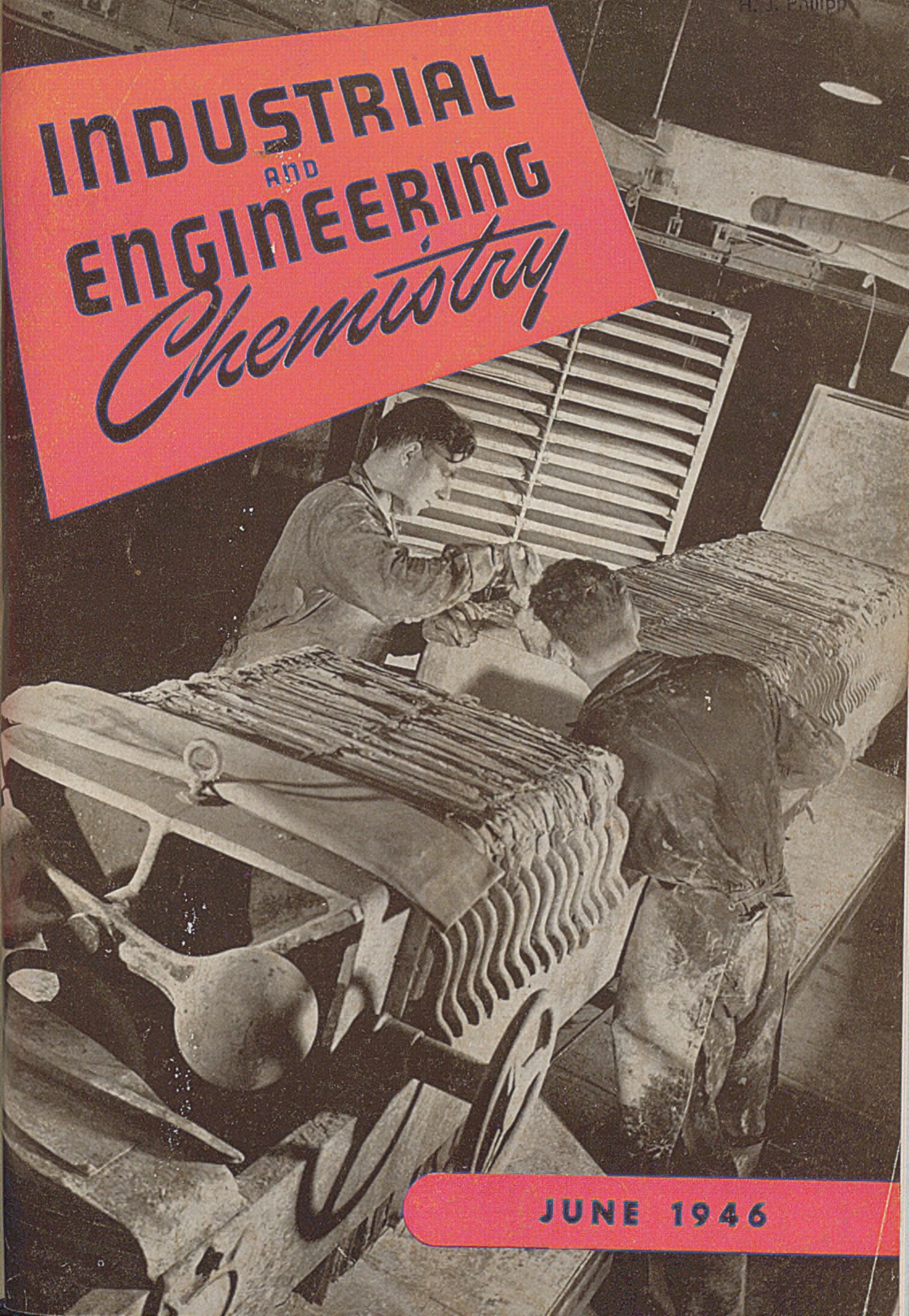
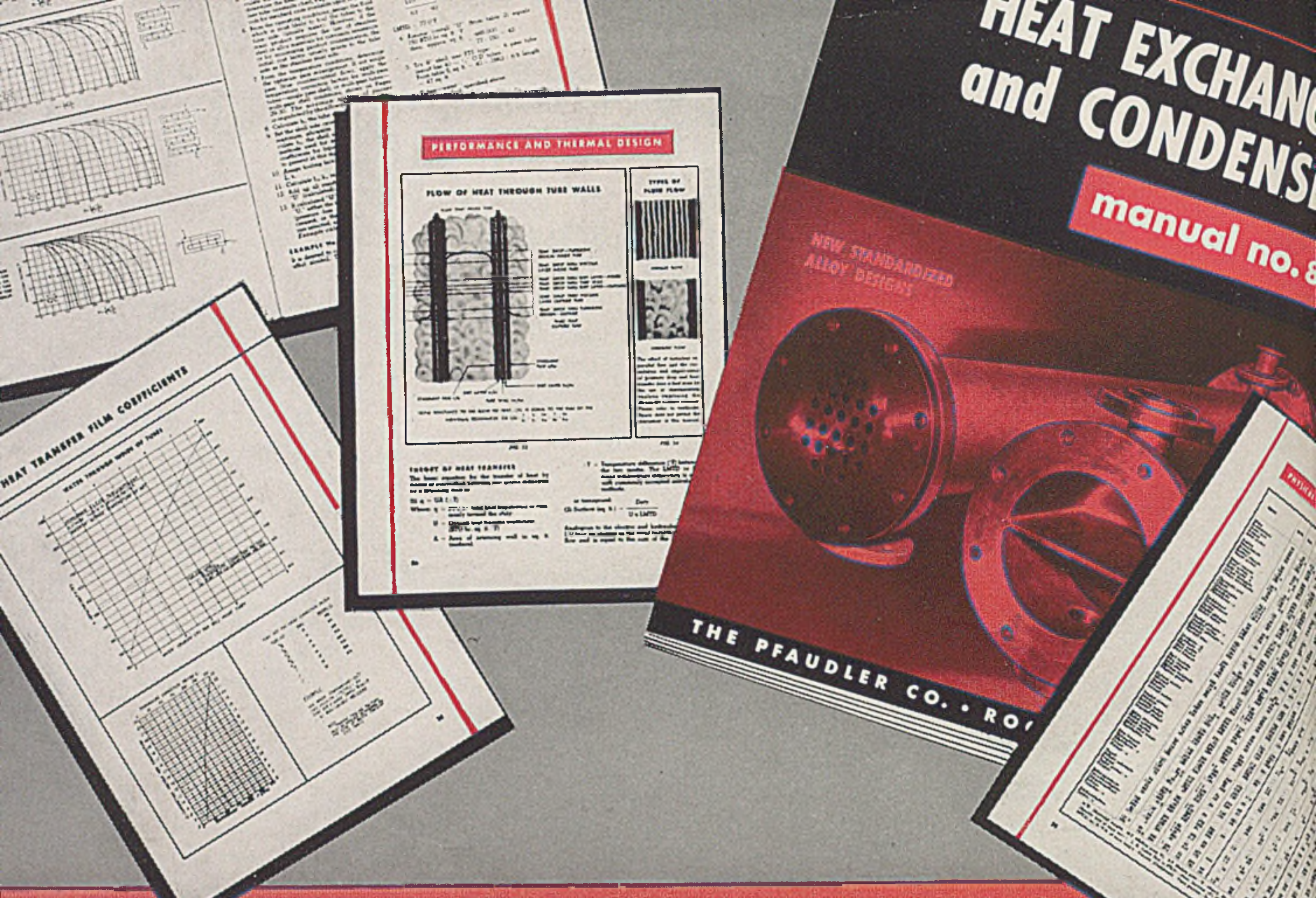
INDUSTRIAL AND ENGINEERING Chemistry



JUNE 1946


HEAT EXCHANG
and CONDENS
manual no. 8
NEW STANDARDIZED ALLOY DESIGNS
THE PFAUDLER CO. • RO
PERFORMANCE AND THERMAL DESIGN
FLOW OF HEAT THROUGH TUBE WALLS
HEAT TRANSFER FILM COEFFICIENTS

H. J. Philipp

INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

VOLUME 38, NUMBER 6 ● ISSUED JUNE 10, 1946 ● CONSECUTIVE NUMBER 11

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We acknowledge with thanks the action of Patterson Foundry and Machine Company in releasing the front cover of this issue for editorial purposes.

This month's cover photo depicts a filtration step in pigment manufacture. It was taken by Robert Yarnall Richie in a plant of E. I. du Pont de Nemours & Company, Inc.

Departments

* Indicates page number in the advertising section.

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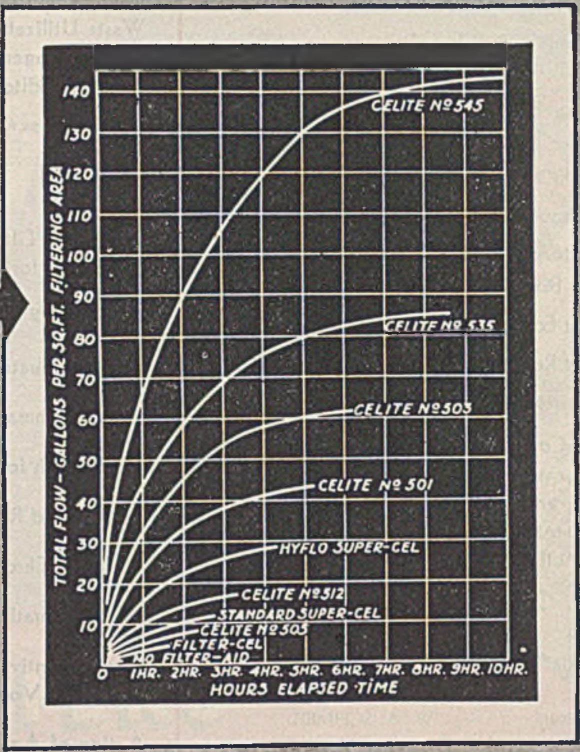
TOTAL FLOW – GALLONS PER SQ. FT. FILTERING AREA
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CELITE Nº 501
HYFLO SUPER-CEL
CELITE Nº 512
STANDARD SUPER-CEL
CELITE Nº 505
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HOURS ELAPSED TIME

INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

War and Postwar

Water and G. I. Salads. When the Army puts into effect a plan it is cooking up for American troops in Japan, we predict that the average soldier will turn military tradition topsy-turvy by bragging of the newest raw deal he has had. And if he writes home about the luscious tomatoes he has seen on the "sacred isle", probably he will be referring to the great improvement in quality of the fresh vegetables and salads served him at G.I. messes. They will be grown on the Island of Honshu in Army-operated hydroponic farms, the largest in existence.

The Army first used hydroponics at Coral Gables, Fla., where a small unit, patterned after commercial American installations, was built as a diversion for patients of a convalescent hospital. The potentialities of the unit for providing fresh food in out-of-the-way places were recognized by the Army Air Forces. Larger installations were constructed later, first on Ascension Island (2 acres), then on Coconut Island of the Hawaiian group (1 acre), Iwo Jima (2 acres), Georgetown, British Guiana (3.25 acres), etc. These projects now are not solely for the AAF, but are operations of the entire theater in which they are located.

Less than 14% of Japan is arable, and that area has been farmed to death; also, Japanese fertilizing practices posed a serious sanitation problem for the foods that are eaten raw. Many of those foods do not ship well, and it seemed apparent that it was better to use water as a nutrient carrier in Japanese farms than to use it to float food ships from America.

The basic unit of the installation in Japan is a gently sloping, rectangular, shallow concrete bed, 9 to 11 inches deep and 4 feet wide, divided into sections 120, 100, and 80 feet long. The beds are filled within 2 inches of the top with $^{3}/_{8}$-$^{5}/_{8}$ inch river pebbles. The plants are grown in these pebbles by periodically moistening them with a water solution of the following fertilizer-grade chemicals per thousand gallons of solution:

Potassium nitrate	9 lb. 3 oz.
Calcium sulfate	6 lb. 6 oz.
Magnesium sulfate	4 lb. 6 oz.
Monocalcium phosphate	2 lb. 10 oz.
Ammonium sulfate	1 lb. 3 oz.
Total	23 lb. 12 oz.

Crop yield is roughly 5 pounds of vegetables per pound of fertilizer. The beds are moistened two or three times daily, usually in the morning, from a 150,000-gallon storage tank serving ninety beds. The first section of the bed is filled from the bottom, drained into the second and then the third sections, and next into a sump, from which it is returned to the storage tank by a 550-gallon-per-minute centrifugal pump. Corrosion is no problem, but if iron pipes are used, enough iron goes into solution to satisfy the plant's trace element requirement for this material. Chemical control of solution composition is extremely simple with colorimetric tests and calibrated charts.

Two farms totaling 1440 beds will be set up—one of 55 acres at Chofu (14 miles from Tokyo) and one of 25 acres at Otsu (6 miles from Kyoto, the unbombed cultural center of Japan). The entire cost of the project will be borne by the Japanese. Of approximately 1000 persons required to operate the farms, only about 70 will be Americans, the remainder Japanese. The farms are designed to satisfy all the raw food requirements of the occupying American forces, and will provide 800,000 individual servings per week. Half of all the crops grown the first year will be tomatoes, another 15% lettuce, and the remainder evenly divided among radishes, cucumbers, peppers, and onions. Carrots and spinach may be added next year. Transportation facilities are good enough so that time from loading point to discharge point anywhere in the American occupation zone is less than that normally allowed between icing points in this country.

When American military occupation of Japan ends, the farms will be returned to the Japanese. Lieutenant Colonel Ewing Elliott, in charge of the project for the Eighth Army, hopes that the results will indicate a way for Japan to produce more of its own food requirements. The water farms may be built on areas unsuitable for conventional agriculture, and 75% of the cost of operation is labor, notoriously cheap in the Orient. In fact, this particular item of reparations could turn out to be a valuable investment in the future economic health of Japan. D.O.M.

(*Continued on page 8*)

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

Your Bulk Material Can Be Economically Elevated By One Of These Units

• Link-Belt engineers have had extensive experience in the design, manufacture and application of bucket elevators for varied service requirements. If your conditions call for the use of a bucket elevator, let Link-Belt show you the most efficiently performing size and type for your needs. Refer to pages 862-916 of our general catalog No. 800 for complete engineering data, specifications and information on how to select bucket elevators.

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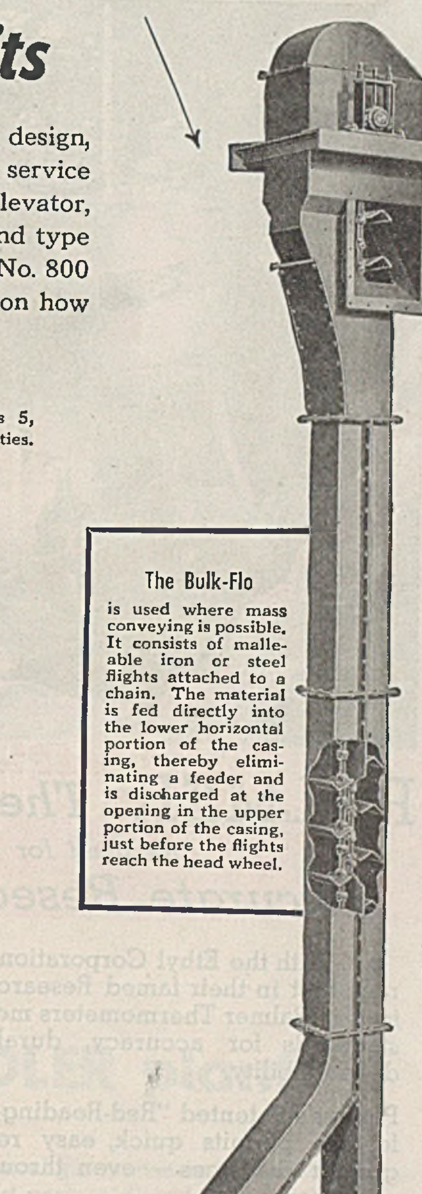
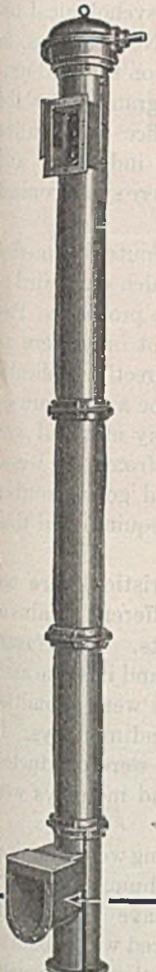


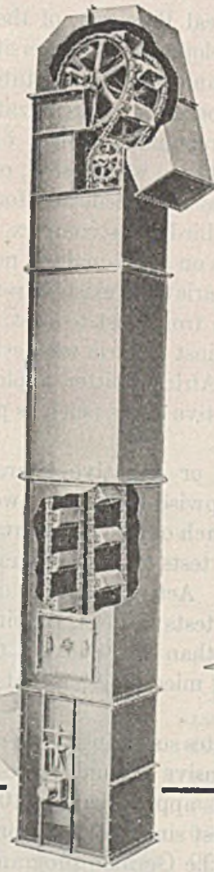
The Bulk-Flo

is used where mass conveying is possible. It consists of malleable iron or steel flights attached to a chain. The material is fed directly into the lower horizontal portion of the casing, thereby eliminating a feeder and is discharged at the opening in the upper portion of the casing, just before the flights reach the head wheel.



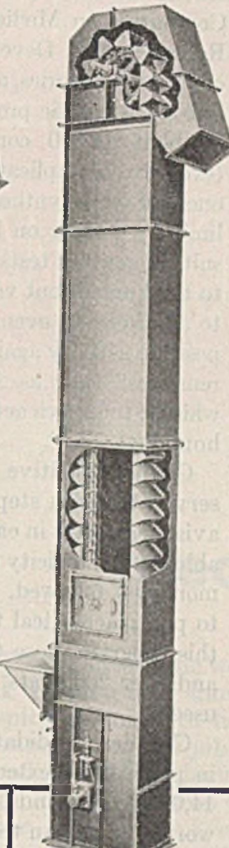
The Rotor Lift

is a Helicoid (screw) elevator which handles many products that normally can be conveyed by a horizontal screw conveyor. It consists of a vertical screw driven from either the top or bottom, operating in a solid or split casing. The material is fed to the vertical screw by screw feeder near the foot of the lift and is discharged at the top or head end.



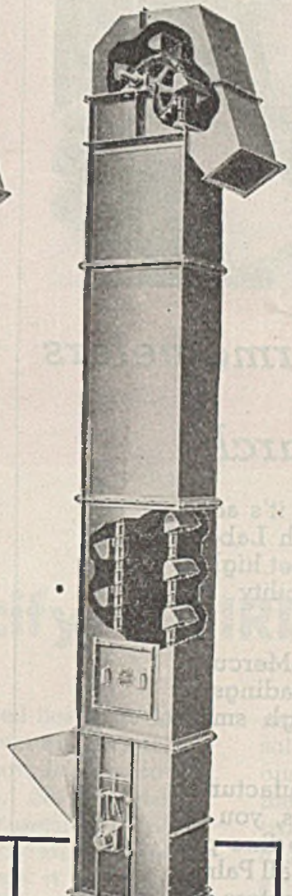
The Perfect Discharge Bucket Elevator

operates at slower speeds and is used where materials will not readily discharge at centrifugal speeds. Malleable iron or steel buckets are mounted between two strands of chain. Material is fed directly into buckets at the foot of the elevator or scooped up in the boot and discharged over a snubbed head wheel which inverts the position of the buckets over the discharge chute.



The Continuous Bucket Elevator

is used where higher capacity at slower speed is desired or where the material is friable. It consists usually of steel buckets mounted on either a chain or belt. Material is fed directly into the buckets at the foot of the elevator and discharged over a head wheel onto the preceding buckets, whose front and projecting sides form a chute, thereby directing the material into a fixed discharge spout.



The Centrifugal Discharge Bucket Elevator

is used for most products. It consists of either malleable iron or steel buckets mounted on either a chain or belt. The material is fed either directly into the buckets at the foot of the elevator or scooped up in the boot and is discharged over the head wheel by centrifugal action.

10,299

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ELEVATORS

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

Operation Antimalarial. Malaria, the most extensive of all maladies in peacetime and a scourge to warm-climate troops, was largely removed from the field of tactical importance in the recent war. This advance was made possible through a program in chemotherapeutic research that was outstanding for its combination of intensity, organization, and cooperation.

Since 1930 a related research program in Germany had failed to improve upon the unsuitably toxic pamaquine (Plasmochin) as a curative, and quinacrine (Atabrine), with its problems of application (partially psychological because of skin coloring) as a suppressive. Nevertheless, in 1940 the National Research Council took action that led ultimately in 1944 to a full scale unified program under the Committee on Medical Research, of the Office of Scientific Research and Development. Universities, industrial and clinical laboratories, and research institutes were synchronized into a systematic program and organization.

About 14,000 compounds, drugs, or reputed remedies (exclusive of duplications) were tested, of which one third to one half were synthesized specifically for the program. Preliminary testing on birds was complex. Not only were results of activity tests on avian malaria not directly applicable to the human, but variations existed from one avian parasite to another and even from host to host. Any material with possible activity against malaria was tested, from "old wives' remedies" such as African bitter apple and good bourbon whisky, to known active drugs (such as pamaquine) and their homologs.

