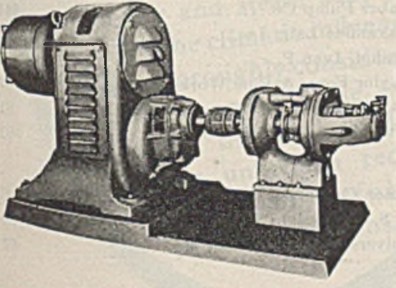

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From the Editor's Desk

Demand for 105 million ounces of silver this year is expected to exceed the estimated supply by about 40–50 million ounces.

★ Chemical output kept pace with national expansion during the war. From 3.9 billion dollars in 1939, it rose to 8.3 billion during 1944.

★ More than 200 million dollars were invested by the Government in ten synthetic ammonia plants which have a combined design capacity of 800,000 tons of fixed nitrogen.

★ During the war Rubber Reserve sold about 5 million dollars worth of ethylbenzene, for making cumene additive to high-octane gasoline, to the Petroleum Administration for War.

★ Canada, one of our chief sources of uranium compounds, actually shipped less uranium to us in 1943 than during the previous two years. The figures are 334, 377, and 211 thousand pounds for 1941, 1942, and 1943, respectively. Radium salts went up from 4412 mg. in 1941 to 22,943 and 90,775 mg. for the next two years.

★ Sodium lactate injected intravenously is effective in overcoming the effects of methyl alcohol poisoning. Navy physicians also found sodium bicarbonate, taken by mouth, to be effective.

★ Although natural rubber is coming into the country in a steady stream, it has not yet equaled the demand.

★ November was the month of largest sales of government surplus property so far. Actual sales amounted to $70,746,000 for property that originally cost $171,274,000.

★ The new rat poison, ANTU (alpha-napthylthiourea), was discovered during taste tests. Crystals of this substance, which was thought to be nontoxic, were placed on the tongues of several rats. To the surprise of the investigators, death resulted within a short time.

★ Construction problems for the chemical industry will not be so acute as for other industries, since much of the war plant is readily adaptable to manufacturing operations without too much alteration. Lumber for building is the narrowest bottleneck, and the supply will be inadequate for the rest of this year.

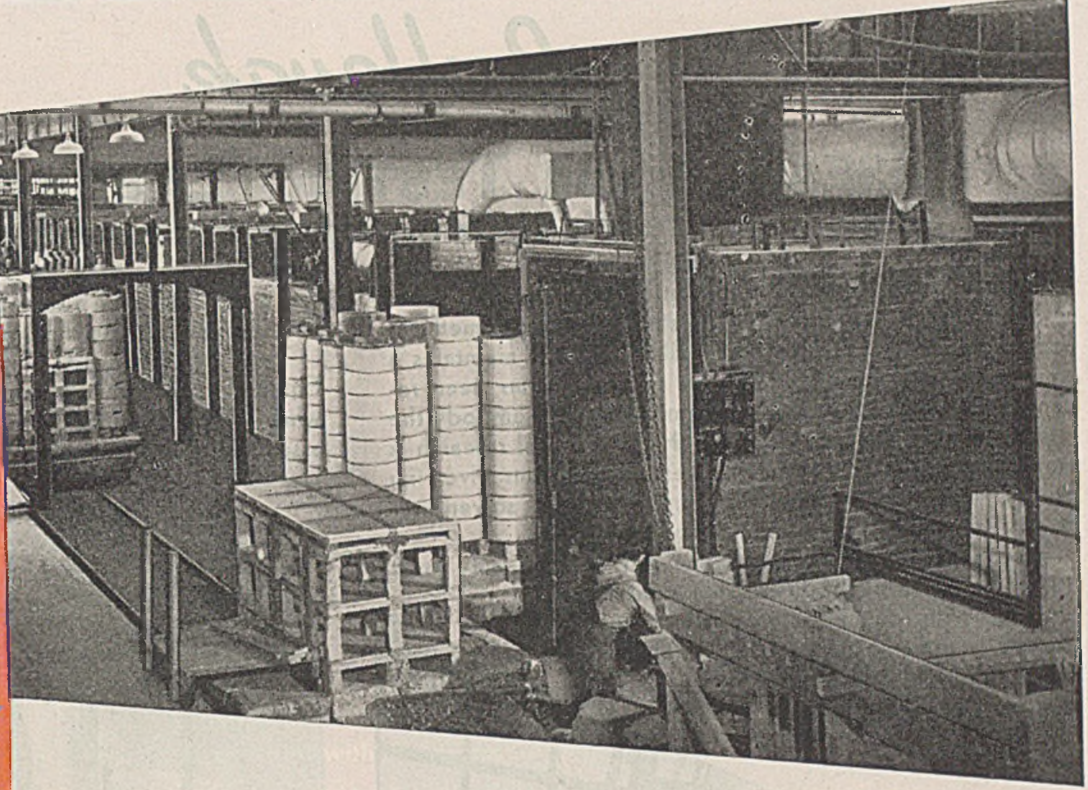
★ Streptomycin has not yet gone into large scale production. Pilot plants are still the principal production units in all producing companies.

★ Last month saw the return of domestic penicillin plants to normal capacity production. There is still a shortage, however, since the whole world must be supplied with this product.

★ The Tariff Commission's first monthly report on phenol shows that October production was 15,565,258 pounds, which indicates an annual figure of almost 187,000,000 pounds. Monthly data were not available either during or before the war. The same report places formaldehyde output in October at 31,934,286 pounds, equal to about 383,000,000 per year.

★ Large quantities of ergot imported from Europe are being held up by the Food and Drug Administration because they are substandard in quality.

★ With more pyridine required for pharmaceutical uses (such as sulfas and vitamins), high-boiling tar bases are being used to make rust inhibitors which formerly depended on pyridine.



VISUAL PYROMETER

ELECTRICAL PYROMETER

PYROMETRIC CONES AND DISCS

Why you can be sure of higher CORROSION-RESISTANCE, positive NON-ABSORPTION *with* LAPP CHEMICAL PORCELAIN

3 THOROUGHLY VITRIFIED BODY PRODUCED IN THE LAPP CONTINUOUS KILN

● You can fully capitalize on the many trouble-saving and money-saving advantages of ceramics *only* by getting the *most* out of ceramic ware. LAPP Chemical Porcelain is different because it offers you all the "natural" advantages of ceramics *developed to their highest degree.* Complete corrosion-resistance to all acids (except HF), positive non-absorption, added mechanical strength and purity are *plus* advantages of LAPP Chemical Porcelain. These are made possible by its *extra* dense, homogenous, *thoroughly* vitrified body. A vitally-important contribution to that body is made by the LAPP Continuous Kiln. In a 380-foot tunnel kiln temperatures exceeding 2250°F are precisely controlled so that the formed clay is slowly brought to the exact molten stage where *complete* vitrification occurs. The clay body is transmuted by fusion into *solid* Porcelain, chemically inert and well beyond the degree of vitrification found in ordinary ceramics or vitreous china.

If you've had trouble with ceramics on a problem that ceramics should solve—it will pay you to experience the difference in LAPP Chemical Porcelain. *LAPP Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.*

LABORATORY QUALITY IN PLANT PRODUCTION WITH

Lapp

Chemical Porcelain

ARMY E NAVY

VALVES • PIPE AND FITTINGS • RASCHIG RINGS • TOWERS • KETTLES • FILTERS • SPECIAL SHAPES

Buflovak

RESEARCH and TESTING LABORATORIES

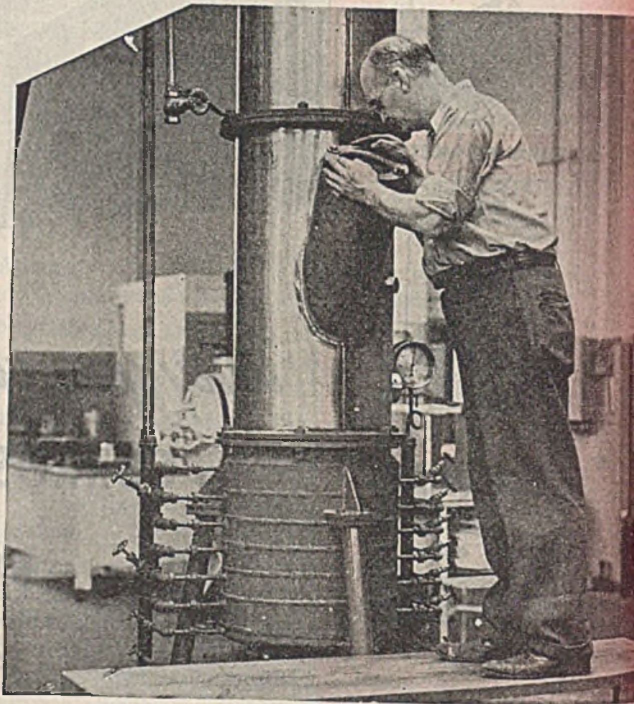
Can aid you in reaching new heights in process production

TO ASSIST customers in the solution of processing problems and to develop more efficient production methods and improved finished products, BUFLOVAK maintains a Research and Testing Plant. New equipment has been recently installed. These modern, semi-plant units embody the latest and most advanced design. Here practical research is employed in the solution of processing problems involving drying, evaporation, extraction, impregnation, solvent recovery, crystallization and food processing.