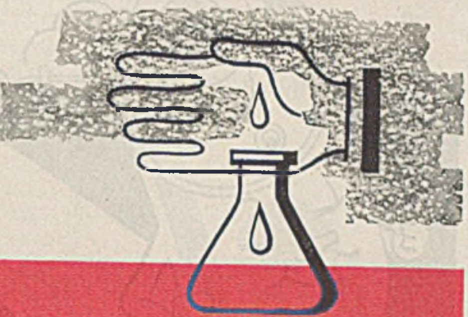
Critical positive or negative characteristics were observed through stepwise testing on two different strains of avian parasites in each of two different hosts. With favorable results, toxicity tests on mice and rats (and in some cases monkeys) followed. Active tolerable drugs were submitted to pharmacological tests in dogs, rabbits, and monkeys. In this program more than 25,000 avian tests were conducted, and over 2000 rats, mice, dogs, rabbits, and monkeys were used.

Chemical candidates surviving this screening were examined in precise and extensive chemical tests in humans. Of the 14,000 compounds, approximately 100 have been found worthy of human test since 1942, as compared with about 25 carried that far in the German program of the past twenty-five years.

The system yielded results. Well over sixty series of compounds of a wide variation of structures showed activity against avian malaria, and at least ten have been found active for man. This was a scientific advance, as it had previously been the concensus that only quinoline type structures were effective (quinine, pamaquine, and quinacrine are thus related). Practical results were gratifying, as there are now at least three curative drugs which appear superior to pamaquine: SN 13276 or 6-methoxy-8-(5′-isopropylaminopentylamino)-quinoline; SN 13429 or 6-methoxy-8-(4′-isopropylamino-1-methylbutylamino)-quinoline; and SN 9972 or 4,8-isopropylamino-1-methylbutylamino-5,6-dimethoxyquinoline. Three drugs gave strong indications of being superior to quinacrine as suppressives: SN 7618 or

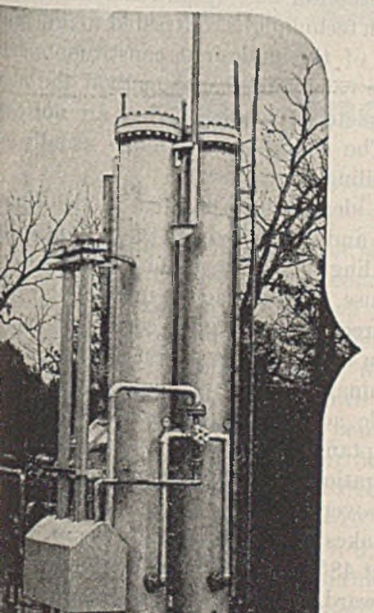
(*Continued on page 10*)

For effective, economical



DEHYDRATION

OF GASES AND LIQUID HYDROCARBONS



specify a GIRDLER plant

THE automatic well-head gas dehydration unit shown at the left is a typical example of how it pays to get GIRDLER on the job. No operator is needed for this factory assembled "package" unit . . . fifteen minutes attention once each week keeps it in running order. The only utility required is a minute fraction of the gas for fuel. No steam. No electric power. No solutions. There are practically no moving parts.

Dehydration plants of every size—solid dessicant systems (like the one illustrated), diethylene glycol systems, refrigeration systems or combinations of these—have been designed for simple operation and built for economical performance by Girdler specialists in gas processing. Girdler dehydration plants are being used for high pressure natural gas transmission lines, liquid or solid carbon dioxide production, various chemical operations involving gases, metallurgical operations involving controlled atmospheres, and for the dehydration of special gases such as nitrogen, hydrogen, and carbon monoxide.

For direct evidence of what this wealth of experience means to you, write today giving a brief outline of your specific dehydration problem.

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

Technology

7-chloro-4-(4′-diethylamino-1-methylbutylamino)-quinoline, a drug made by the Germans who, apparently, did not fully appreciate its efficacy; SN 8137 or 7-chloro-4-(3′-diethylamino-2-hydroxypropylamino)-quinoline; and SN 10751 or 4-(7-chloro-4-quinolylamino)-α-diethylamino-*o*-cresol. In addition, at least one other drug in each class has been shown superior in avian activity tests to those listed, and they are now being tested pharmacologically and clinically.

Much has been achieved, but a great deal of additional work is needed before malaria finally can be brought under firm control. OSRD is disbanding, and no means of support is now in view for completing the program, particularly the costly but indispensable clinical tests. The benefits of this enterprise already are far-reaching: if it is carried through to completion, the malaria menace may be banished entirely.

R.L.K.

Less Mercaptan, More Octane. In striving to rid gasoline of mercaptans, the refiner has leaned rather heavily on aqueous caustic wash and the procedure known as doctor sweetening. These methods have disadvantages. Caustic treatment alone does not eliminate all of the mercaptans, and those which remain in gasoline become a costly nuisance. Their most undesirable characteristic (even when they are converted to odorous disulfides) is that they inhibit lead susceptibility. In the sweetening process, as a result, the octane number of gasoline may be lowered one or two points.

This will explain the growing interest of the oil industry in the caustic-methanol method of mercaptan removal. In all respects it is an extraction technique as contrasted to processes based upon conversion of the undesired constituents into other materials. In the caustic-methanol method the mercaptans are almost completely removed. They are not converted to disulfides. The use of caustic alone usually removes only the lower boiling mercaptans.

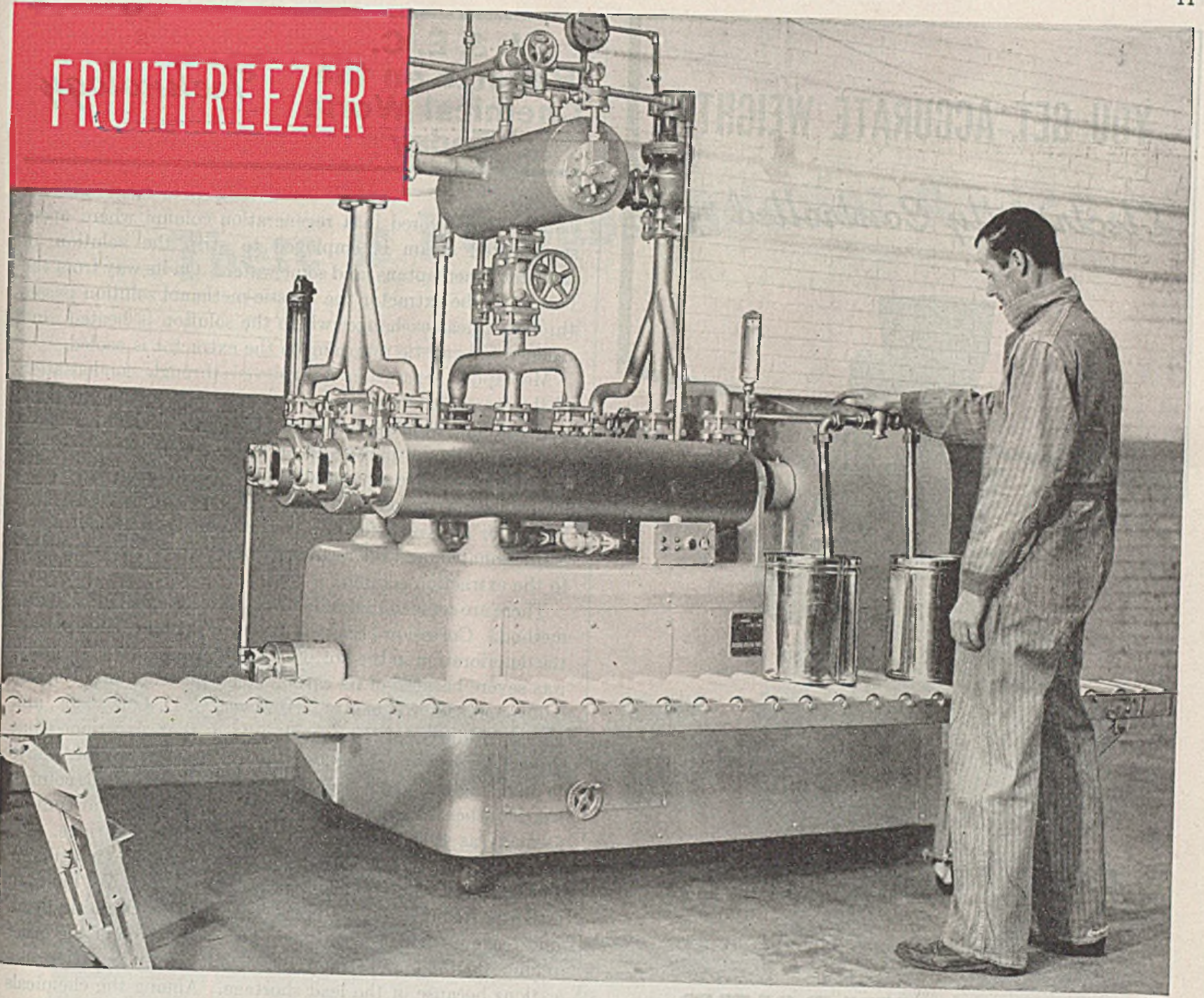
The caustic-methanol idea, as incorporated in the Unisol process, was originated and developed by the Atlantic Refining Company; according to Universal Oil Products Company which licenses its use, eight extraction units of this type are in operation while three others are under construction.

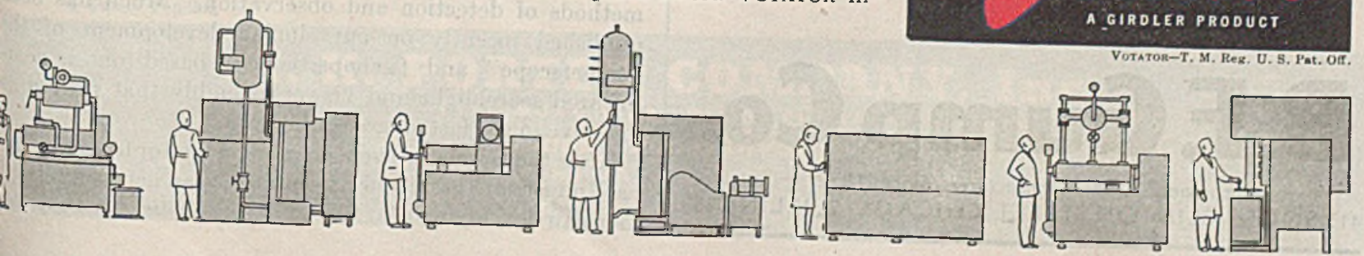
The Unisol mercaptan removal process consists essentially of five steps: (1) preliminary caustic washing to remove hydrogen sulfide, aliphatic acids, and (if desirable) phenols; (2) extraction of mercaptans and removal of methanol from the gasoline; (3) regeneration of caustic; (4) mercaptan separation; (5) methanol recovery.

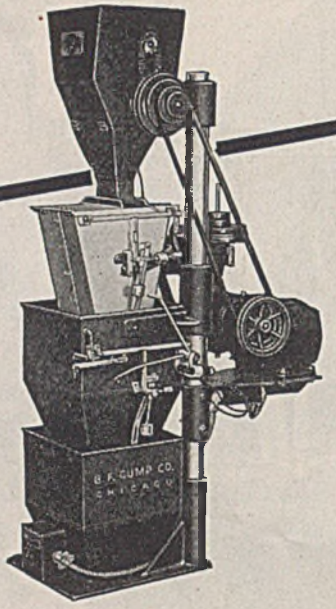
Mercaptan removal takes place in a packed column with a caustic solution of about 48° Bé., introduced at the top of the column. It flows downward, countercurrent to gasoline rising from the bottom of the column. Methanol, about 30 to 40% by volume of the caustic solution, is introduced at the midpoint of the column and divides it in two sections.

Mercaptan extraction takes place in the lower half of the column while dissolved methanol is removed from gasoline in the upper half with fresh caustic. Gasoline leaves the top of the column free of caustic, and the reagent shows no tendency to absorb the fuel.

(*Continued on page 12*)


FRUITFREEZER





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

Technology

Caustic is recovered in a regeneration column where open, superheated steam is employed to strip the solution of methanol, mercaptans, and some water. On its way from the bottom of the extractor the caustic-methanol solution passes through a heat exchanger where the solution is heated, and regenerated caustic returning to the extractor is cooled.

Mercaptan separation is achieved through condensation of the mercaptan-methanol-water vapors from the regeneration column, which produces a two-phase system—a lower aqueous methanol phase and an upper mercaptan oil phase. The two phases are separated by skimming off the mercaptan oil, which is run off into a disposal system in which it is burned or recovered for sale. The aqueous methanol phase is fractionated, and the recovered methanol is circulated back to the extraction column.

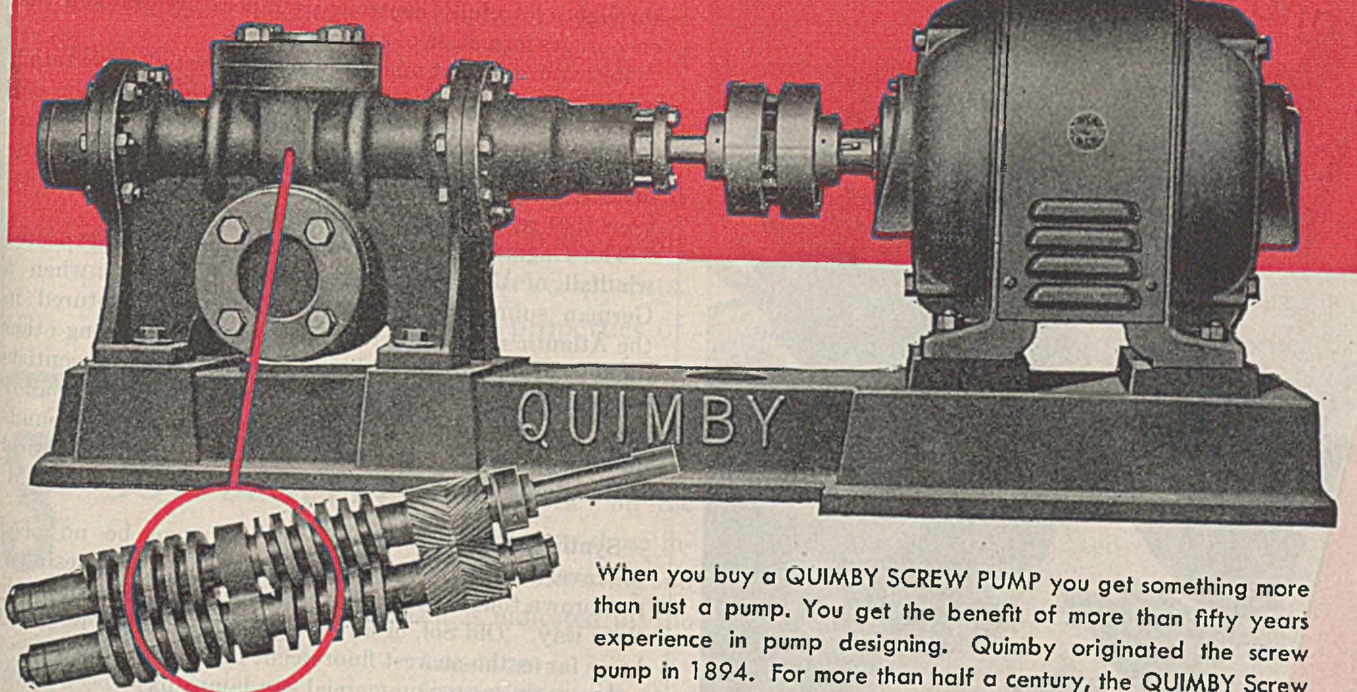
There are some undesirable features of the caustic-methanol method. Corrosion became a problem in the earlier plants; the deterioration in the bottom of the caustic recovery section was severe because of its carbon steel construction. Repairs had to be made frequently. However, C. D. Lowry, Jr., and F. C. Moriarty of Universal advise that experience has proved corrosion may be avoided by the use of proper alloys in the high temperature zones. The extraction column also is rather tall, and the installations made thus far contain as many as 40-54 vertical feet of carbon Raschig rings.

On the other hand, there are distinct advantages in utilizing the Unisol process for mercaptan removal. H. W. Field, of Atlantic Refining, says it conserves gasoline, tetraethyllead, and reagents, which would be lost through some of the other refining methods. Tetraethyllead today is under strict allocations because of the lead shortage. Among the chemicals saved are litharge, caustic for doctor sweetening, and copper salts for copper sweetening processes. The gasoline losses, according to Lowry, are so low that they approximate the volume of the mercaptans removed. Caustic consumption is low, extractor temperatures run between 80° and 100° F., and the total cost of chemicals and utilities in the process is within the range of 1 to 1.5 cents per barrel. The methanol, being volatile, can be recovered if it becomes necessary to discard the caustic because of contamination with sulfide or aliphatic acids in the feed. H.W.S.

Cats' Eyes from Rat Poison. When the Allies' wartime research on radar became too great to hide completely from the Germans, our counterespionage service obligingly "let slip" that the operating principle was based on infrared radiation. This effectively diverted the enemy from radar research as we knew it, but boomeranged by spurring them on to the highly successful development of infrared methods of detection and observation. Much has been published recently on our similar development of the "sniperscope" and "snooperscope", based on a near-infrared searchlight and viewer assembly that proved so effective in the last stages of the war.

After the German surrender an investigator from Technical Industrial Intelligence Committee ran across a related German development

(Continued on page 14)


QUIMBY

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

Technology

utilizing infrared radiation. The collecting lens system for this instrument consists of elements ground from single crystals of a eutectic mixture of 42% thallium iodide and 58% thallium bromide. The result is a beautiful rose-colored crystal, soft enough to be cut with a sharp knife and sawed, yet capable of being ground and polished like glass. The refractive index is high (about 2.2 to 2.5) both in the visible and infrared spectra. The Germans claim it is transparent to infrared radiation up to 30-micron wave length. Scientists of the Engineer Board, Fort Belvoir, Va., have successfully made single crystals up to 2 inches in diameter and hope to make them up to 8 inches. The method used is Massachusetts Tech's *Stockbarger* process, which consists essentially of lowering a molten mixture of the material through a carefully controlled temperature gradient that encourages formation of a single crystal.

Research aimed at uncovering other crystalline materials with similar properties is planned. In this work the emphasis will be on water-soluble salts, which in general are easier to grow than the thallium compound crystals. So little is known about fundamental chemical-optical relations that research now is in the pioneering stage.

The Engineer Board investigators had an unexpected windfall of thallium shortly before V-E day, when a German submarine bound for Japan was captured in the Atlantic off the North American coast. Among other items in a cargo that must have made our military scientists lick their chops in delight were 200 pounds of a 50-50 alloy of lead and thallium. But most of the thallium compounds used in our country's studies of this intriguing new optical material was obtained from rat poison. D.O.M.

Synthetic Sun Tans. There will soon be no need to travel to Florida or California to acquire that desirable nut-brown tone on your skin—that is, if the chemists have their way. Old Sol, or a reasonable facsimile thereof, will be as far as the nearest fluorescent light fixture.

For some years commercial sun lamps have been available which utilize a high intensity mercury discharge to emit radiation that will tan the body. These lamps, however, consume 100 to 500 watts or more of power and have a low efficiency in converting this into useful sun tan radiation. In addition, their operation requires specialized equipment.

An extensive investigation of ultraviolet emission by means of fluorescent lamps was undertaken some years ago by the Sylvania Electric Products Company, and it was found possible to convert electrical power to a desired radiation with fluorescent powders or phosphors. It was also discovered that this conversion was more efficient than the conventional one, since it was capable of producing the same sun tan radiation with about half of the usual power consumption. The problem was essentially a physical-chemical one of producing a stable powder that will emit radiation of the desired wave length and brightness with maximum conversion efficiency.

(*Continued on page 16*)

Furfural-on the THRESHOLD OF CHEMICAL PROGRESS...

To the chemist of today Furfural and the other available Furans offer the same opportunity for chemical discovery as did benzene seventy years ago. For many years chemical industry has neglected Furfural and its derivatives, primarily because they frequently did not behave in the manner which would have been predicted from consideration of the ring substituent. Chemists are now beginning to realize that this unorthodox behavior might open up interesting and valuable developments.

In the meantime the physical properties of Furfural, such as its preferential solvent action on unsaturated compounds, its effectiveness as a dispersant, as a wetting agent and bactericide have so extended its use and reduced the cost of manufacture that Furfural is the cheapest pure aldehyde available today.

Because of its low price and because of its chemical activity which is a function of both the unsaturated ring and the aldehyde group, chemists will find it worth while to work with Furfural. Samples of Furfural will be furnished when requested on your business letterhead.

3 *Bulletins*

in a series on the Furans are also available to those interested. They contain interesting and informative data as indicated by the titles:

Bulletin 201
General Information About Furfural.

Bulletin 202
Introduction to the Chemistry of the Furans.

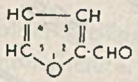
Bulletin 203
Physical Data on Furfural.

Bulletin 201 is of general interest to all users of chemicals. Bulletins 202 and 203 contain information of interest primarily to the research worker.

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.

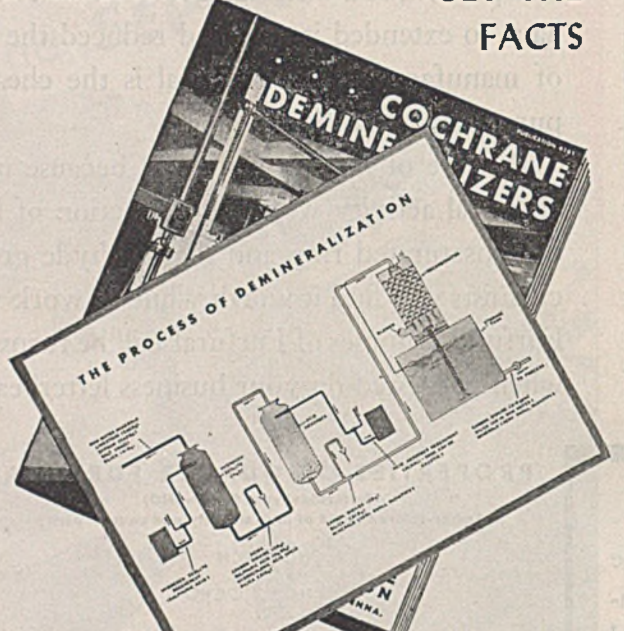
†ODT requires maximum loading

Drums non-returnable

The Quaker Oats Company CHEMICALS DEPT.

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

URFURAL • FURFURYL ALCOHOL • FUROIC ACID • TETRAHYDROFURFURYL ALCOHOL



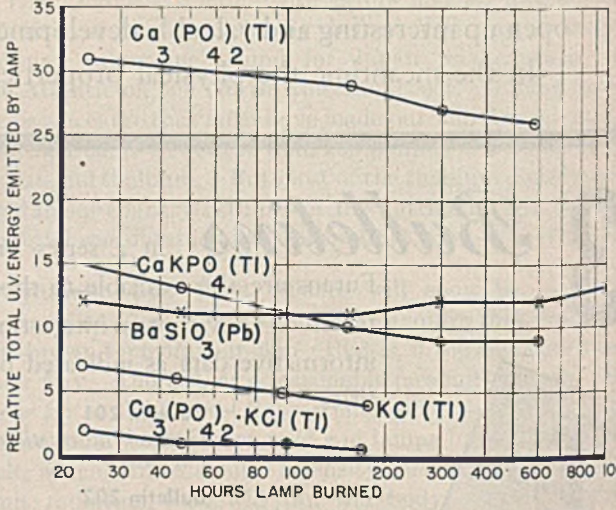
I. & E. C. Reports on the Chemical World Today

Technology

It was noticed that, when a phosphor was subjected to radiation of a given wave length, the fluorescent radiation emitted always had a longer wave length than the incident radiation. A common example is the irradiation of certain phosphors by "black light" of 3400–3800 Å. wave length and the spontaneous emission by these phosphors of visible light with wave lengths anywhere from 4000 Å. (blue) to 7000 Å. (red).

The choice of the phosphor depends upon the desired application, since it is necessary to consider the effects of air, ozone, heat, and gaseous discharges upon the phosphors during either utilization or manufacture. The adaptability of the powder to mechanical treatment such as milling and grinding for use in paints or other suspensions must also be taken into account.

In the main, the phosphors investigated consisted of metallic phosphates or silicates activated by thallium, lead, or cesium. A representative lot of optimum composition of each of the types studied was prepared in a lacquer suspension and applied to glass bulbs in a conventional manner. Lime glass was used in the case of the black light phosphors, and germicidal glass passing all wave lengths down to approximately 2000 Å. (in the ultraviolet range) was employed for the sun tan phosphors.



These bulbs were then made into lamps and subjected to a series of tests, including spectral energy distribution studies and lamp life observations. A phosphor of composition $Ca_3(PO_4)_2$ (thallium-activated) showed a reasonably high output value of good maintenance characteristics. With a redesigned model of the two-lamp fixture using aluminum reflectors with an increased amount of current flow, it was possible to produce with 140 watts an erythema (sunburn) of a pinkness comparable to that obtained by a 300-watt mercury type lamp.

It is expected that installations of this lamp can be adapted to bathroom use to give automatic 5-minute exposures during shaving or more general exposures during showering. Although no immediate tourist trade upheaval is foreseen, the American bathroom may become competition for the winter resort of the future. R.L.D.

Remember 1942? Aviation gasoline was critically needed, and the muscles of the petroleum refining industry flexed. But, looming as a major menace to the program, was a shortage of iso-butane. Something had to be done... and fast.

A new process to convert abundant normal butane to iso-butane was adopted. Then, Porocel Corporation was assigned the job of perfecting the manufacturing technique and producing the vital isomerization catalyst* in large quantities. Within six months the technique was perfected, a special plant was built to produce the catalyst, and the first car-load was rolling to the refiners. Because of prompt action in an emergency, a gravely needed product was made available in ample quantities. Furthermore, high operating flexibility of the catalyst resulted in iso-butane production records of double the anticipated capacity in many plants. The way was paved for a substantial increase in the flow of aviation gasoline.

This is one example of the results obtained when Porocel Corporation's laboratory research, practical experience and flexible plant facilities are applied to problems of catalyst manufacture. It is a typical example, too, of the superiority of Porocel as a catalyst carrier. Its natural ore ruggedness, high adsorptive activity, uniform dispersal qualities, freedom from impurities, inertness and extremely low cost are the characteristics that insure economy and operating efficiency.

New applications for Porocel, either as catalyst carrier or direct catalyst, are regularly being discovered. It is possible that we can perfect and manufacture the catalyst you need. Whatever your catalytic problem, our staff of experienced engineers will be glad to assist you.

Just address: Attapulgus Clay Company *(Exclusive Sales Agent)*, Dept. C, 260 S. Broad St., Phila. 1, Pa.

Anhydrous $AlCl_3$ impregnated on Porocel (Deironed, activated bauxite) and sold under the trademark* **ISOCEL

POROCEL CORPORATION, BAUXITE CATALYSTS, CATALYST CARRIERS, ADSORBENTS and DESICCANTS

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

U.S.I. CHEMICAL NEWS

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

Two Phenolic Resins Now Are Available for Immediate Shipment

100% Rosin-Free, They Provide Durability, Chemical Resistance

Arofene 700 and Arofene 775, two well-known U.S.I. pure phenolic resins, are now available for immediate shipment. Both resins are entirely free from rosin and rosin derivatives. Used principally in spar varnishes, chemical-resistant finishes, ethyl cellulose finishes, and in varnishes for fortifying alkyds, they impart excellent durability and remarkable resistance to salt water, acids, strong alkali, and other corrosive substances. Products made with these resins exhibit good color and drying properties.

Arofene 700

Arofene 700 is a heat-hardening, heat-reactive 100% phenolic resin which, in combination with drying oils, gives hard durable finishes. It provides outstanding resistance to chemical reagents in a wide variety of formulations, and produces varnishes of maximum durability. Varnishes made with this resin are unusually pale and exhibit far less after-yellowing than is normally expected from a pure phenolic. They possess good gloss, and with tung or oiticica oils, the inclusion of small amounts of linseed oil produces highest gloss.

To obtain the best results, Arofene 700 should be processed with a preponderance of "hard oils," such as tung or oiticica. Varnishes with oil contents composed largely of "soft oils," such as linseed or dehydrated castor, are practical, but are much slower drying.

The addition of Arotene 700 to other resins in varnish formulations, reduces the cooking cycle of the varnish, or enables the manufacturer to acquire high varnish viscosities which otherwise would be impossible. Its incorporation in this manner, also adds to the durability and resistance of the varnish.

Manufacturers have found Arofene 700 ideal for super spar varnishes, alkali-resistant

(*Continued on next page*)

Improved Thyroid Product Prepared by New Process

To minimize many of the objectionable physiological effects of thyroid preparations used to combat excess weight, a new brominated thyroid compound has recently been invented. This compound is reported to lessen the increased pulse rate, palpitations, emotional upsets, and muscle tremors which sometimes follow thyroid injections.

According to the patent, the brominated product is prepared by treating a commercial powdered thyroid with ethyl alcohol and bromine at room temperatures. After standing over night, the mixture is filtered, and the solid material is allowed to dry at room temperature. The final product is stated to be no different from the original desiccated glandular material, except that it contains 0.2% to 15% added bromine.

U. S .I. Opens New Laboratory To Evaluate Wide Range of Products

Installs Complete Facilities For Evaluation Of Chemicals and Insecticides at Baltimore, Maryland

As one of the first steps in its broad program of expansion, U.S.I. has organized an unusually complete laboratory for the evaluation of a wide range of products. The new laboratory, located at Baltimore, Maryland, occupies more than 9000 square feet of floor space and is equipped with the last word in chemical, physical, and entomological testing facilities.

Four major fields of activity are now being investigated in the laboratory: the study of solvents and plasticizers; the testing of anti-freeze compounds and other automotive products; technical service for customers; and evaluation, compounding, and development work on insecticides and insectifuges.

Proceeding on the belief that the success of any new-product program depends in large measure on the accurate evaluation of the commercial performance of new products, U.S.I. has assembled an exceptionally fine staff of chemists, biologists, and entomologists to carry on this work. Activities of the new Technical Development Laboratory will be closely integrated with those of the company's research groups at Stamford, Conn., Baltimore, Md., Newark, N. J., and with the Dodge and Olcott laboratory at Bayonne, N. J.

This ingenious distillation set-up provides accurate analyses of organic solvents quickly.

THE MONTH IN INSECTICIDES

Coats for seeds, containing built-in insecticides, fungicides, fertilizers, and hormones may have far-reaching effects . . . Benzene hexachloride is reported to be seven times more effective against flies than DDT . . . The effectiveness of rotenone oil sprays in combating California red scale is said to be increased by the addition of butyl phthalate . . . Methyl bromide is used to control the pineapple mealybug . . . The Army's smoke apparatus is now being used to deliver superheated oil vapors for treating vegetation . . . A rapid field method for assessing the spreading power of antimalarial oils is developed . . . Cyclopentenylamines are identified as a new group of insecticides . . . Another effective insecticide for house flies is made from Sabidilla seeds . . . A series of new insecticides are used for chicken louse control.

Rats' Cancer Killed By Alcohol Extract

An alcoholic extract which destroys tumors and cancers and sets up immunity against their growth in inbred albino rats has been announced in a technical paper published recently. The extract has been tested successfully on rats, but is not ready for use on humans, the authors said. They stated further that theirs were the first successful experiments of this type.

The Administrative Group of U.S.I.'s Technical Development Laboratory maps out the tests which will determine the performance-value of a new product. Left to right: N. C. Schultze, Assistant Director of the Laboratory, W. E. Dove, Director of the Entomological Division, D. G. Zink, Director of the Technical Development Department, N. C. McAlister, Jr., Assistant to

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

JUNE ★ U.S.I. CHEMICAL NEWS ★ 1946

Makes Alcohol Solutions Of Hydrogen Peroxide

A recently-issued patent describes a method by which strong alcohol solutions of hydrogen peroxide can be prepared. These solutions are reported to be useful in many industrial organic processes in which the aqueous hydrogen peroxide of commerce has been found unsuitable. Hydrogen peroxide is of particular value as a catalytic reagent in many polymerization reactions, and as an oxidizing agent for use in oxidizing and decolorizing certain types of compounds.

The process of preparing the solution consists, basically, of treating the boron ester of an alcohol with commercial aqueous hydrogen peroxide. Boron hydroxide precipitates, leaving a nonaqueous solution of the peroxide. Ethyl, butyl, and amyl alcohol are stated to produce satisfactory solutions.

Phenolic Resins

(*Continued from preceding page*)

varnishes, and ethyl cellulose finishes. It has also been used widely as a fortifying resin to increase the alkali and moisture resistance of alkyds and other resins.

Arofene 775

Manufactured to meet U. S. Navy Specification 52R11, Arofene 775 is an oil-soluble, 100% phenolic resin of the type which is nonreactive with oils. As the sole resin component in the manufacture of varnishes, it insures excellent chemical resistance and durability, as well as good color and drying properties. As a fortifier in modified resin varnishes, it improves the durability and resistance of the original product.

Arofene 775 can be used with all the usual varnish oils, although it should not be used with straight tung oil. All tung oil varnishes should contain 20% or more of an oil such as linseed. Since this resin is readily soluble and "non-reactive" with oils, relatively simple cooking procedures can be employed with excellent results.

Outstanding spar varnishes and marine paint vehicles are produced using Arofene 775. This phenolic has also been employed widely in the manufacture of finishes resistant to boiling water, salt-spray, alkali, organic solvents, and acids. In addition Arofene 775 has been used advantageously in fortifying a wide variety of varnish formulations.

Specifications and samples of both resins are available on request.

New Laboratory

(*Continued from preceding page*)

Two of the many tests which are necessary for the proper evaluation of an anti-freeze are being conducted here. On the left, the laboratory worker is determining the effectiveness of anti-freeze corrosion inhibitors. The technician on the right is measuring the foaming tendency of an experimental anti-freeze by means of a set-up that simulates the worst possible foaming conditions encountered in an automobile.

All known insecticides and insectifuges and many experimental products run the gamut of tests in the Entomological Laboratory. The jars shown here contain all stages of the common species of cockroaches. Results of tests performed on these insects help guide researchers in the development of tomorrow's insecticides.

One section of U.S.I.'s Baltimore Laboratory is devoted to the product-evaluation of all types of plasticizers. The technician shown here is testing a plasticizer in the "creep box."

TECHNICAL DEVELOPMENTS

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

To cure troublesome foaming, a new compound is marketed which is said to be effective in concentrations as low as 1 part per million. It is described as a viscous, tasteless, colorless, chemically inert, and non-volatile organic material. **(No. 073)**

USI

To impart crispness to fabrics, a new textile-treating resin is offered which is claimed to eliminate the necessity of starch. It is said to perform satisfactorily on such cotton garments as shirts, children's playclothes and women's house dresses, and to be permanent. **(No. 074)**

USI

A new multi-purpose plasticizer, which the manufacturer claims can be used as a softener, and as an impregnant for waterproof and grease-proof paper coating as well, is described as a viscous, clear-amber, resinous oil. **(No. 075)**

USI

To remove paint and enamels is the purpose of a new compound which is stated to be non-inflammable. It is claimed that this compound can penetrate, loosen, and remove 8 coats of paint in approximately 30 minutes. **(No. 076)**

USI

A new wool dye is said to be equally fast to washing, sea water, and sea water spotting. It is described as a metallized dye, recommended for men's and women's wear, tropical suitings, bathing and sweating yarns, and upholstery fabrics. **(No. 077)**

USI

A self-curing neoprene putty for patching parts of goods molded from Neoprene, Buna S. Hycar, and rubber, and for use as a caulking and gasket cement, is now available. It is stated to have good water, oil, acid, alkali, and flame resistance. **(No. 078)**

USI

A weatherproof and waterproof glue, claimed to be inexpensive and to have superior binding strength, is claimed to last longer than the pieces of plywood which it bonds. It is stated to have passed the 3-hour boiling test with surplus strength. **(No. 079)**

USI

A resilient floor covering is claimed to have the cushioning feel of an expensive deep-pile rug, and yet be washable and tough enough to withstand the heavy traffic of offices and lobbies. It is described as being composed of a durable plastic surface on an 8-inch layer of sponge. **(No. 080)**

USI

A new textile preservative, claimed to be the most versatile, efficient, and long-lasting textile preservative thus far known, is said to afford durable protection against fungi, soil-inhabiting organisms, and jungle rot. It is described as being unaffected by water sprays, weather exposure, sunlight, and laundering, and to be compatible with water-repellent and fire-retardant finishes. **(No. 081)**

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
  Alpha-acetylbutyrolactone
  5-Chloro-2-pentanone
  5-Diethylamino-2-pentanone
  Ethyl Acetoacetate
  Ethyl Benzoylacetate
  Ethyl Alpha-Oxalpropionate
  Ethyl Sodium Oxalacetate
  Methyl Cyclopropyl Ketone

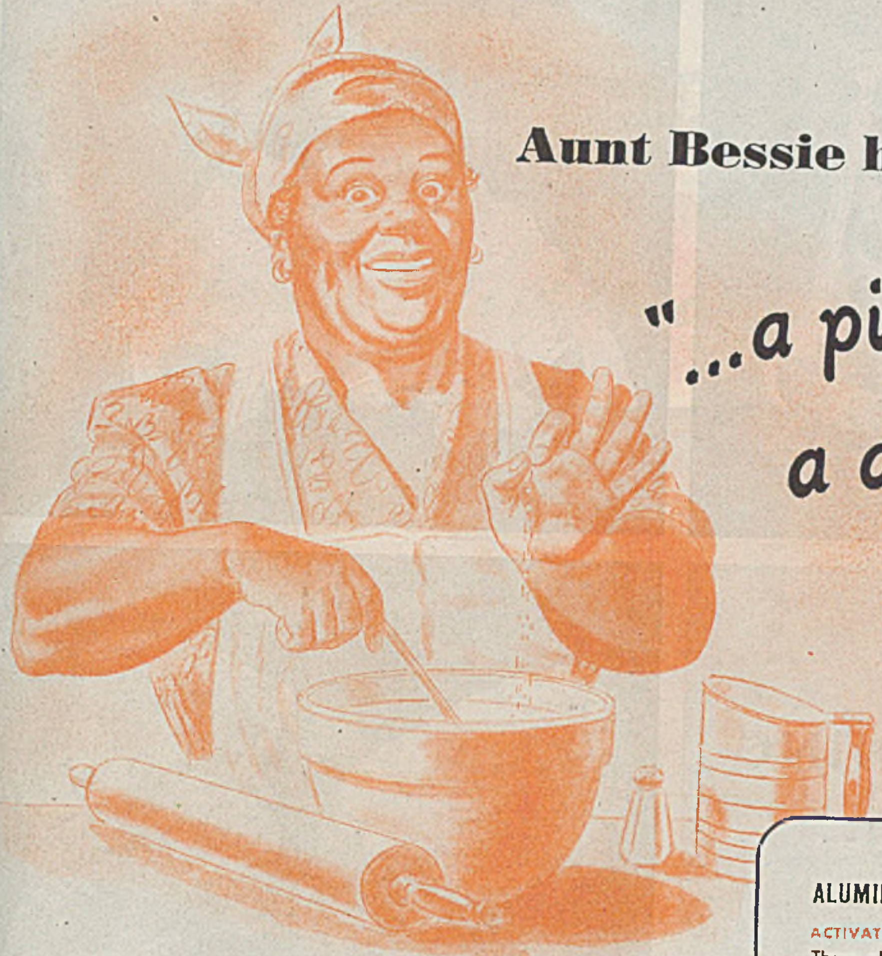
ETHERS
  Ethyl Ether
  Ethyl Ether Absolute—A.C.S.

FEED CONCENTRATES
  *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



Aunt Bessie had a lot of luck—

"...a pinch of this, a dash of that"

You're not depending on **LUCK** when you employ chemically controlled Alorco Aluminas

Nature's a lot like Aunt Bessie—probably averages out well as a compounder, but likely to vary enough to make individual results mighty uncertain.

There's no such uncertainty when you're working with Alorco Aluminas in your catalytic processes—as catalysts, carriers, and auxiliary catalysts. Each lot is exactly like the previous one, because of our accurate control of production.

Refer to the list of Alorco Aluminas shown in the table and decide what characteristics you need. We'll send samples for trial and then make certain that you get identical properties time after time. ALUMINUM ORE COMPANY, Subsidiary of ALUMINUM COMPANY OF AMERICA, 1911 Gulf Building, Pittsburgh 19, Pa.

ALUMINAS FOR CATALYTIC PURPOSES

ACTIVATED ALUMINAS (F SERIES)

These aluminas produced from crystalline aluminum tri-hydrate are catalytically active. Hard granules are available in graded mesh sizes up to one inch. Various grades are distinguished by surface area, porosity and soda contents as low as .1%.

ACTIVATED ALUMINAS (H SERIES)

These aluminas are largely amorphous. They have high surface area and sorptive capacity, high resistance to heat and live steam. Experimental lots are now available in minus-20 mesh particles or as spherical balls ¼" to ½" in diameter.

TABULAR ALUMINAS (T SERIES)

These aluminas are a form of corundum, having high strength and resistance to abrasion. They are unaffected by high temperatures. They are available in graded mesh granules and as spherical balls. Balled and granular forms have porosity of either less than 10% or approximately 30%.

OTHER ALUMINAS

Hydrated Aluminas, C-700 Series, have particles less than .5 micron. They become active after being heated to approximately 300°C. Monohydrated Aluminas, D Series, have particles approximately one micron in diameter. They are substantially inactive catalytically but have considerable porosity.

ALUMINUM ORE COMPANY

ALORCO

Aluminas and Fluorides

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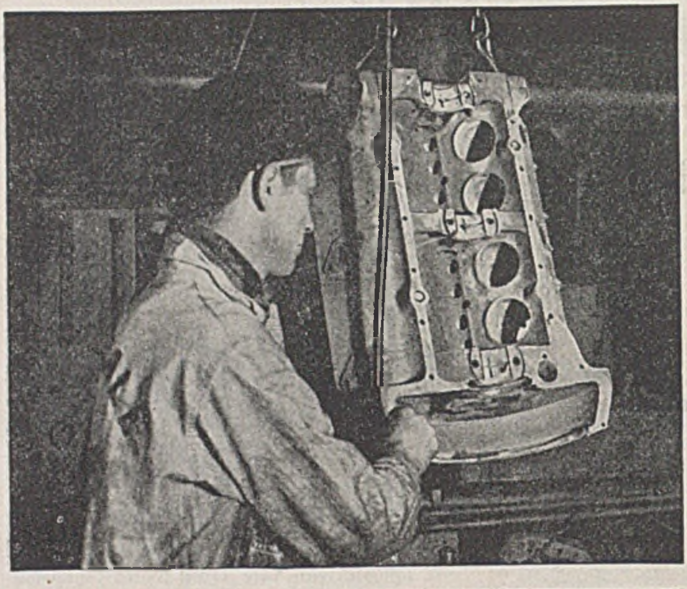


FOR
HIGHER CLEANING
STANDARDS—
BE
SPECIFIC

say Metso!

Upper: Left, cleaner motors. *Right,* whiter coveralls. *Lower:* De-inked paper stock. *Left,* with Metso; *right,* with caustic.

Motors, paper pulp, floors, coveralls—no matter what it is—it must come cleaner when given a Metso Detergent bath. Here's why. The balanced components of Metso, one part of sodium oxide combined and working with one part soluble silica insure accelerated cleaning. This alkaline power, plus the properly proportioned soluble silica speeds up wetting action, emulsification, deflocculation; and then soluble silica performs the added unique function of preventing the removed dirt from redepositing on the cleaned object.