These facilities can save you time and money. They show the commercial possibilities of a contemplated process, with data on production cost, capacity, and the characteristics of the finished product. Results are definite, because each test is conducted on a semi-plant scale, with equipment which gives accurate indexes of full production results.

These tests safeguard your investment in BUFLOVAK Equipment by showing unmistakably, right at the start, what will be obtained from a given process. It is your assurance of the most efficient type of equipment.

A Special research evaporator scientifically equipped for the study of evaporator performance.



Evaporator for concentrating materials in sufficient quantities to gi indexes of the characteristics of the finished product.

BUFLOVAK EQUIPMENT

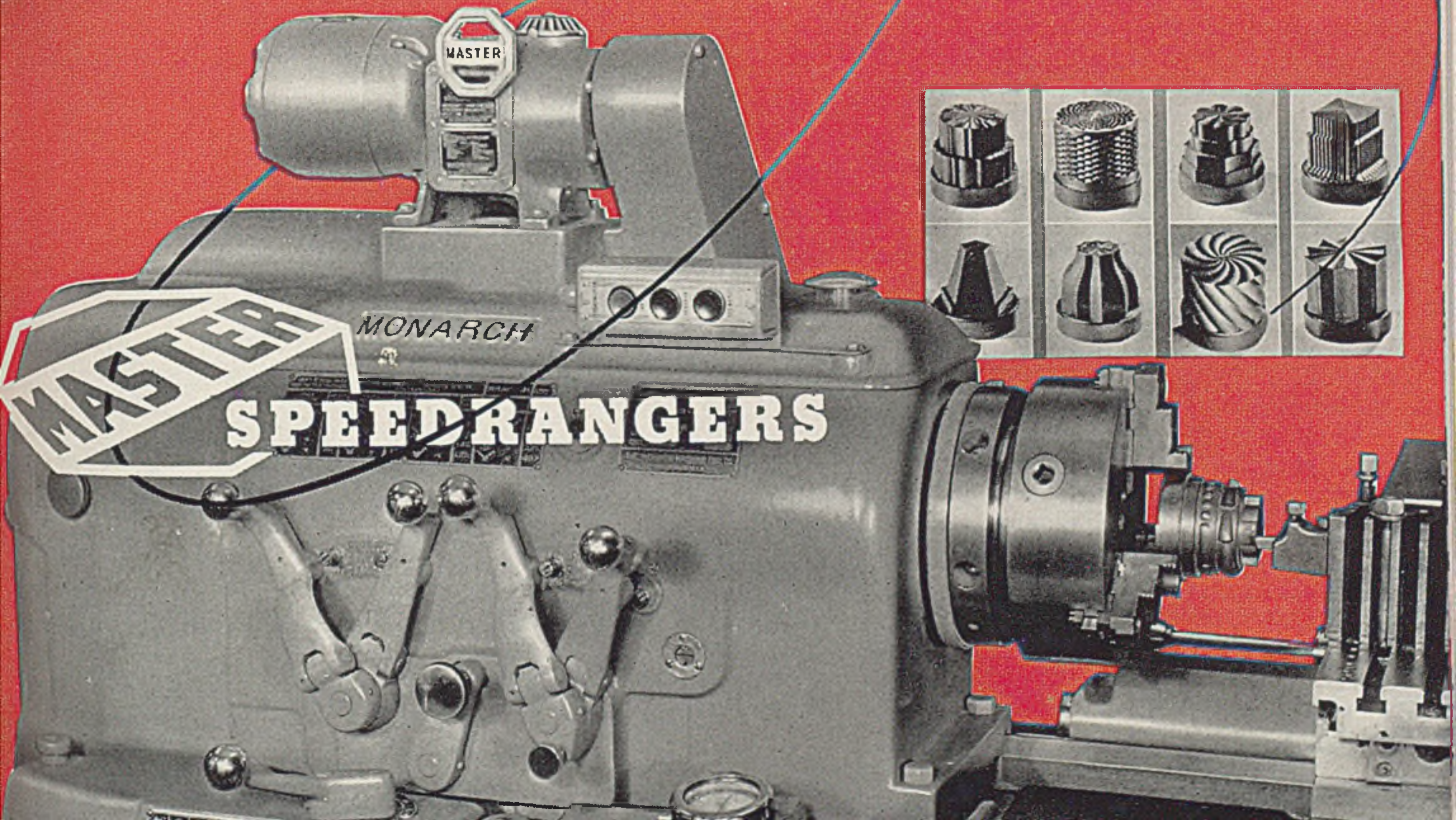
DIVISION OF BLAW-KNOX CO.

1549 FILLMORE AVE. BUFFALO 11, N. Y.

See Our Exhibit

NEW YORK

FEB. 25 TO MARCH 2, 1946
GRAND CENTRAL PALACE
TWENTIETH EXPOSITION
CHEMICAL INDUSTRIES
BOOTH 6


MASTER
MONARCH
MASTER
SPEEDRANGERS

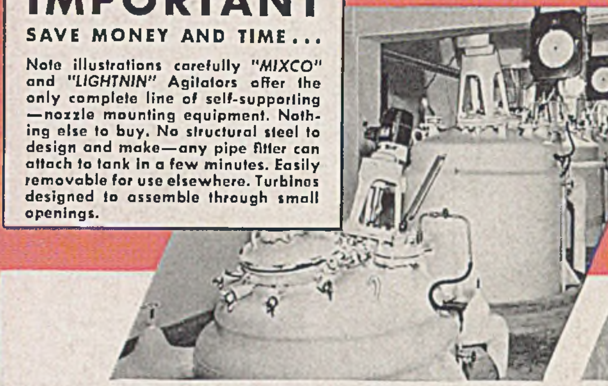
Process Adapted Agitation FOR

PRESSURE VESSELS Self-Supporting, Factory-Assembled and Permanently Aligned

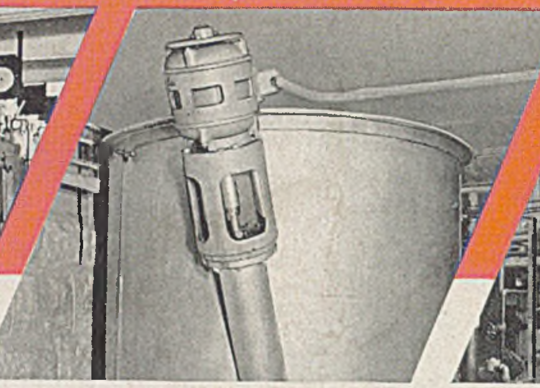
IMPORTANT

SAVE MONEY AND TIME . . .

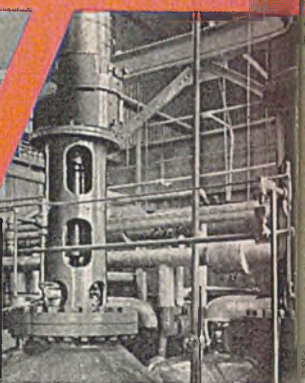
Note illustrations carefully "MIXCO" and "LIGHTNIN" Agitators offer the only complete line of self-supporting —nozzle mounting equipment. Nothing else to buy. No structural steel to design and make—any pipe fitter can attach to tank in a few minutes. Easily removable for use elsewhere. Turbines designed to assemble through small openings.



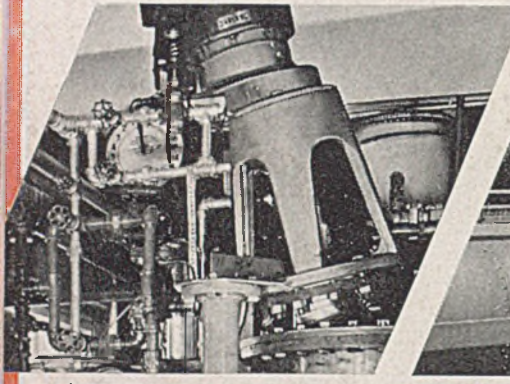
Nozzle mounting propeller-type agitator mounted in off-center position. Needs no baffles—permits freedom of head design. Sanitary construction—used in Blood Plasma production. Simplified installation—no external supports.