Start now to evaluate these benefits of Metso balanced soluble silica cleansers in a detergent operation in your plant. Specify Metso.

"Metso Granular" (Na_2SiO_3: $5H_2O$). Original sodium metasilicate. U. S. Patent 1898707. White granular product, free flowing. Packed in 100 lb. bags and 300 lb. barrels.

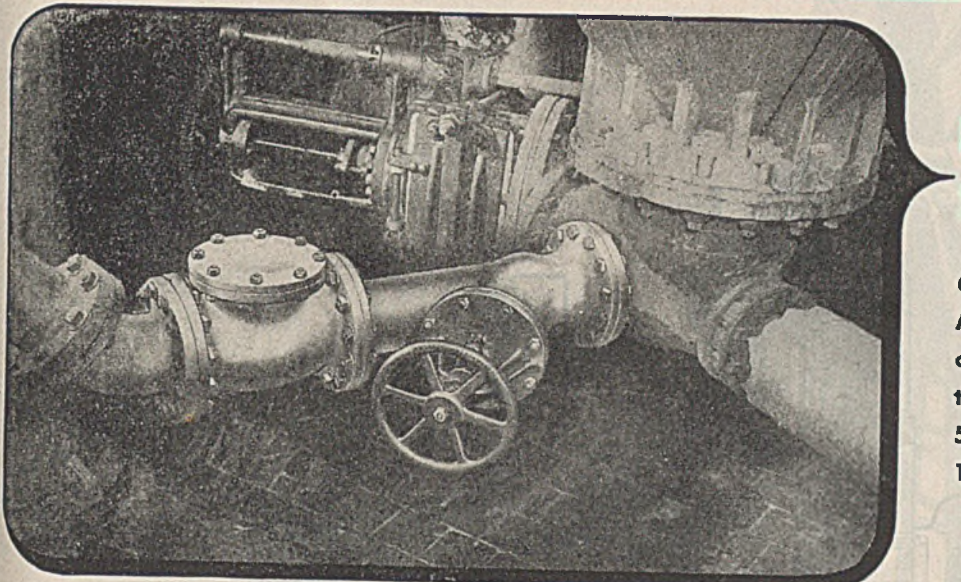
"Metso 99" (Na_3HSiO_4: $5H_2O$). Sodium sesquisilicate. U. S. Patents 1948730, 2145749. White, granular and free flowing. Packed in 400 lb. steel drums.

PHILADELPHIA QUARTZ COMPANY
Dept. C, 119 South Third Street, Phila. 6, Pa.
Chicago Sales Office: 205 West Wacker Drive

metso BALANCED DETERGENTS

ALOYCO STAINLESS STEEL VALVES

.. Install them and forget them



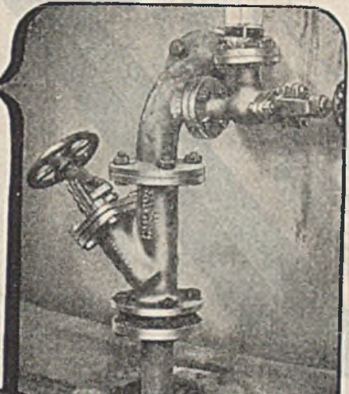
HANDLING HOT SULFITES SINCE NOVEMBER 18, 1929

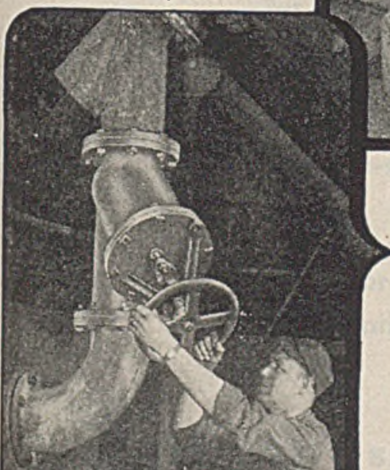
6″ Aloyco Check Valve and 6″ Aloyco "Y" Valve handle hot calcium bisulfite solution containing 6 to 7% total SO_2, and 5 to 6% free SO_2. Also, note 10″ Aloyco Blow Valve in rear.

Photos Courtesy of Eastern Corporation

ALSO INSTALLED NOVEMBER 18, 1929

2½″ Aloyco Side Relief Valve handles hot calcium bisulfite solution containing about 3% total SO_2. The ¾ inch angle sampling valve shown is also an Aloyco.





HOT RELIEF AND COLD ACID

This 8″ Aloyco "Y" Valve handles relief containing up to 85% SO_2 and cold acid.

● Are you valve conscious? Do corrosion, contamination, abrupt temperature changes and other rigorous service conditions give you valve trouble? If so, it will pay you to get in touch with us and find out how Aloyco Valves in the correct analysis of stainless steel can help you "install them and forget them."

The photographs here show Aloyco Stainless Steel Valves in operation in the paper mills of Eastern Corporation since 1929—and still going strong. They are used in the toughest spots in the sulfite mill for blowdown and relief line service.

Aloyco Valves are available in a wide range of stainless steels and corrosion resistant alloys. Large selection of types and sizes for 150 p.s.i. to 600 p.s.i. service. Write today for detailed information.

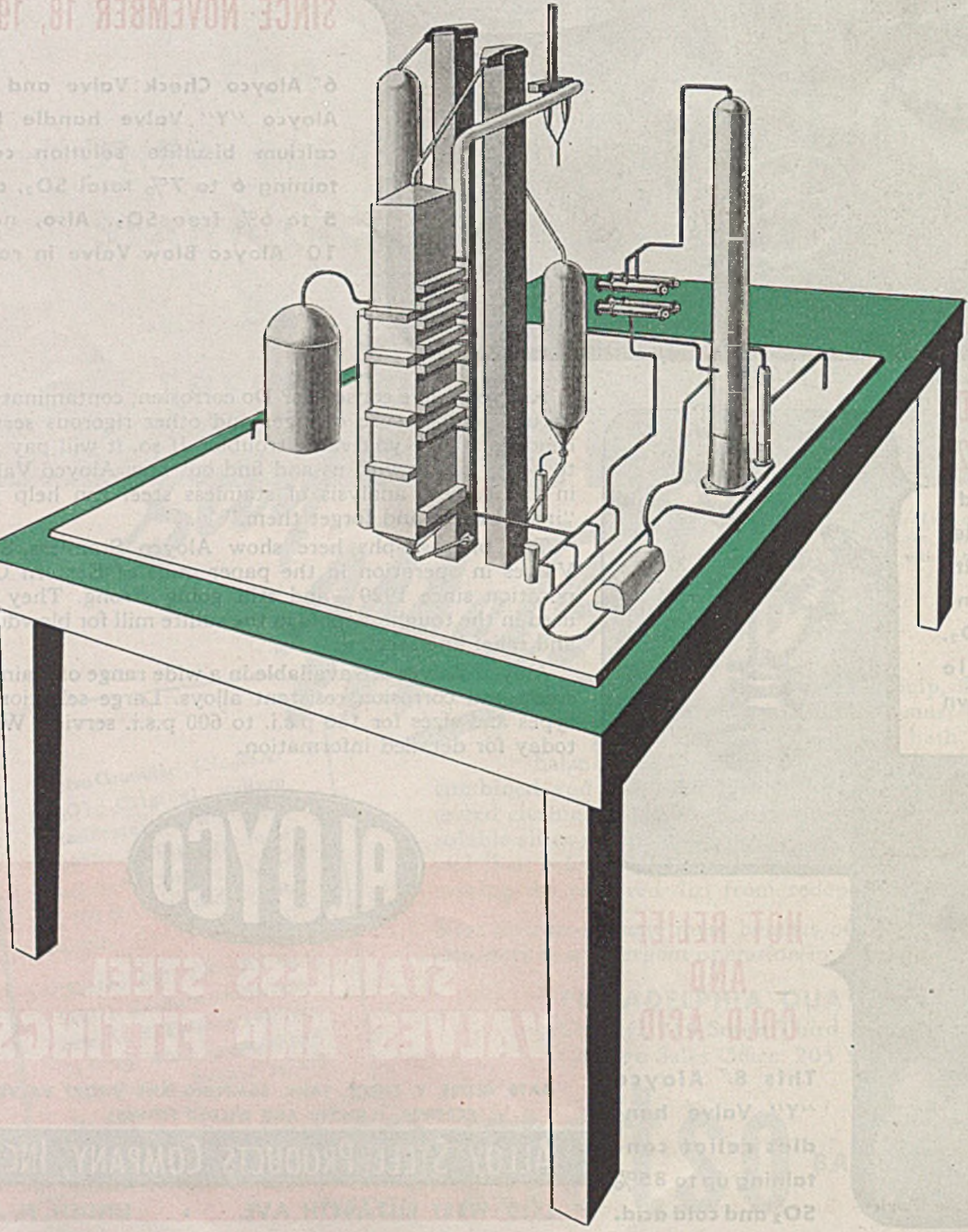
ALOYCO

STAINLESS STEEL VALVES AND FITTINGS

GATE, GLOBE, Y, CHECK, TANK, SAMPLING AND V-PORT VALVES
SCREWED, FLANGED AND WELDED FITTINGS

ALLOY STEEL PRODUCTS COMPANY, INC.

1310 WEST ELIZABETH AVE. • LINDEN, N. J.



A *Glass*

WITH UNEXPECTED

PROPERTIES

Unlike the familiar orthophosphates and pyrophosphates, Calgon* is a glassy rather than a crystalline sodium phosphate.

Hidden in the unknown structure of this sodium phosphate glass are properties of great industrial utility. Calgon sequesters metallic ions in the form of soluble complexes; it aids in the dispersion of pigments; it is adsorbed on metal surfaces, thus inhibiting corrosion.

These properties are developed in Calgon by the method of preparation. Soda ash and phosphoric acid are fused together, and this red-hot melt is cooled quickly, to prevent crystallization. Let the melt cool slowly, so that crystallization *does* take place—and these useful properties are lost.

Fundamental scientific knowledge concerning the "why" of Calgon's exceptional properties is still far from complete, but sixteen years of experience have provided the "how" of effective and economical application of these properties in the conditioning of water for the most varied uses and in the processing of industrial products of the most varied types.

Our chemists will be glad to give you any information which is available concerning the use of Calgon in processes in which you are interested.

X-ray diffraction patterns—which "fingerprint" distinctively each crystalline substance—show Calgon to be devoid of crystalline structure.

1 WATER-SOLUBLE SODIUM METAPHOSPHATE

2 WATER-INSOLUBLE SODIUM METAPHOSPHATE

3 CALGON GLASS

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

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CORROSION problems encountered in handling acid vapors are readily solved through the use of SK corrosion resistant Steam Jet Vacuum Pumps. Lined with Karbate, Haveg or other corrosion resisting materials, destructive vapors never come in contact with the metal bracing which supplies strength and shock-resistant qualities.

SK High Vacuum Ejectors for corrosive service are made in single and multistages with stoneware, Haveg, rubber lined or plastic lined inter-condensers for absolute vacua as low as 1 m/m of mercury and less.

You can have confidence in SK Corrosion Resistant Ejectors as they are backed by many years' experience in the design and manufacture of jet equipment. The Schutte & Koerting Company have pioneered the development of High Vacuum Ejectors and leadership in this field has been maintained by constant product improvement.

SK engineers are ready to help in solving your vacuum problems. Write today for Bulletin 5-EH which illustrates and describes many types of SK Steam Jet Vacuum Pumps.

corrosive vapors cause no trouble . . .
in these SK High Vacuum Ejectors

ET APPARATUS • HEAT TRANSFER EQUIPMENT • STRAINERS • CONDENSERS AND VACUUM PUMPS • OIL BURNING EQUIPMENT • ROTAMETERS AND FLOW INDICATORS ADIATIN TUBES • VALVES • SPRAY NOZZLES AND ATOMIZERS • GEAR PUMPS

SCHUTTE & KOERTING CO.
Manufacturing Engineers
1160 Thompson Street Philadelphia 22, Pa.

COOLING TOWER PERFORMANCE CAN BE MEASURED

THE COOLING TOWER is one of the most critical pieces of equipment affecting overall plant operation. Despite this fact, comparatively few users of Cooling Towers have ever attempted to determine whether or not the towers purchased were doing the job specified. *The most exacting specifications are useless if the manufacturer's performance guarantees are never tested.*

After years of field tests, under widely varying conditions, we of the FLUOR Corporation have proved to our satisfaction and that of many customers that the Power Test Code, 1929 Series, as adopted by the A.S.M.E., provides the measurement standards necessary for testing any Cooling Tower—regardless of design or make.

Don't take our word for it. Test your Cooling Towers. Or, if you prefer, FLUOR Engineers are available to make an unbiased and unprejudiced test of any Cooling Tower you operate.

All Fluor Cooling Towers Carry This Performance Guarantee

FLUOR Cooling Towers are guaranteed to perform in accordance with the design conditions set forth herein when tested as specified by the A.S.M.E. Power Test Code, 1929 Series, using the following procedure: the wick of the wet bulb will be wetted with water from the Cooling Tower basin; the wet bulb temperature for test purposes will be measured on the windward side of the tower at intervals not to exceed the width of each individual cell along the longitudinal axis of the tower at a distance not to exceed 50 feet from the various air intakes and not over 6 feet above the basin curb. The average of the several wet bulb temperatures taken as described here will be used as the wet bulb for tower performance......

BE SURE
with
FLUOR

FLUOR AERATOR AND COUNTERFLOW COOLING TOWERS

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

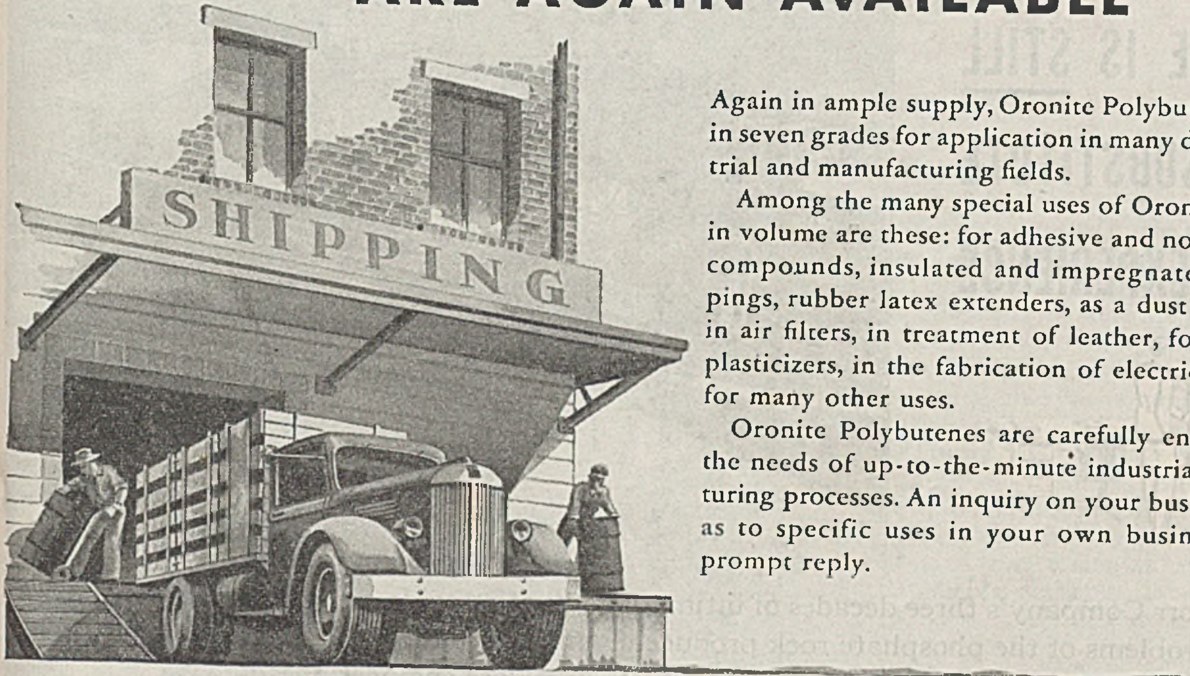
SINCE 1890

ENGINEERS • MANUFACTURERS • CONSTRUCTORS

ORONITE CHEMICALS
Reg. U. S. Pat. Off.

THE NAME TO WATCH IN CHEMICALS

ORONITE POLYBUTENES ARE AGAIN AVAILABLE



Again in ample supply, Oronite Polybutenes are offered in seven grades for application in many diversified industrial and manufacturing fields.

Among the many special uses of Oronite Polybutenes in volume are these: for adhesive and non-drying gasket compounds, insulated and impregnated paper wrappings, rubber latex extenders, as a dust trapping agent in air filters, in treatment of leather, for paraffine wax plasticizers, in the fabrication of electrical devices, and for many other uses.

Oronite Polybutenes are carefully engineered to fill the needs of up-to-the-minute industrial and manufacturing processes. An inquiry on your business letterhead as to specific uses in your own business will bring prompt reply.

1240

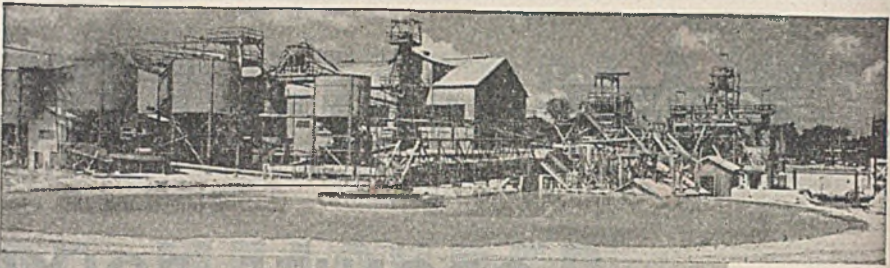
TYPICAL TESTS:

	No. 8	No. 12	No. 16	No. 20	No. 24	No. 32	No. 64
Flash Point, Clev. °F.	315	340	360	380	435	500	540
Viscosity 100°F. SSU	358	3390	5425	17160	49750	167500	347600
Viscosity 210°F. SSU	52	154	210	528	1060	3065	6075
Viscosity Index	71	75	80	100	104	115	119
Pour Point °F.	—30	—5	0	10	20	40	55
Solid Point °F.	—35	—10	—5	5	15	35	50
Gravity, API	35.4	32.0	31.0	29.8	27.9	26.0	25.0
Spec. Gravity	.8478	.8654	.8708	.8772	.8877	.8984	.9042
Lbs. Per Gallon	7.059	7.206	7.251	7.305	7.392	7.481	7.529
Molecular Weight	370	530	600	700	900	1200	1500
Neut. Number	.10	.10	.10	.05	.02	.01	.01
Sap. Number	.3	.3	.2	.2	.2	.1	.1
Carbon %	0	0	0	0	0	.01	.02
Sulphur %	.01	.01	.01	.02	.02	.02	.04
Sligh Oxidation Test	0	0	0	0	1	1	2
Color ASTM (Max.)	1½	1½	1½	2	2	2	2
Dielectric Strength	35,000	35,000	35,000	35,000	35,000	35,000	35,000

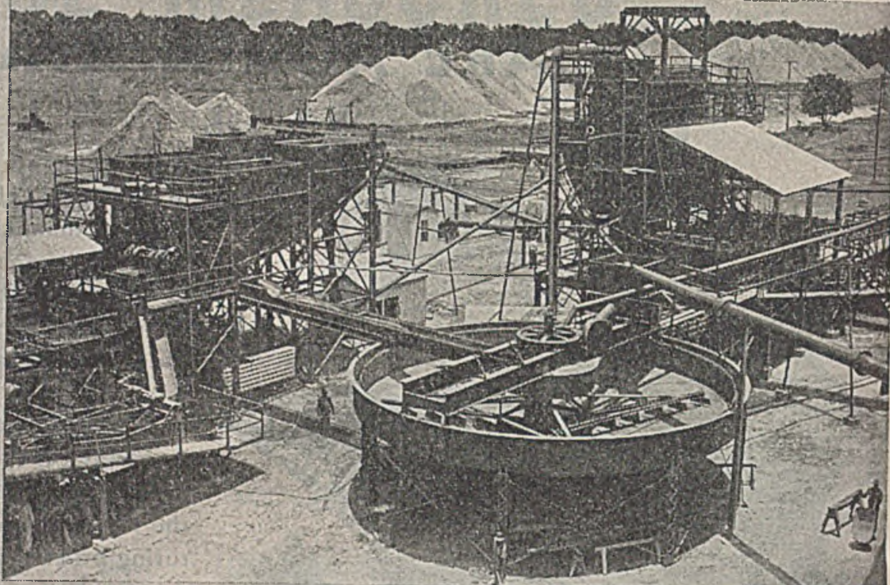
ORONITE CHEMICAL COMPANY

Russ Building, San Francisco 4, California
White-Henry-Stewart Bldg., Seattle 1, Wash.

30 Rockefeller Plaza, New York 20, N.Y.
Standard Oil Bldg., Los Angeles 15, Calif.



In Phosphate Rock Processing THERE IS STILL NO SUBSTITUTE FOR EXPERIENCE



The Dorr Company's three decades of intimate and nation-wide assistance with problems of the phosphate rock producers, and of producers in similar high tonnage, low profit margin fields, gives the Dorr engineer an advantage which you as an operator can thoroughly appreciate.

To augment his own knowledge, he has behind him a corps of widely experienced engineers and the accumulated data from a wide variety of similar jobs.

Whether you are considering Classifiers, Sizers, Hydroseparators or Thickeners, you will do well to call in the Dorr Company and have one of its engineers explain how some of the newer machines may improve recovery and lower the "per ton operating cost".