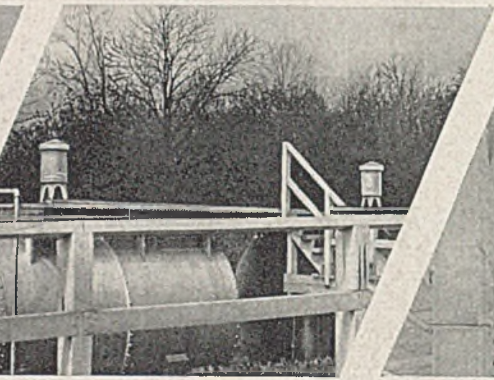
Simple side branch pipe adaptor provides support and closure combined for Agitator used under "no-head room" conditions. Imagine the difficulty of designing supports if the mixer had been furnished with drive, separate from the stuffing box.



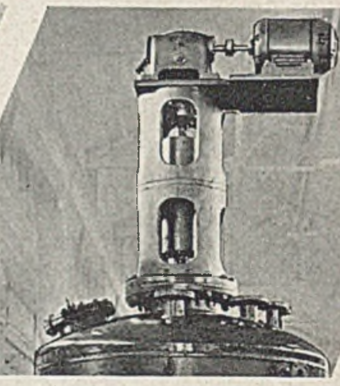
Turbine-Agitator. Simple, reliable nozzle mounting s ports entire mixer without separate structural st Factory aligned—integral construction assures prop stuffing box performance on this difficult high pressure job.



Nozzle mounting agitator leaves more room for other fittings on vessel head. Note how structural steel supports would have complicated piping layout and increased head room, if mixer were not complete and integrally mounted.



For outdoor service, self-supporting, nozzle mounting agitators pay extra dividends in lower overall cost, lower maintenance and simplified, accessible installations.



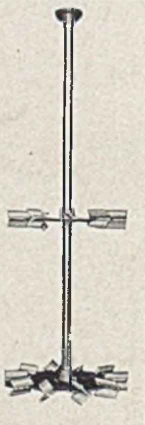
Turbine-Agitator. Right-angle drive, complete and self-supported on tank nozzle. Prominent process vessel builder appreciates integral construction with stuffing box already aligned and unit ready to install. Note: designer has been able to locate all other fittings without interference with usual structural steel supports.

PORTABLE M
ERS: ⅛ to 10 H.
for rim attachme
to open tanks. Ge
and direct drives
Many exclusive co
veniences. Off-cente
positioning. Extende
bearing sealed against o
and grease leaks.

TOP ENTERING MIXERS

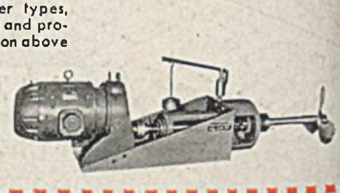
Where to use them. In problems involving mixing under pressure, vacuum, airtight, vapor proof and other similar conditions, a Top Entering "*LIGHTNIN*" or "*MIXCO*" Agitator—*properly engineered for the specific job*—is the answer. Because the operation takes place in a closed tank, the agitation must be fitted to the job with due consideration for all factors including tank size, viscosity of materials, results required, etc., etc.

"*LIGHTNIN*" and "*MIXCO*" Top Entering Agitators are available in ¼ to 50 H.P. direct or gear drive for agitating liquids up to 20,000 centipoises at mixing temperature. A wide variety of propellers and turbine type impellers are available to give maximum efficiency on various materials under a specific set of conditions and requirements.



TOP ENTERING MIXERS: A wide range of sizes for large or small tanks—¼ to 50 H.P. for vertical use on pressure or vacuum vessels. Integral mounting, all Impeller types, Radial Turbines and propellers. Illustration above for open tank.

SIDE ENTERING MIXERS: 1 to 25 H. for horizontal use. Any size tank. Pr peller type only. Many models o drives. In use on tanks up to 5,000,00 gallons capacity.



The Basis of Our Recommendations

Twenty-five years of experience have resulted in an organization, research facilities and skill which qualify Mixing Equipment Company as a leading authority in the whole broad field of agitation. Mixing Equipment Company offers its services in the solution of any problem involving controlled recirculation of liquids to produce physical and chemical changes, as included in the following table:

Mixing Equipment Company Offers

Complete coverage of industrial areas with service for both individual user and engineers or equipment manufacturer.

Assumption of responsibility for selection of mixer size, types, performance, characteristics within limits of existing technology.

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

See our Exhibit—Booths 273 and 274
at the Chemical Show.

MIXING EQUIPMENT CO., INC.

MIXING EQUIPMENT CO., INC.
1062 Gerson Ave., Rochester 9, N. Y.

Please send me the literature checked:

☐ B-66 and B-76 Side Entering Mixers
☐ B-78—Top Entering Mixers
☐ B-75—Portable Mixers (*Electric and Air Dr*
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet

Name...
Title...
Company...