The Dorr engineer is an "experienced hand" in phosphate rock processing and for this experience of his there exists no substitute.

1514

DORRCO

THE DORR COMPANY, ENGINEERS
NEW YORK 22, N. Y. . . 570 LEXINGTON AVE.
ATLANTA 3, GA. . . WILLIAM-OLIVER BLDG.
TORONTO 1, ONT. . . . 80 RICHMOND ST. W.
CHICAGO 1, ILL. . . . . 221 NO. LA SALLE ST.
DENVER 2, COLO. . . . . COOPER BUILDING
LOS ANGELES 14, CAL. . . . 811 WEST 7TH ST.
RESEARCH AND TESTING LABORATORIES
WESTPORT, CONN.
SUGAR PROCESSING
PETREE & DORR DIVISION
570 LEXINGTON AVE., NEW YORK 22, N. Y.

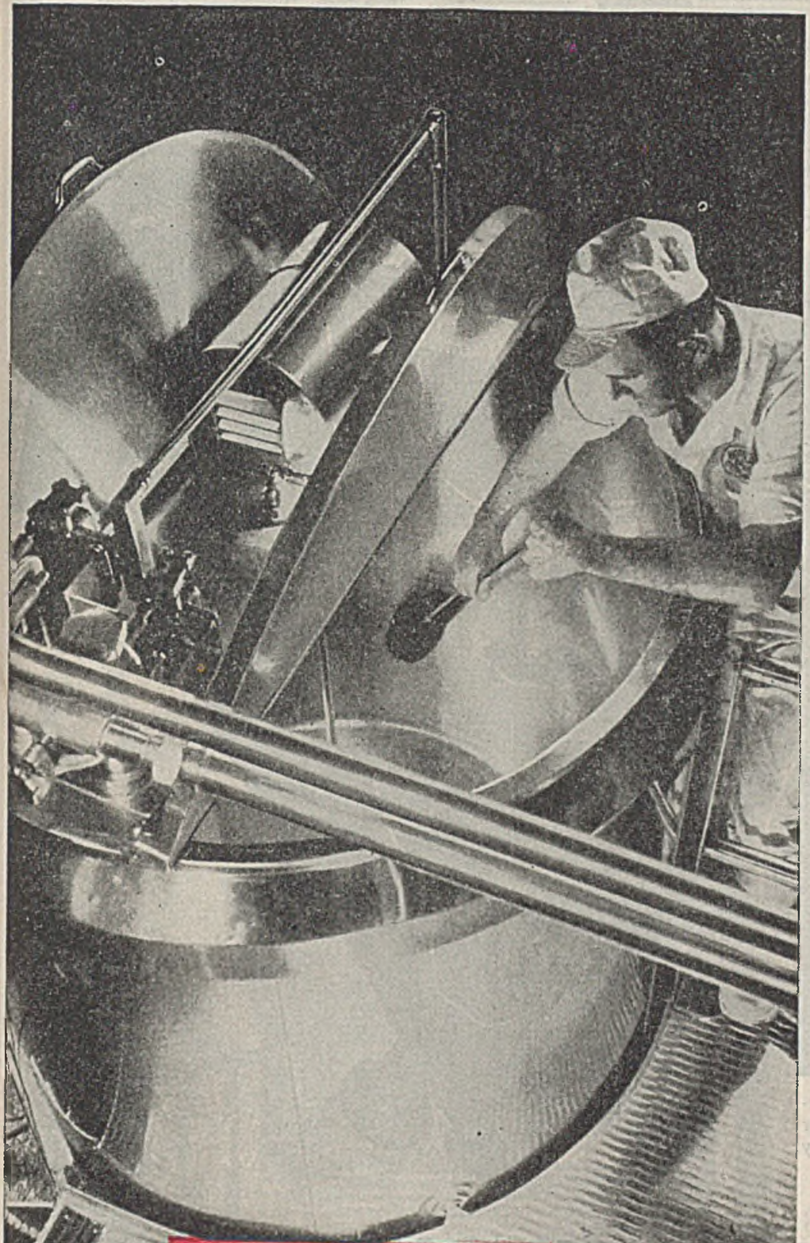
DORR

RESEARCH ENGINEERING EQUIPMENT

ADDRESS ALL INQUIRIES TO OUR NEAREST OFFICE

TO CUT DOWN CLEANING TIME AND COSTS

—nothing equals Stainless Steel!



Ask anybody—the man on the street, the housewife, your plant manager, chemical engineer or maintenance man, especially ask the men who operate your equipment—what is the first thing that comes to mind when Stainless Steel is mentioned. The answer is always the same—*"It's clean. It's easy to keep clean."*

True enough. And this well-recognized attribute of Stainless results in important savings in time, money and labor.

A less well-known property that goes hand-in-hand with "cleanness" and which has similar highly desirable cost-cutting effects is Stainless Steel's *ability to resist adherence.*

It's a fact that many materials which adhere quite readily to common steel, or to coatings with which such steels are protected against corrosion, will not adhere to Stainless Steel.

These materials include a number of food products, dyes, gums from rayon and other textile products, wood gums and resins, and various materials encountered in chemical processing.

Stainless Steel rejects corrosion or solution by these materials to the point where they will not seize upon it.

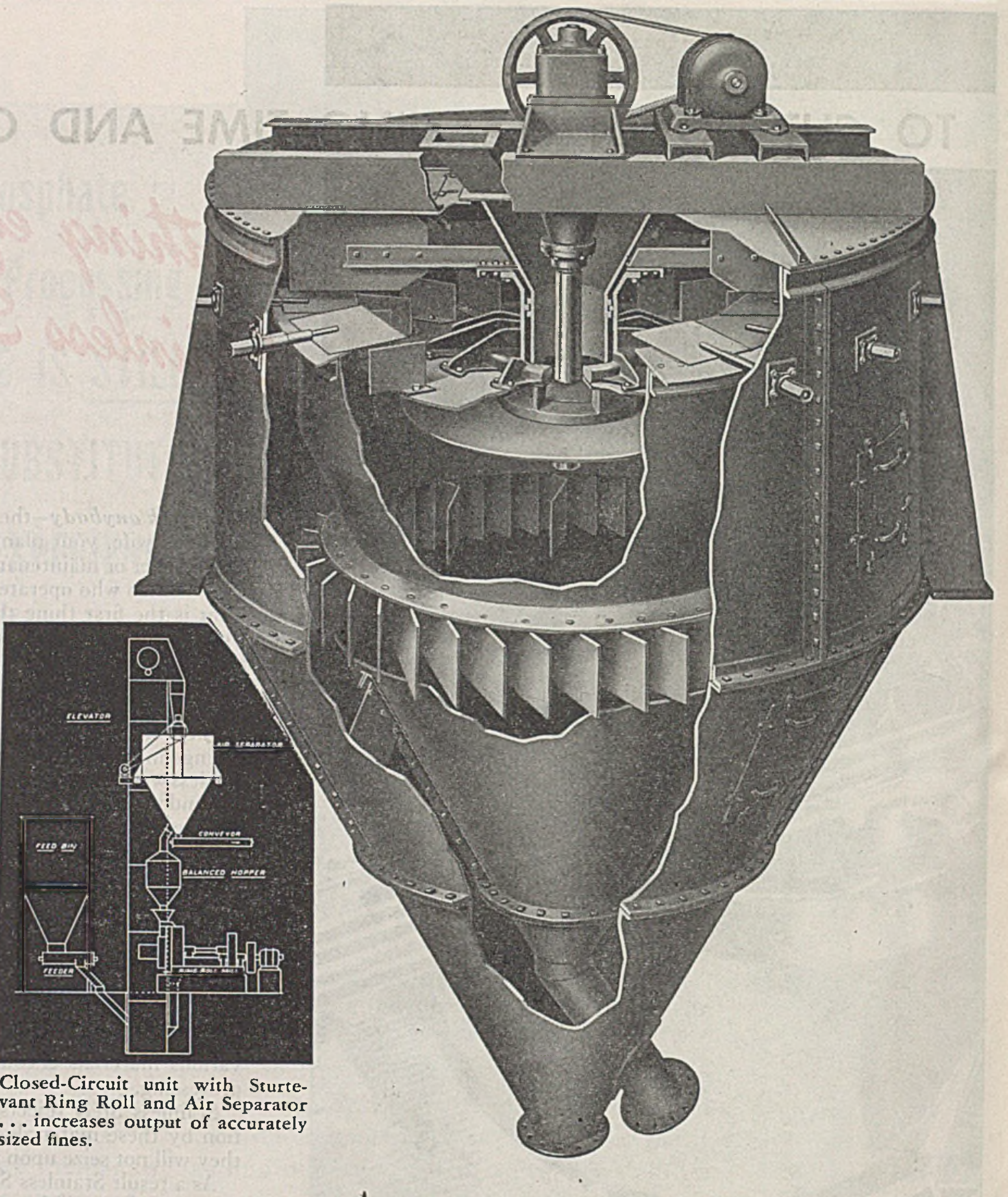
As a result Stainless Steel equipment can be run for much longer periods without cleaning—errors in control of process temperatures cause less damage to equipment—spoiled materials can be cleaned and scoured away with less time and labor and with less damage to equipment.

All the money-saving advantages of Stainless Steel you can obtain at top perfection in U·S·S Stainless. Our engineers are specialists in solving new and unusual problems in the use of Stainless Steel—their wide experience is backed by the laboratory and research facilities of the world's largest producer of fine steel. Both are at your service to help you obtain optimum results with U·S·S Stainless.

U·S·S STAINLESS STEEL

AMERICAN STEEL & WIRE COMPANY, *Cleveland, Chicago and New York*
CARNEGIE-ILLINOIS STEEL CORPORATION, *Pittsburgh and Chicago*
COLUMBIA STEEL COMPANY, *San Francisco*
NATIONAL TUBE COMPANY, *Pittsburgh*
TENNESSEE COAL, IRON & RAILROAD COMPANY, *Birmingham*
United States Steel Supply Company, Chicago, *Warehouse Distributors*
United States Steel Export Company, New York

UNITED STATES STEEL


ELEVATOR
AIR SEPARATOR
CONVEYOR
FEED BIN
BALANCED HOPPER
FEEDER
RING ROLL MILL

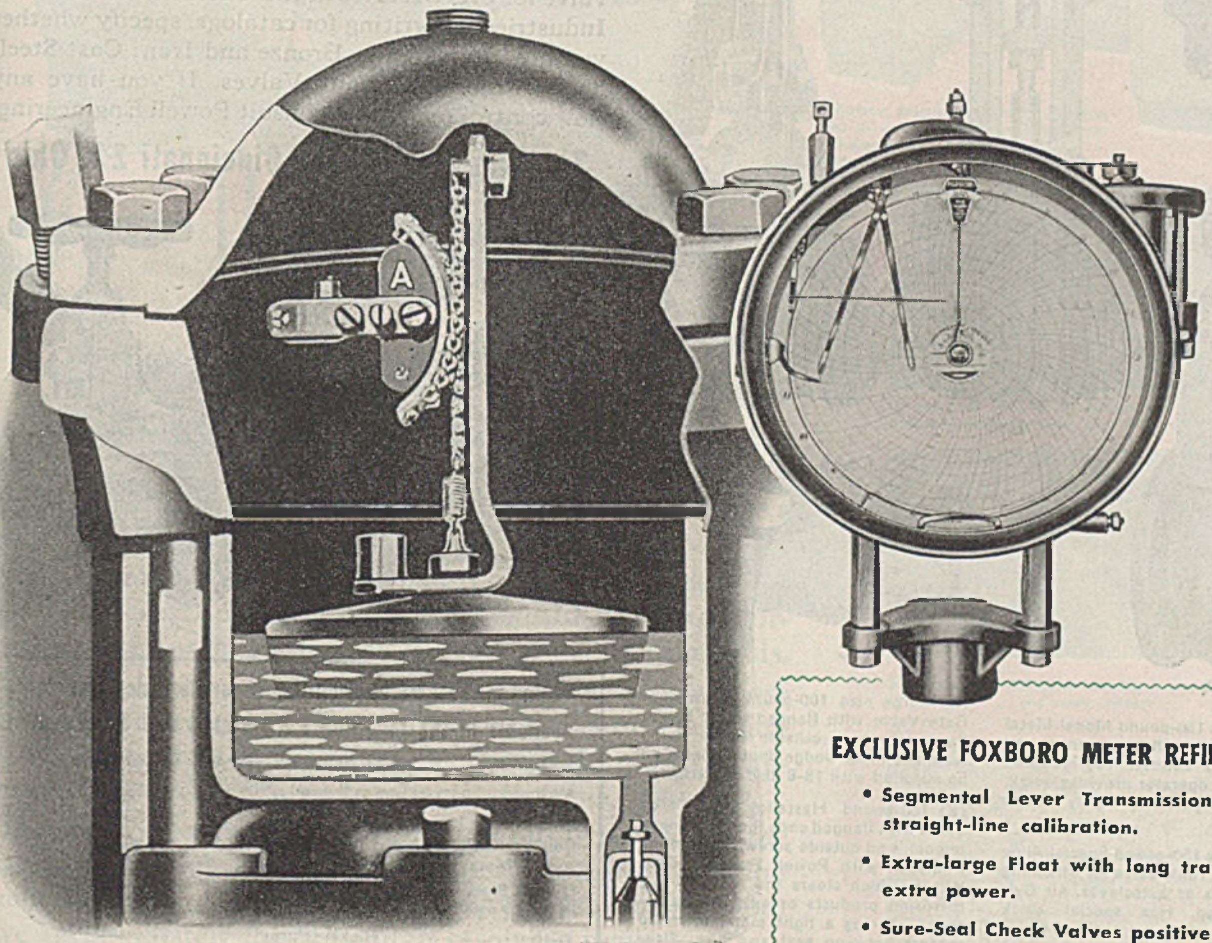
Yes... THERE IS A DIFFERENCE IN FLOW METERS!

In any piece of critical equipment you select, better-engineered design and construction make an important difference in the service it will give you. Flow meters are no exception.

For example, an important refinement found only in Foxboro Differential Meters is the patented Segment Transmission that gives straight-line calibration. It eliminates angularity errors of common levers and avoids the excess friction and lost motion of rack-and-pinion movements. Slightest changes in flow are recorded without error!

When you buy a Foxboro Meter, you get the extra value of many such exclusive features. In metering results, this better engineering gives you added accuracy and dependability . . . without added cost.

Write for Bulletin 200-7 which contains detailed information. **The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U. S. A.** Branches in principal cities.



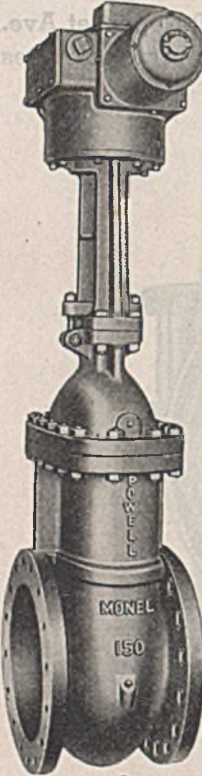
The patented Foxboro Segment (A) produces straight-line calibration. The vertical motion of the float is transmitted through a unique, patented ladder-chain, giving positive transmission of the linear to rotary motion variables. Functions like a rack-and-pinion, but without the friction and lost motion of gear teeth.

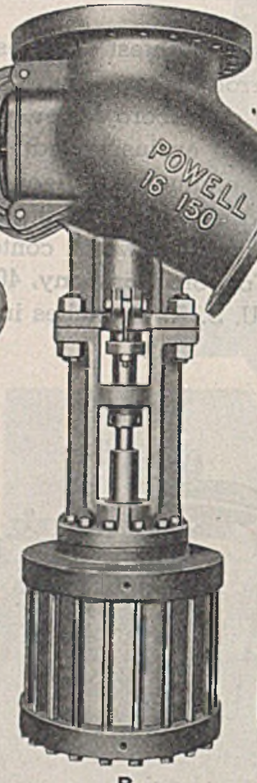
EXCLUSIVE FOXBORO METER REFINEMENTS

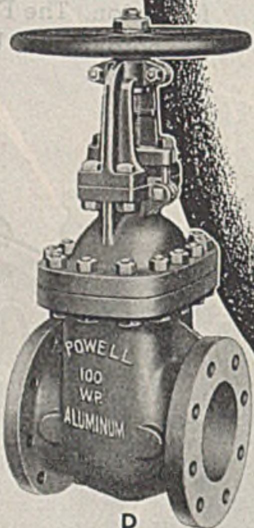
- **Segmental Lever Transmission gives straight-line calibration.**
- **Extra-large Float with long travel for extra power.**
- **Sure-Seal Check Valves positively prevent mercury losses.**
- **Pressur-Tite Bearing eliminates stuffing box and packing.**

FOXBORO
REG. U. S. PAT. OFF.

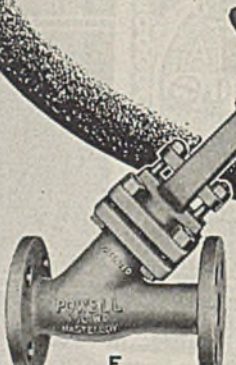
DIFFERENTIAL-TYPE FLOW METERS

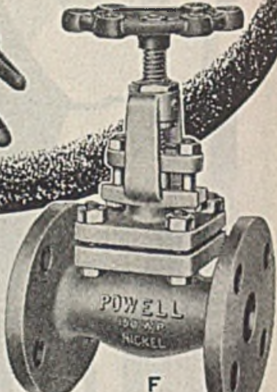

POWELL
MONEL
150
A


POWELL
16 150
B


POWELL
100
WP
ALUMINUM
D


POWELL
C

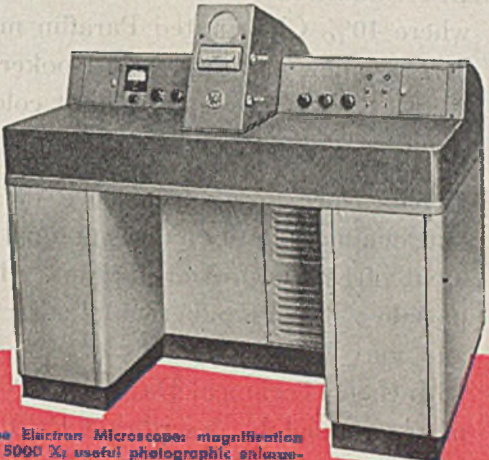

POWELL
E


POWELL
100 WP
NICKEL
F

Speed research...see things you've never seen before...improve product quality

These RCA electron microscopes will multiply your vision 100,000 times

"Universal" Electron Microscope: adjustable magnifications up to 20,000 X. Sharp photographic enlargement to 100,000 diameters.



Console-type Electron Microscope: magnification 500 X and 5000 X; useful photographic enlargement to 100,000 diameters.

IF A DIME were magnified 100,000 times it would be more than a mile in diameter; a human hair would be the size of a giant redwood tree; a blood corpuscle would resemble a sofa pillow.

This magnification power, made possible by these RCA electron microscopes, has opened up a wealth of new opportunities for research, production, process control, and analysis.

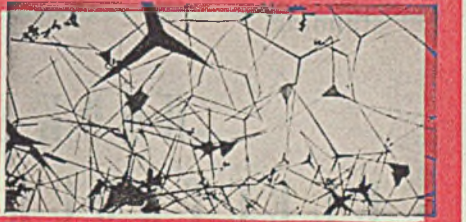
During the few short years they have been available, these remarkable instruments have solved hundreds of vitally important problems relating to metals, chemicals, plastics, rubber, textiles, and petroleum products—to name just a few.

The RCA electron microscope comes in two models: the de luxe "Universal" type incorporating an electron diffraction camera and the compact, less expensive desk model. Both have approximately the same high resolving power.

We'll be glad to help you appraise the possibilities of these instruments in connection with your work. Write Dept. 39-F.

A polished face of a diamond 7,700 X—Note residual polish marks and pits in elevations.*

Surface of a used roller bearing (inner surface of the outer cone).*



Zinc Smoke (ZnO) magnified 2,750 times.

*A collodion replica, metal-shadowed to produce three-dimensional effect. Courtesy R. W. G. Wyckoff and R. C. Williams.

SCIENTIFIC INSTRUMENTS

RADIO CORPORATION of AMERICA

ENGINEERING PRODUCTS DEPARTMENT, CAMDEN, N.J.

Hooker CP-40, A New and Improved Chlorinated Paraffin

In formulations for flame and water repellency where 40% Chlorinated Paraffin may be used, here is a new and improved Hooker product. It is an exceptionally stable, light colored viscous liquid with an extremely low iron content.

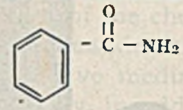
Hooker specialized experience in chlorinating long chain aliphatics has resulted in the development of this improved product. CP-40 is compatible with a number of film forming resins, and may be used as a plasticizer or extender with them. Technical Data Sheet No. 731 which more completely describes CP-40 is available when requested on your company letterhead.

Physical Properties	CP-40
Chlorine Content.	42 ± 1%
Specific Gravity, 15.5°/15.5°C . .	1.185 ± .01
Viscosity at 210°F (Saybolt Universal).	160 to 180
Acidity as HCl.	0.006% max.
Iron.	10 ppm. max.
Color, Union Colorimeter ASTM	1.5 to 2.5
Thermal Stability (6 hours at 300°F).	0.15% HCl max.

Where the formulation calls for a 70% chlorinated paraffin, Hooker CP-70 is available for similar uses. This material is a brittle amber colored resin. It is crushed and shipped as a white powder which does not agglomerate on standing.

HOOKER RESEARCH ***Presents***

BENZAMIDE



Benzamide (Amide of Benzoic Acid) is a white, free-flowing monoclinic crystalline material.

Its physical and chemical properties suggest its application in the fields of organic synthesis, including plastics, pharmaceuticals and dyestuffs. It is compatible with a limited number of resins including cellulose acetate and nitrocellulose with which it forms a firm transparent film.

For more complete information write on your letterhead for Technical Data Sheet No. 361 which lists the physical properties and a number of the reactions which Benzamide will undergo.

Because of its relative chemical inertness CP-70 is suggested also in formulations for fireproof paints, adhesives, linoleum, etc. In protective coatings and paints it does not adversely affect the rate of drying. Technical Data Sheet No. 763, describing more fully the properties of this chemical, is available when requested on your company letterhead.

Physical Properties	CP-70
Analysis (typical)	
Chlorine.	69 to 73%
Free HCl.	0.05 max.
Iron.	0.01 max.
Softening Range.	90° to 100°C
Acid Number, mg. KOH/gm.	0.50 max.

HOOKER
ELECTROCHEMICAL
COMPANY

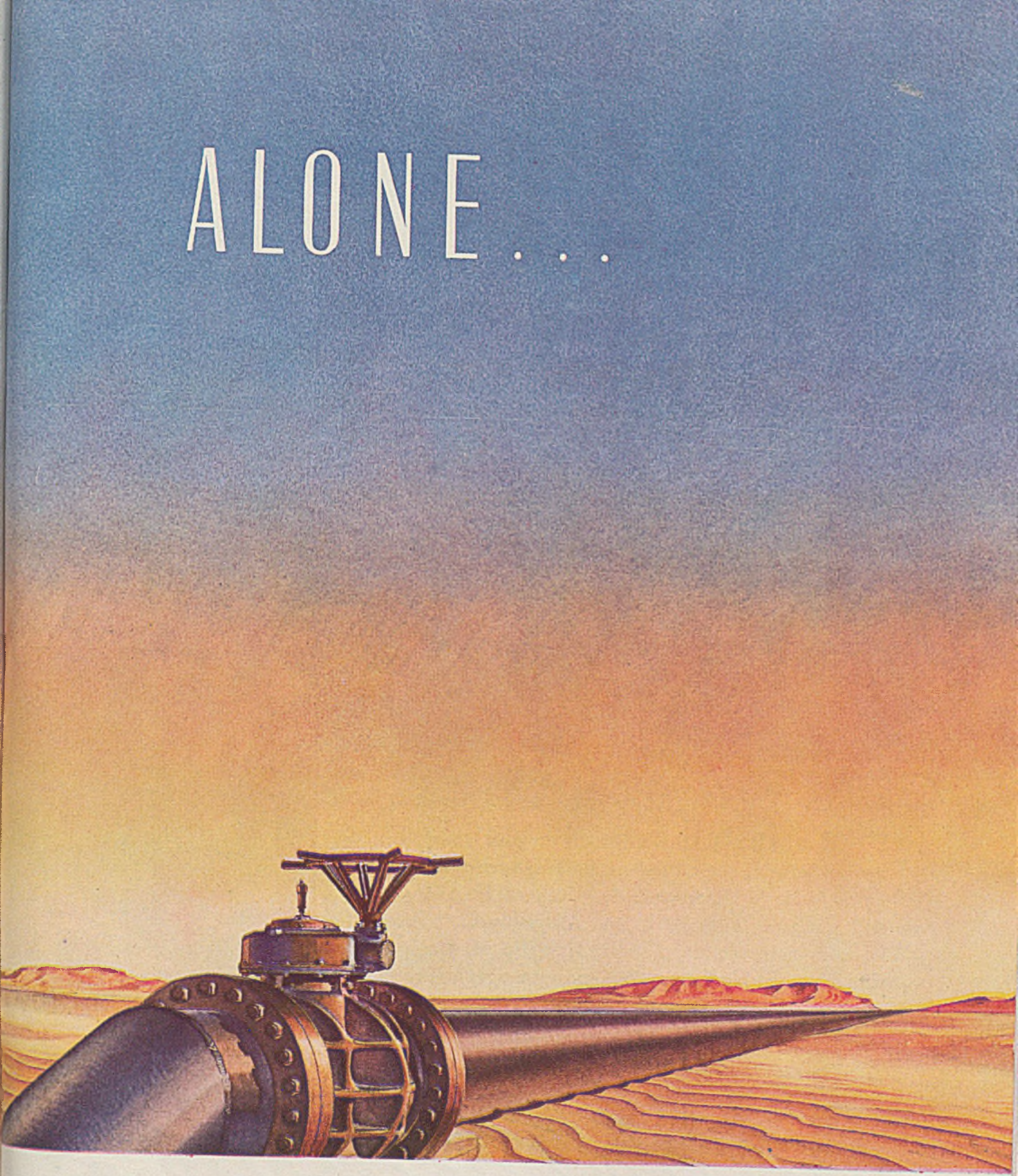
9 Forty-seventh St., Niagara Falls, N. Y.

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

Caustic Soda · Muriatic Acid · Sodium Sulfide
Paradichlorbenzene · Chlorine · Sodium Sulfhydrate

HOOKER CHEMICALS

8318

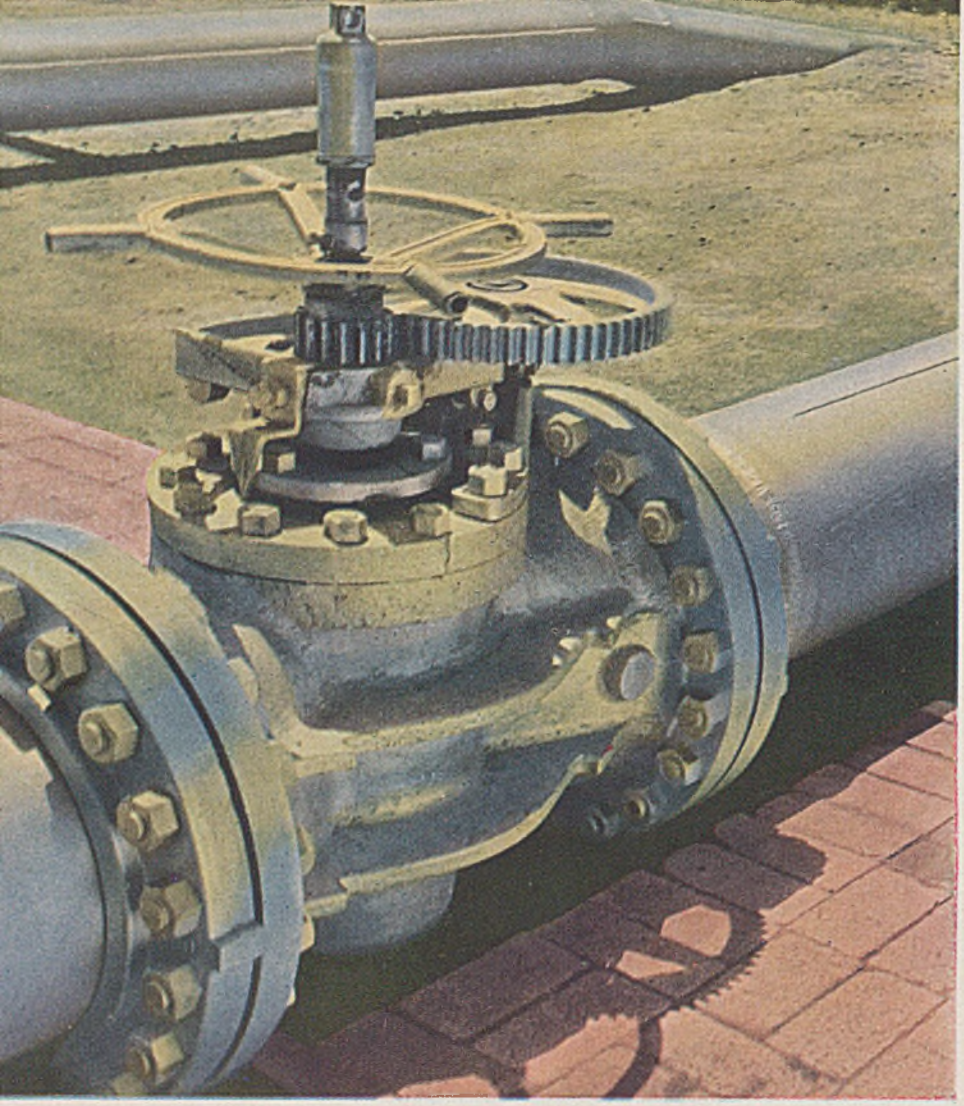


It cannot plead for help; it must stand alone; solitary sentry of the far-flung pipe line. It must not fail when emergency arises, nor deteriorate in the face of the elements. Built for rough, out-in-the-open service, the Nordstrom Valve stands as a bulwark of safety; always ready for instant operation, with no fear of sticking.

The prime credential of valve integrity is *leakproof endurance*. There is nothing so certain of seating as a lubricated, tapered-plug valve. With pressure lubrication hydraulically directed, the Nordstrom Valve brings the tapered-plug principle of leakproof closure to its fullest scope of achievement. Nordstrom builds sizes up to 30".

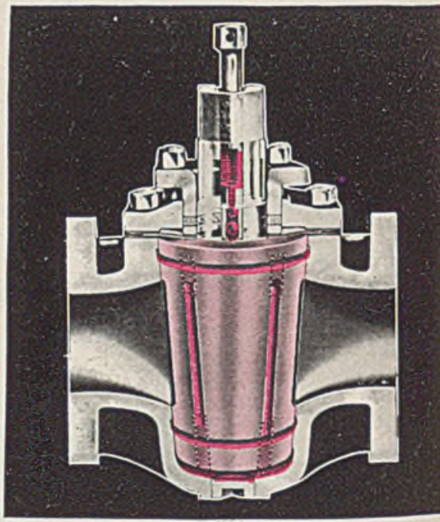
NORDSTROM LUBRICATED VALVES

KEEP UPKEEP DOWN



Unbeatable pipe line control

Often heard in plant and field is the expression, "*They make it tough on Nordstroms.*" On lines where no other valves will satisfactorily operate, Nordstroms do the job. In operations where temperature, fluids, corrosion and erosion take heavy toll, count on Nordstrom to "*do the trick.*" Everything is under control with these unbeatable valves.



Install Nordstroms on your tanks, flow lines, circulating lines, transmission lines—everywhere for *safety*. Made in all pressure classifications to ASA and API standards. Sizes ½" to 30". Adaptable for manual and automatic remote controls. May also be equipped with locking devices, extensions and water tight housings.

Nordstrom

LUBRICATED VALVES

FOR *ALL-PURPOSE* SERVICE

Sealdport Lubrication

NORDSTROM VALVE COMPANY – ***Division of Rockwell Manufacturing Company***
WORLD'S LARGEST MANUFACTURERS OF LUBRICATED PLUG VALVES
Main Office:
400 North Lexington Ave. Pittsburgh 8, Pennsylvania

Ease your "Profit Squeeze"

SPECIFY INGACLAD STAINLESS-CLAD STEEL FOR LOWER-COST PROTECTION AGAINST CORROSION, ABRASION, OXIDATION, CONTAMINATION

IF YOU use or plan to use stainless steel in your plant or processing equipment, see how IngAclad Stainless-Clad Steel can help you *ease your profit squeeze* three ways—

1 IngAclad, with its 20% cladding of solid stainless steel, *provides 100% stainless protection* on the contact side.

2 IngAclad *costs much less* than the solid stainless metal.

3 IngAclad, with its permanently bonded backing of mild steel, is *easier to fabricate* than solid stainless.

Whatever the application, if stainless protection is called for or desired only on the contact side, IngAclad offers substantial savings in equipment cost—*plus,* frequently, a profitable improvement in the quality of the finished plant product. Why not see what IngAclad can do for you?

Check these Uses of IngAclad in the Chemical Industry

- Lined Tanks
- Dryers
- Filter Units
- Mixing Kettles
- Processing Kettles
- Conveyor Troughs
- Drums and Shipping Containers
- Dehydrators
- Laboratory Tables, Sinks
- Stills
- Condenser Bodies
- Evaporators
- Storage Tanks
- Hoppers
- Ducts
- Fume Hoods
- etc.

INGERSOLL STEEL DIVISION
BORG-WARNER CORPORATION
310 South Michigan Avenue • Chicago 4, Illinois
Plants: Chicago, Illinois • New Castle, Indiana • Kalamazoo, Michigan

NEERING B-W PRODUCTION

Originators and Producers of

INGACLAD

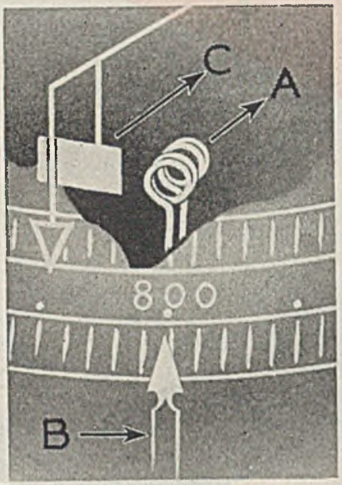
STAINLESS-CLAD STEEL

Q. WHY BUY WHEELCO *Electronic* Controls?

A. THEY'RE BETTER, *Because*:

THEY'RE FASTER

operate at the speed of light — no mechanical link between indicating and control sections — high speed means greater accuracy and sensitivity.



THEY'RE SIMPLER

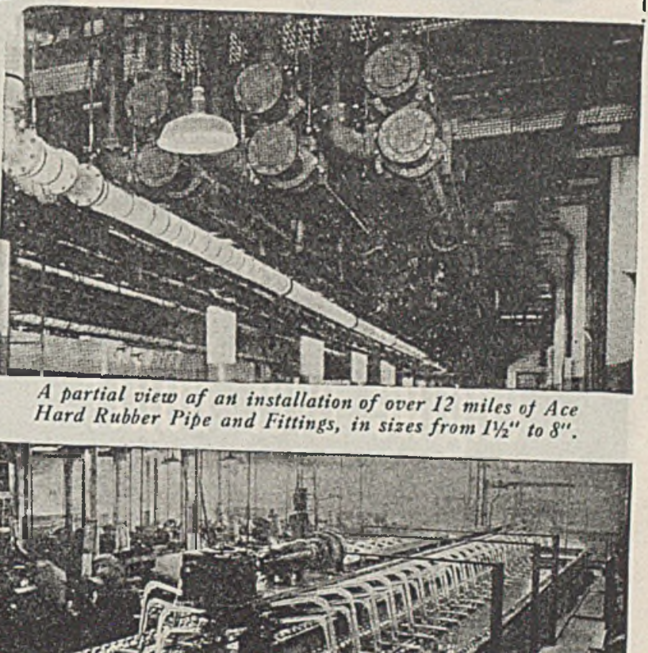
flexible plug-in assemblies permit streamlined construction, operation and installation — simple electronic action — no mechanical cams and gears.

THEY'RE MORE SERVICEABLE

interchangeable unit construction permits replacement or servicing on location without dismounting the instrument — flexibility of design assures uninterrupted operation.

WHEELCO INSTRUMENTS COMPANY
373 W. Harrison St., Chicago 7, Ill

WHEELCO *Electronic* CONTROLS

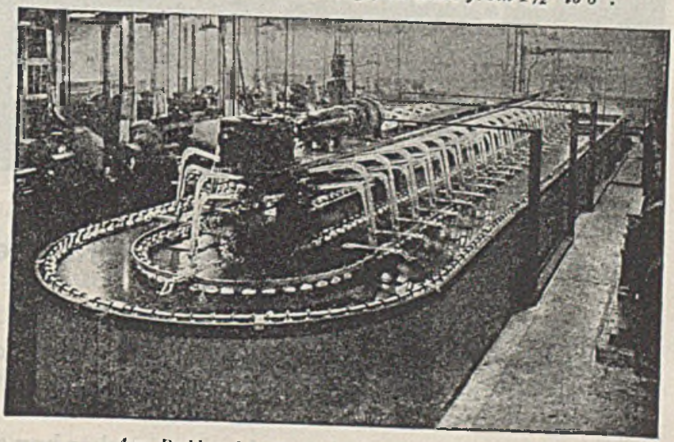


A partial view af an installation of over 12 miles of Ace Hard Rubber Pipe and Fittings, in sizes from 1½" to 8".

With Ace Rubber Protection it's a mighty sound investment

Ace Rubber Protection adds years to the life of plant equipment handling corrosives. In so doing it helps prevent costly breakdowns as it protects not only equipment but the finished product as well. Ace Rubber Protection has proven itself *on the job* in many installations which we have provided in over 75 years of service to American industry!

American Hard Rubber Company
General Sales Office: 11 Mercer St., New York 13, N. Y.
Branch Sales Offices:
111 W. Washington St., Chicago 2, Ill.
Akron 9, Ohio



Ace Rubber lined return type plating tank

PLANT EXECUTIVES:

Write for free copy of 64 page handbook containing invaluable information about anti-corrosion equipment.

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

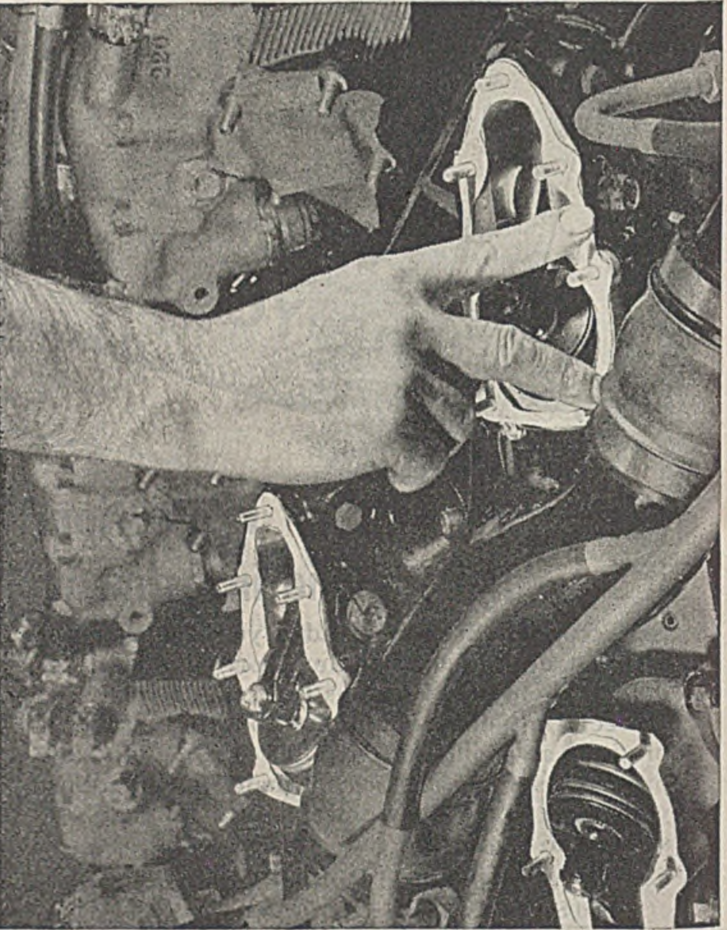
DC
DOW CORNING
SILICONES

SILASTIC
FLUIDS
VARNISHES
RESINS
GREASES

withstand heat
resist oxidation
exclude moisture

SILASTIC* GASKETS

for the most powerful aircraft engine ever built!



chosen best among all gasket materials tested for service at 450°F.

Silastic gaskets fabricated from Dow Corning silicone rubber by the Connecticut Hard Rubber Co. seal 56 rocker boxes of the 28-cylinder Pratt & Whitney Wasp Major.

"*NOTHING BUT THE BEST!*" That's the policy followed by Pratt & Whitney in selecting materials for the powerful new 28-cylinder, 3650 h.p. Wasp Major.

That's why Silastic was chosen for these rocker box gaskets. Factors in the choice were Silastic's resiliency at the 450°F. operating temperature, resistance to the hot oil, and convenience in handling.

Silastic will fly with the Wasp Major in such giant new airliners as the Boeing Stratocruiser, Douglas Globemaster, Martin Mars, and Republic Rainbow.

If you need a rubber-like material that's resilient up to 500°F. and flexible down to −70°F., call for "Silastic Facts" No. 1A—and *TRY SILASTIC!*

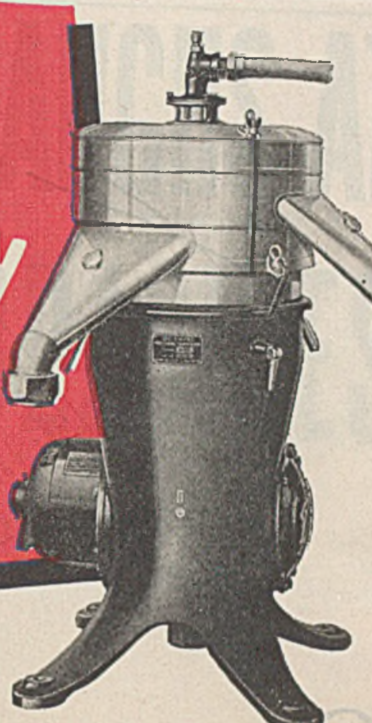
*Trade Mark, Dow Corning Corporation

DOW CORNING CORPORATION • MIDLAND, MICHIGAN

Chicago Office: Builders' Building Cleveland Office: Terminal Tower
New York Office: Empire State Building
In Canada: Dow Corning Products Distributed by Fiberglas Canada, Ltd., Toronto

Dow Corning
FIRST IN SILICONES

Is your problem of CONTINUOUS SEPARATION *similar to these?*



ACID SLUDGE
BLOOD
CAUSTIC SODA
CHICLE
CITRUS JUICES
COOKING FAT
ESSENTIAL OILS
FIRE EXTINGUISHER FLUID
FISH OIL
FORMALDEHYDE
GLUE LIQUOR
GLUTEN
IRISH MOSS
LACQUER
LATEX
LIVER OIL
OLIVE OIL
PAINT & VARNISH
PENICILLIN
PHARMACEUTICALS
PRINTING INK
PROTEINS
SERUM
STARCH
STREPTOMYCIN
TOMATO JUICE
VEGETABLE OIL
WAX
WOOL GREASE
YEAST

OPPORTUNITIES for simplifying processes by changing from old fashioned gravity or filtration systems to the ***faster, more efficient,*** continuous separation with De Laval centrifugals come up every day. The list at the left is far from complete, nor are all the applications "new" — but it does show the wide variety of problems of separation, clarification, or concentration that De Laval engineers have solved.

Perhaps you have always regarded your problem as different or especially difficult. Yet from De Laval's large line of highly specialized machines, which includes more than a dozen distinct types, usually each problem of applying centrifugal force can be met in the most efficient, economical manner.

In addition to speeding up operations by converting a process to a continuous basis, De Laval centrifugals have two additional advantages worth noting: (1) they effect material savings and (2) generally, if not invariably, they improve the product.

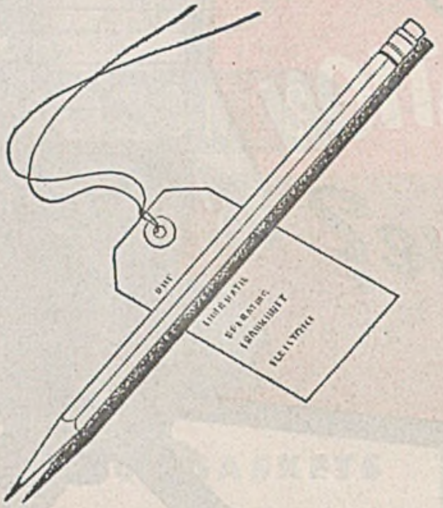
In writing De Laval, it will be helpful if you specify whether you are interested in separation, clarification or concentration. Ask for Bulletin No. 225.

★

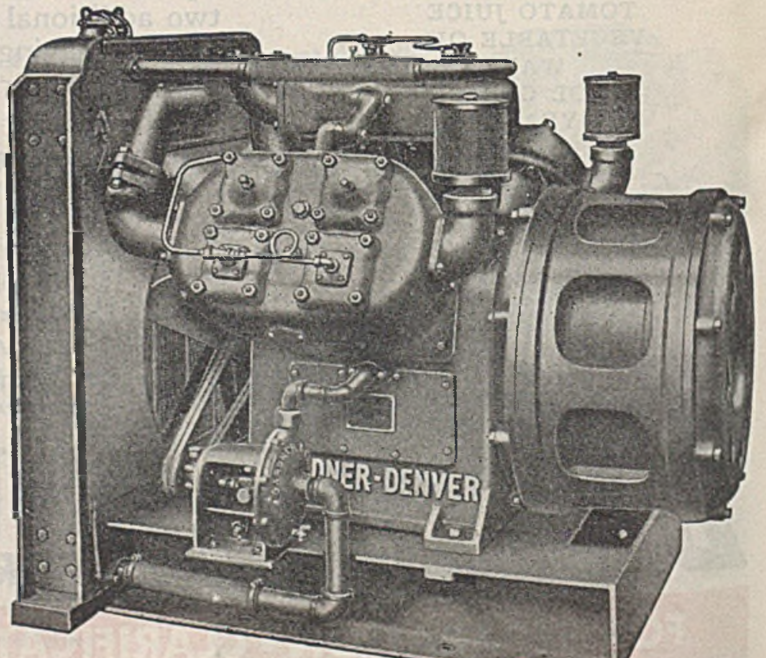
THE DE LAVAL SEPARATOR COMPANY
165 Broadway, New York 6 427 Randolph St., Chicago 6
DE LAVAL PACIFIC CO., 61 Beale St., San Francisco 19
THE DE LAVAL COMPANY, Limited
MONTREAL PETERBOROUGH WINNIPEG VANCOUVER

DE LAVAL CENTRIFUGAL MACHINES FOR PROCESSING SYSTEMS

FOR SEPARATION • CLARIFICATION • CONCENTRATION

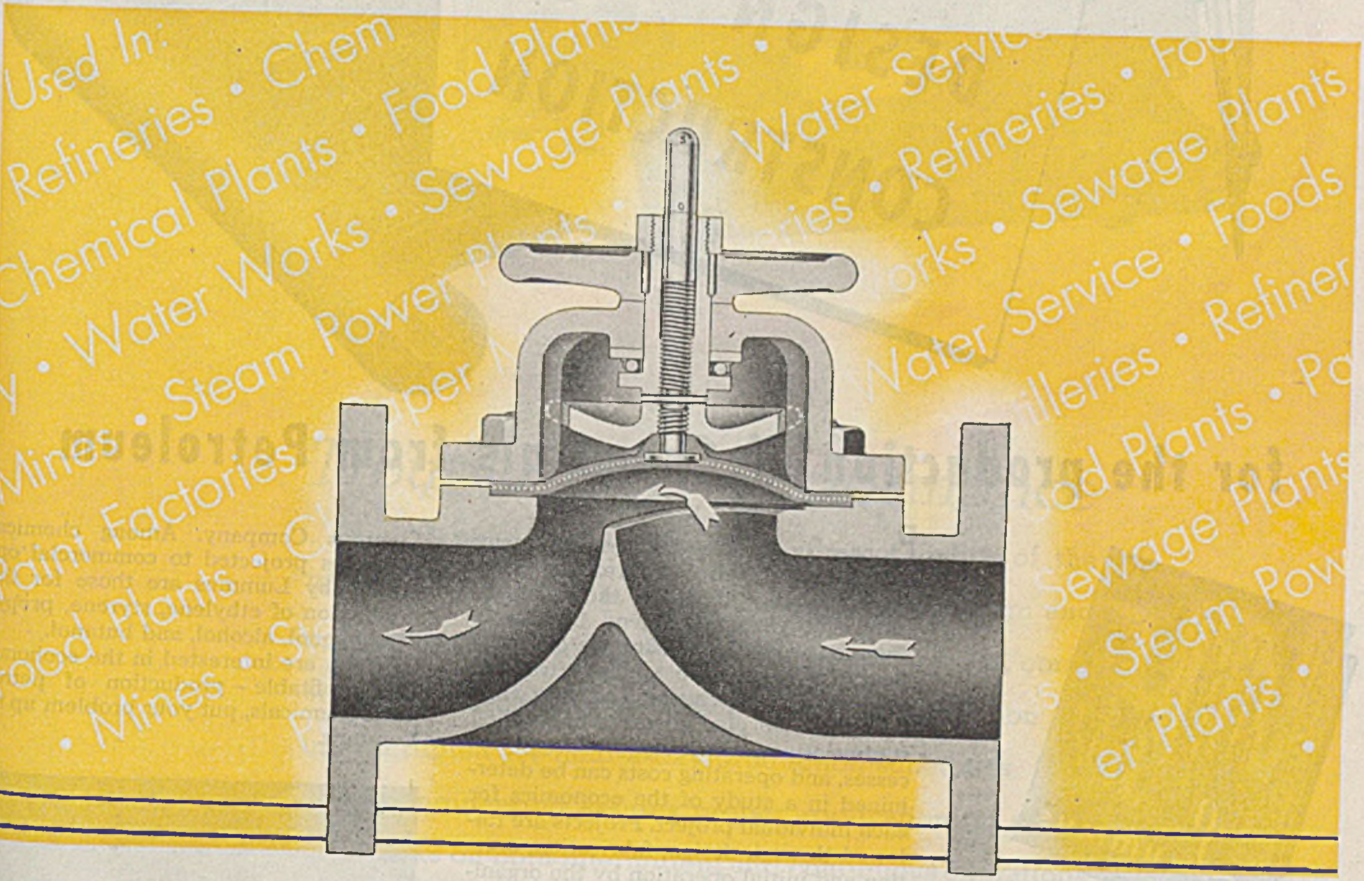



USE
COMPRESSED
AIR FOR
SAFETY
CONVENIENCE
FLEXIBILITY


NER-DENVER

NOW...A VALVE THAT LAUGHS AT CORROSIVES AND ABRASIVES

...and cannot LEAK, "FREEZE" or JAM!



McAlear No. M-1455 Diaphragm Valve

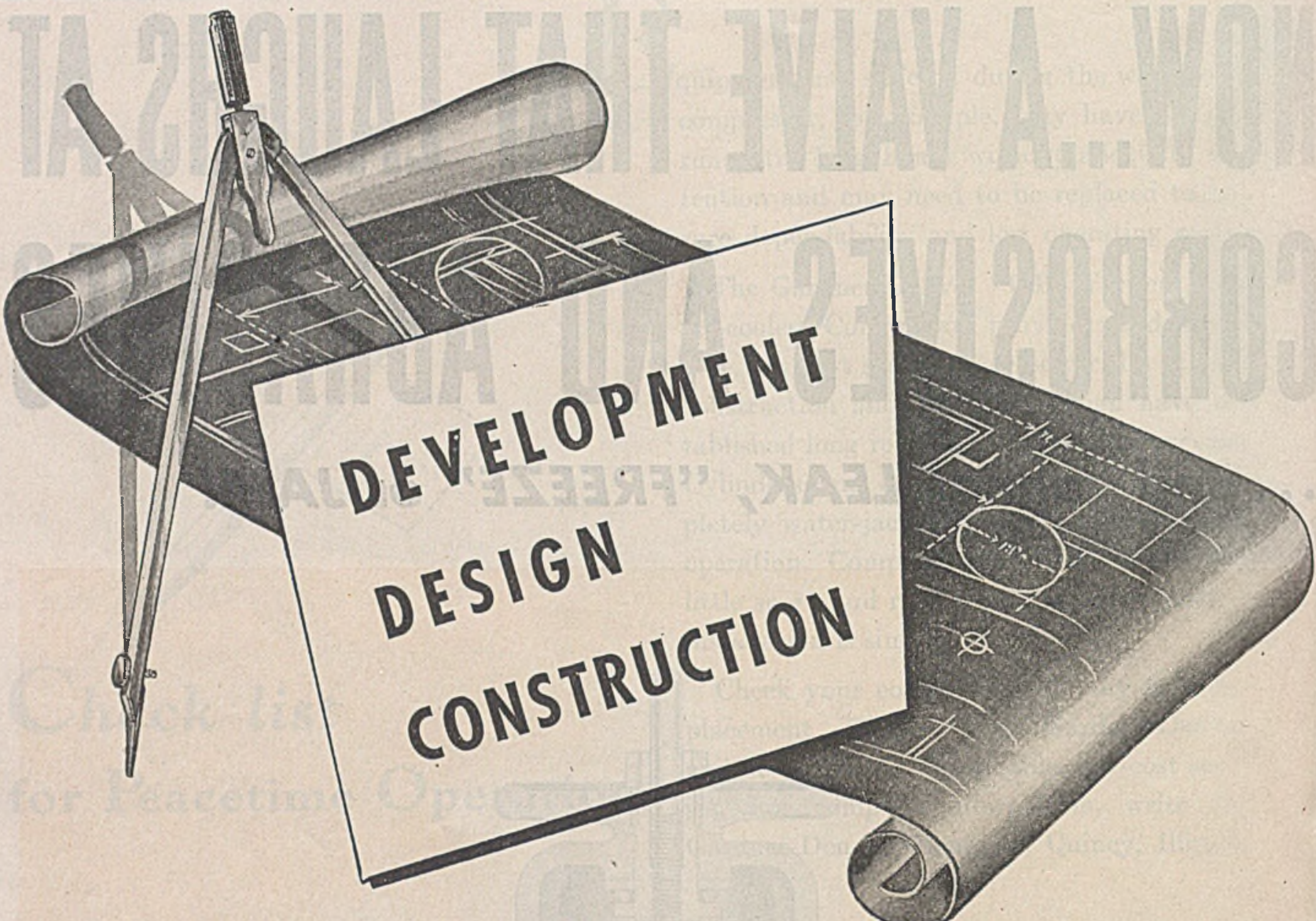
★ Pressures, Vacuum to 150 lbs. ★ Temperatures to 150° F. ★ Sizes ½" to 6".

- Applicable for air and water lines and special services.
- Used in *every* industry that handles corrosive or abrasive fluids.
- Diaphragm separates mechanism *completely* from fluids handled.
- Shut-off positive—even with solids trapped on seat.
- Closure not dependent on metal-to-etal contact.
- Cannot leak in any position.
- Requires no re-packing.
- Requires no re-seating.
- Diaphragm replaceable with valve in line.
- Special pressure operated types for automatic or pilot control.

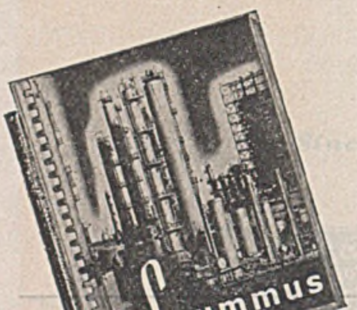
FOR BULLETIN giving complete data, write McAlear Manufacturing Company, Automatic Control Division of Climax Industries, 1925 S. Western Ave., Chicago 8, Illinois.

CLIMAX INDUSTRIES

McALEAR
PRESSURE · FLOW · LIQUID LEVEL · TEMPERATURE
controls
for STEAM, WATER, AIR, OIL and GAS



for the production of Chemicals from Petroleum

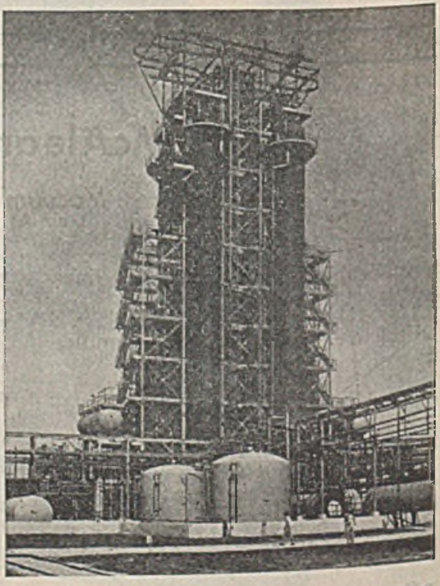


For further information on petroleum chemicals, send for a copy of the latest edition of "Petroleum Refining Processes;" 56 pages of data, flow sheets and photographs.

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 chemical processes projected to commercial operation by Lummus are those for the production of ethylene, styrene, propylene, phenol, alcohol, and butanol.

If you are interested in the economical — profitable — production of petroleum chemicals, put your problem up to 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.

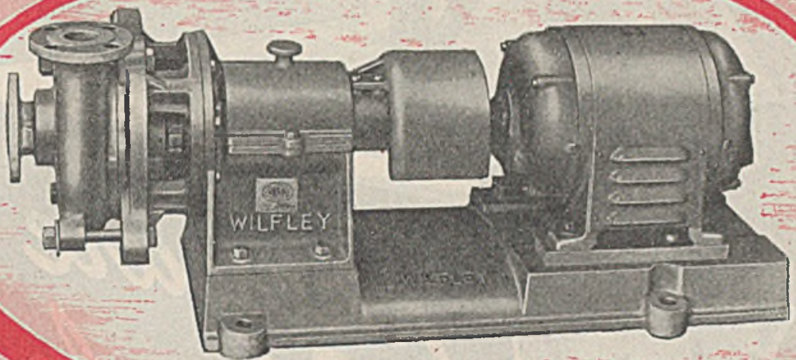
634 South Spring Street
Los Angeles 14, Calif.

Mellie Esperson Bldg.
Houston 2, Texas

78 Mount Street
London, W. 1. England

Lummus
PETROLEUM REFINING PLANTS

For Acids...



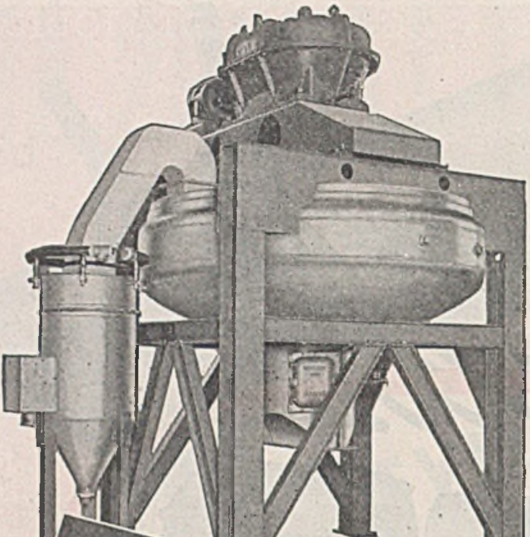
Trouble-Free Performance

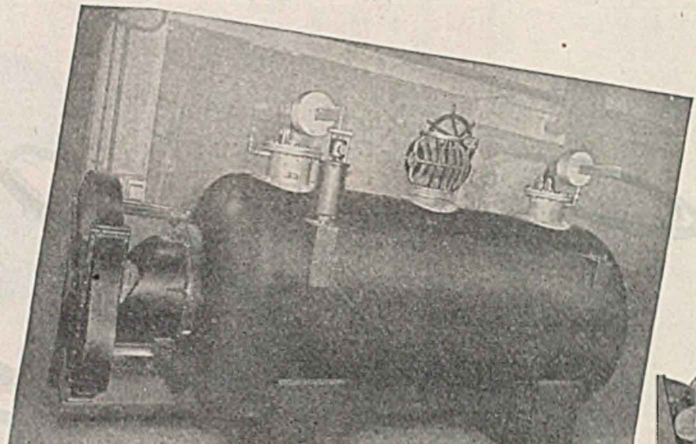
...and dependability are notable characteristics of the WILFLEY Acid Pump. Exclusive features of design and construction enable the WILFLEY to handle acids, corrosives, hot liquids, mild abrasives without attention on uninterrupted 24-hour-a-day production schedules. Individual engineering assures proper application on every job. Works on both intermittent and continuous operations. 10- to 2,000 G.P.M. capacities; 15- to 150-ft. heads and higher. It's the pump to buy when you want low costs. Write or wire for further details.

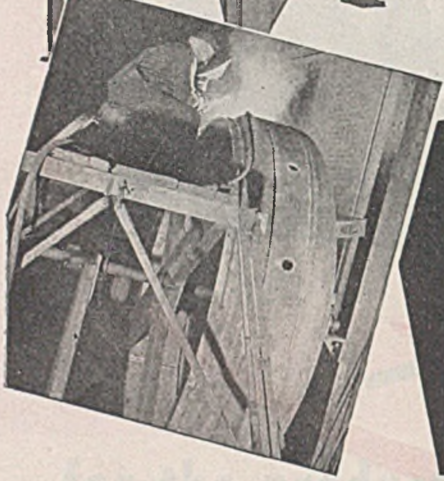
WILFLEY

centrifugal PUMPS

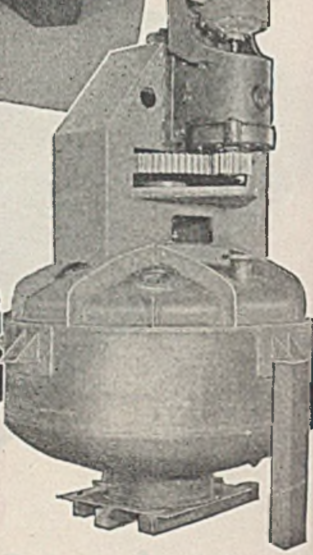
A. R. WILFLEY & SONS, INC., Denver, Colorado, U.S.A. New York Office: 1775 Broadway, New York City







Pressure Vessels...



TO MEET YOUR INDIVIDUAL REQUIREMENTS

● Typical of Bartlett-Snow construction is an Autoclave, pictured above, for conducting a pressure reaction at 150 P.S.I. gauge on 5 tons of material. This vessel, 8′ 0″ in diameter and 18′ 0″ long, is charged through a worm operated 12″ lubricated plug valve. Double screw-driven agitators stir the charge during treatment, and when completed, sweep the material through 16″ lubricated plug type discharge valves. The equipment, like all others of Bartlett-Snow construction, is built in accordance with A.S.M.E. Code for Unfired Pressure Vessels, and carries Hartford Steam Boiler Inspection & Insurance Company's certificate, and National Board approval and number.

Whether yours is a problem of catalyst crystallization, oxidation, or reduction . . . pressure reaction . . . or merely a simple drying, calcination, or heat treatment, call the Bartlett-Snow Heat Engineers. Their technical, mathematically exact approach to problems of surface evaporation or diffusion, corrosion, abrasion, dust condition, etc., and the skill of Bartlett-Snow welders who are qualified to weld pressure vessels conforming to A.S.M.E. Code for Unfired pressure Vessels U-68, U-69 and U-70, is your assurance that the equipment supplied will prove thoroughly suited to all phases of your requirement.

Our Bulletin No. 89—more than 50 pages—and profusely illustrated—contains much technical data on heat processing of interest to development and operating men. Send for a copy.

THE C. O. BARTLETT & SNOW CO.

6207 HARVARD AVENUE • CLEVELAND, OHIO

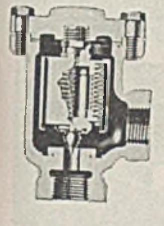
Engineering and Sales Representatives in Principal Cities

DRYERS • CALCINERS • KILNS • PRESSURE VESSELS

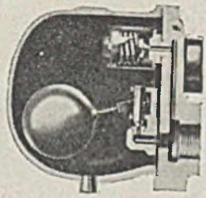
COMPLETE MATERIAL HANDLING FACILITIES TO MEET ANY REQUIREMENT
ONE CONTRACT • ONE GUARANTEE OF SATISFACTORY PERFORMANCE • UNIT RESPONSIBILITY

WHEN YOU SEE - THIS

SOMEBODY LOSES—THREE WAYS



No. 9-100 thermostatic steam trap



Float-thermostatic steam trap

It's an innocent looking little stream of water, sometimes with a lot of vapor and at others quite cold. But it runs all day, and there are a score or more places in your plant where this is taking place, although most of them are not visible.

Occasionally an operator will do something about it but mostly it runs merrily on, wasting heat or cooling water—and indicating a loss in productive capacity.

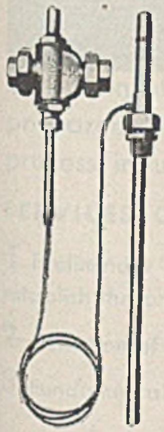
YOU DON'T HAVE TO PUT UP WITH IT

In a few hours and at a cost that will soon be forgotten, you can connect one or more of the Sarco products shown at the left. From then on, winter and summer, noon or midnight, there will be no wasted heat or water; no lost production.

YOUR PRODUCT WILL BE IMPROVED

Whether it's heating, cooking, drying, cooling or refrigeration, both the *quantity* and the *quality* of the product will be improved because the temperature is always at its best.

The Sarco representative near you can tell you how.



TR-21 Temperature Control

TR-52R Temperature Control

Water Blender

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

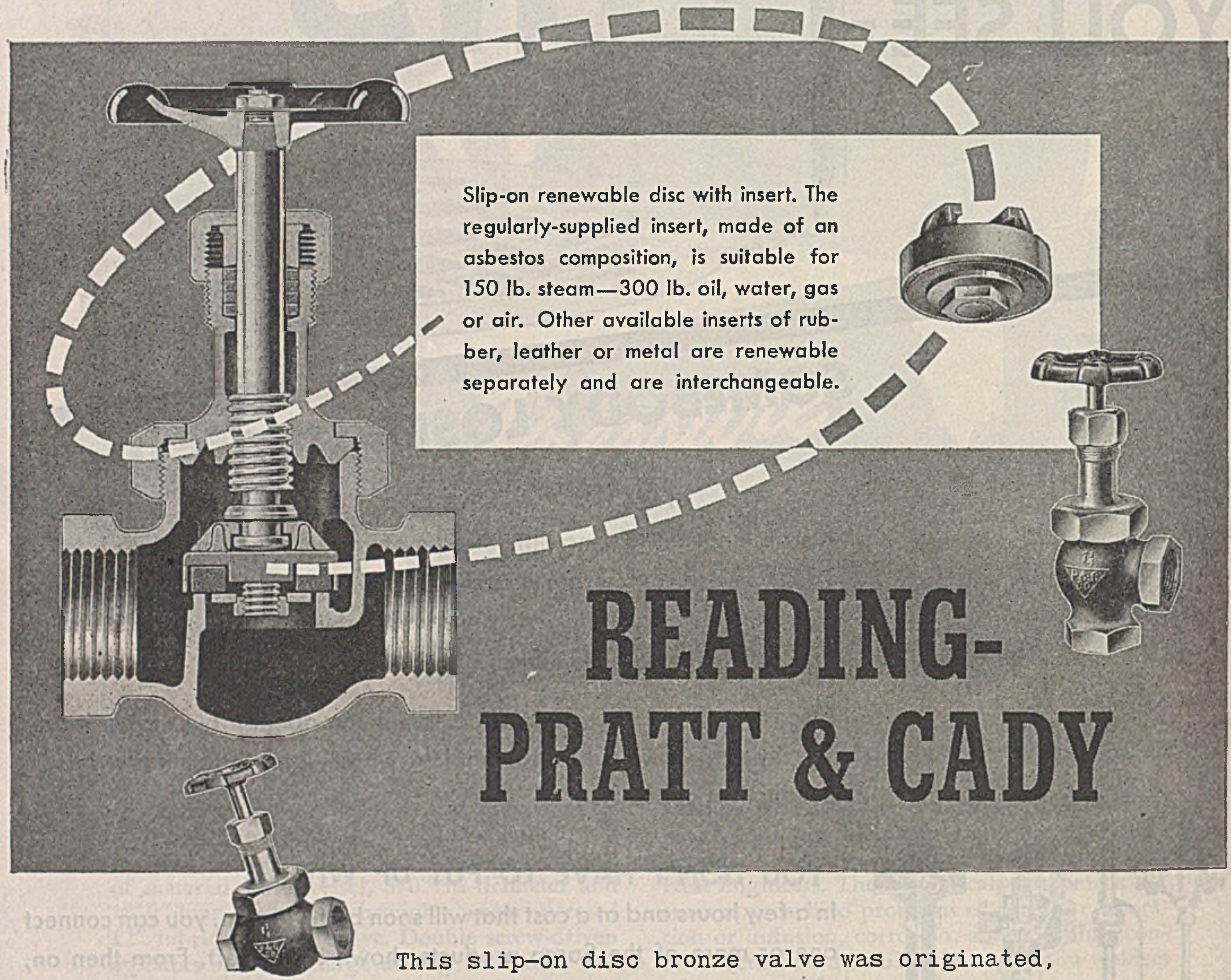
SARCO SAVES STEAM

Represented in Principal Cities

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

Dependable • • Long-lasting • • Versatile

GLOBE and ANGLE Valves



Slip-on renewable disc with insert. The regularly-supplied insert, made of an asbestos composition, is suitable for 150 lb. steam—300 lb. oil, water, gas or air. Other available inserts of rubber, leather or metal are renewable separately and are interchangeable.

READING-PRATT & CADY

This slip-on disc bronze valve was originated, developed and improved by Reading-Pratt & Cady. Essential to fullest performance are disc guides, cast in the bodies and machined, which extend down to the body seats. This is a versatile valve because a soft disc insert gives a tight closure in a globe type valve, basically a throttling type.

Reading-Pratt & Cady distributors are located in principal cities.

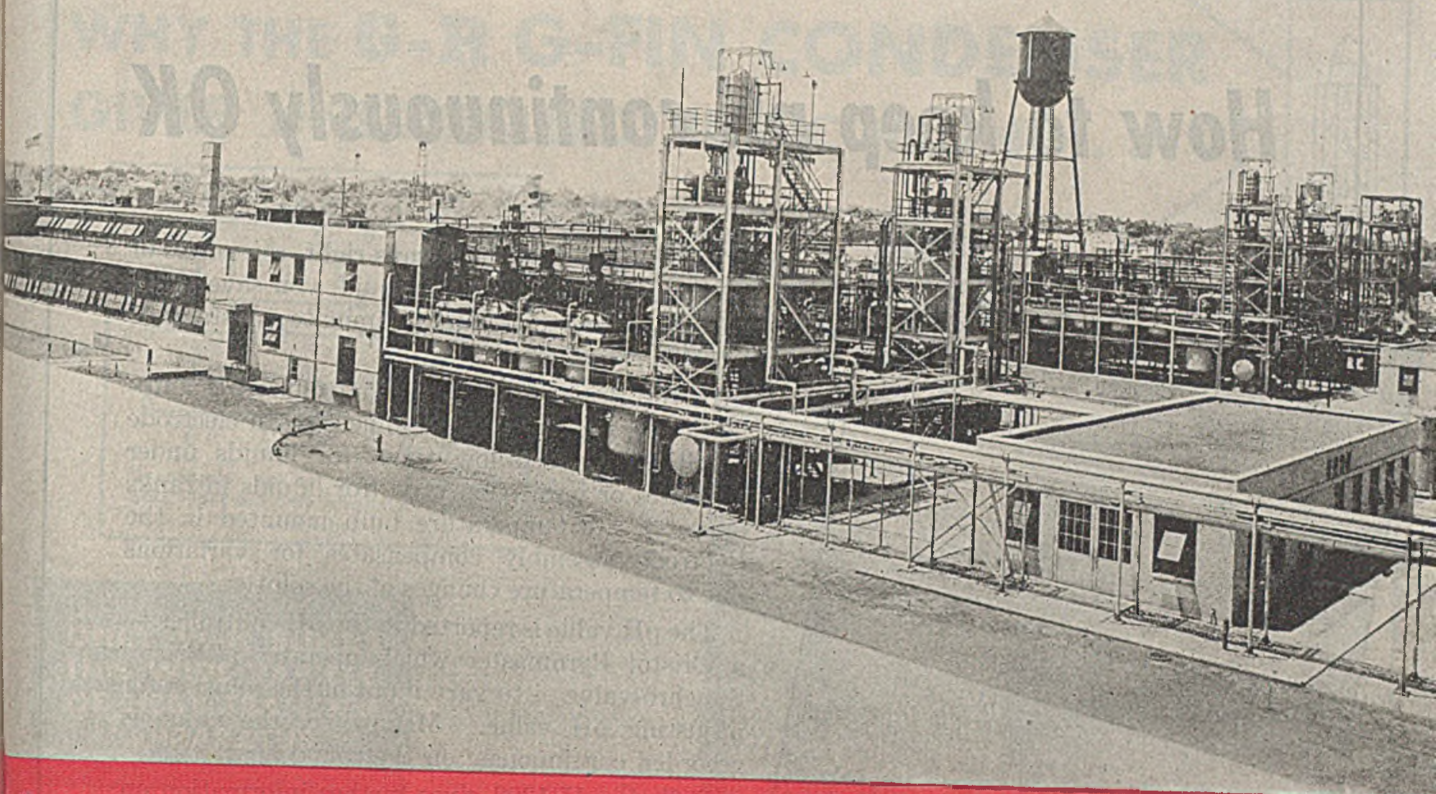
Reading Cast Steel Valves and Fittings • Pratt & Cady Brass and Iron Valves
d'Este Automatic Regulating Valves

ACCO

Reading, Pa. • Atlanta • Chicago • Denver • Detroit • Houston • Los Angeles • New York • Philadelphia • Pittsburgh • Portland, Ore. • San Francisco • Bridgeport, Conn.

READING-PRATT & CADY DIVISION
AMERICAN CHAIN & CABLE

TRADE



PROCESS PLANTS BUILT TO ORDER

From your idea to production—from process determination and assembling of basic data to operation of the completed plant—Blaw-Knox is prepared to carry projects for the chemical process industries *through to completion.*

SERVICES OFFERED:

1 Preliminary design study based on available data to establish the process requirements and economics.

2 Selection of processing methods.

3 Fundamental engineering: preparation of flow sheets, layouts, sizing of units, material and utility balances, and cost estimates.

4 Detail engineering: design and specification of process vessels, mechanical equipment, piping, instruments, electrification, and structures.

5 Fabrication, procurement, expediting, and inspection of process equipment and materials.

6 Plan for execution of the project which includes schedules for completion of engineering, procurement, and construction.

7 Plant construction including preparation of the site, establishment of necessary construction facilities, erection of structures, installation of equipment, piping, instruments, lighting and power.

8 Initial operation, test runs, and training of operating personnel.

Here is a unified responsibility, covering a full range of services, ready to work for you.

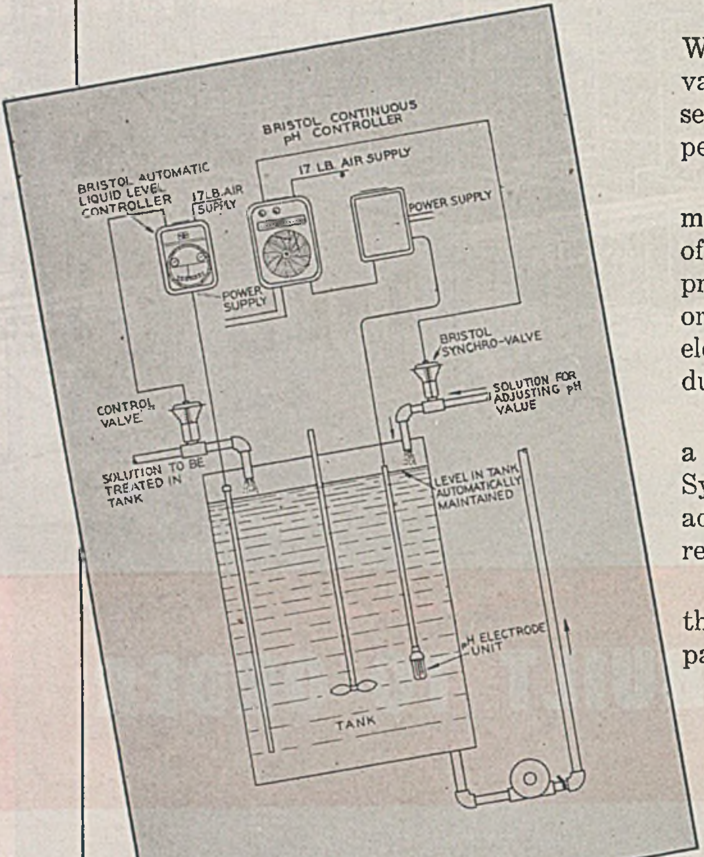
KNOW BLAW-KNOX responsibility

BLAW-KNOX DIVISION of Blaw-Knox Company 2081 Farmers Bank Bldg., Pittsburgh 22, Pennsylvania
NEW YORK • CHICAGO • PHILADELPHIA • BIRMINGHAM • WASHINGTON

BLAW-KNOX *IMPLEMENTS*
THE PROCESS INDUSTRIES

Seven Blaw-Knox plants have been awarded

How to keep pH continuously OK



When you know pH is always right, regardless of variables affecting process liquid, you save yourself worry and can safely eliminate constant or periodic attention.

In the Bristol method of controlling pH automatically, the liquid is examined by an electrode of either enclosed-flow type (for liquids under pressure) or immersion type (for liquids in tanks or vats). A temperature bulb mounted in the electrode assembly compensates for variations due to temperature changes of the solution.

The pH value is reported to the pH controller — a Bristol Pyromaster which operates a Bristol Synchro-valve — to vary input of the solution for adjusting pH value. Meanwhile, the value is recorded continuously on the round chart.

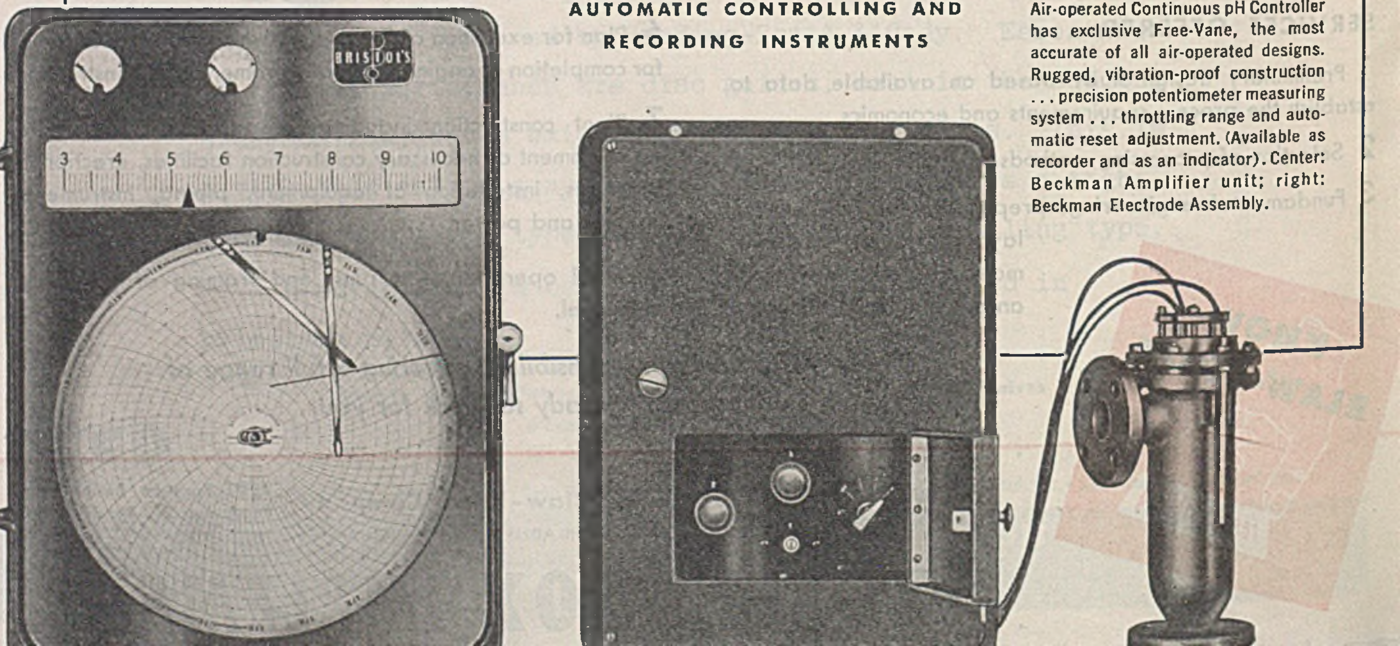
Bulletin pH 1302 gives further information on the complete system. Address The Bristol Company, 110 Bristol Road, Waterbury 91, Conn.

BRISTOL

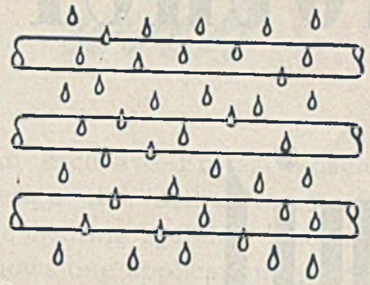
Engineers process control for better products and profits

AUTOMATIC CONTROLLING AND
RECORDING INSTRUMENTS

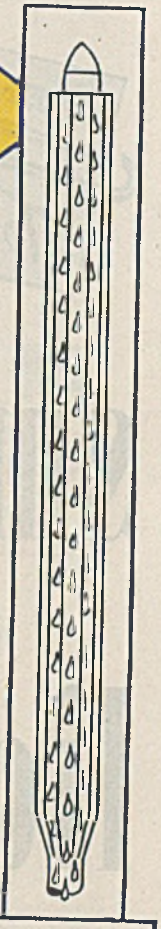
Air-operated Continuous pH Controller has exclusive Free-Vane, the most accurate of all air-operated designs. Rugged, vibration-proof construction . . . precision potentiometer measuring system . . . throttling range and automatic reset adjustment. (Available as recorder and as an indicator). Center: Beckman Amplifier unit; right: Beckman Electrode Assembly.



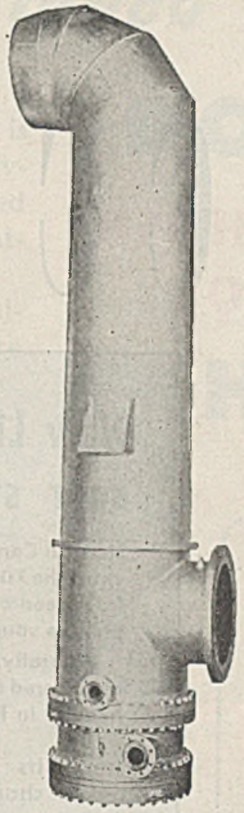
WHY THE G-R G-FIN CONDENSER GIVES UNEQUALLED SUB-COOLING . . .

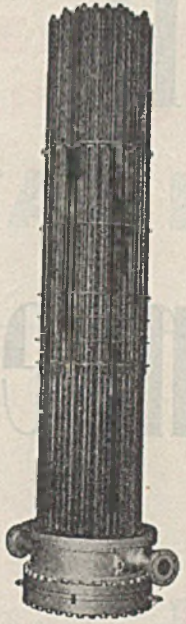


Condensate falling over horizontal bare tubes has only momentary contact with tubes



Condensate falling over vertical G-Fin tubes in constant contact with entire length of pipe





In conventional types of horizontal bare-tube condensers, the condensate, in dropping down over the tubes, is in contact with each tube for only a brief period. As a result, the condensate receives little sub-cooling effect, and some may even be re-vaporized.

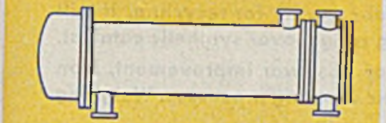
Compare with the G-R G-Fin Condenser. Here, the condensate which forms on the longitudinal fins is guided downward as it hugs the tube surface throughout the entire length of fins and tube—sometimes 20 feet or more in length.

This explains why the G-R G-Fin Vertical Condenser is so far superior to multiple shell horizontal bare tube condensers, and is one of the many reasons why this unit provides better condensing and sub-cooling results at lower cost than any other design.

Write for Bulletin 1625 explaining in detail the exclusive advantages of this unit and the other G-R finned-tube apparatus available for practically every heat transfer service.

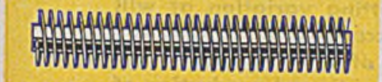
THE GRISCOM-RUSSELL CO.
285 Madison Ave. New York 17, N. Y.

ONLY G-R BUILDS THIS WIDE VARIETY OF HEAT TRANSFER APPARATUS

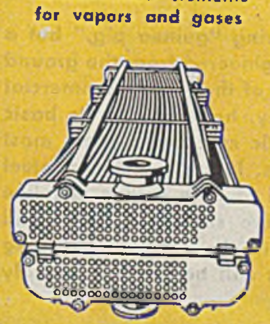


SHELL and BARE TUBE
Heaters, Coolers, Condensers, Heat Exchangers

G-FIN
Longitudinal-finned elements for greater heat conductivity



K-FIN
Helical-finned elements for vapors and gases



BENTUBE EVAPORATOR
Scale-shedding Elements

TUBEFLO SECTIONS
Non-clogging design for residuum and other dirty fluids

GRISCOM-RUSSELL

Pioneers in Heat Transfer Apparatus

MEMO:
To small refiners

...another small T C C unit licensed by Houdry!

New Lion unit will process wide-cut sour stocks over synthetic catalyst

Lion Oil Company, of El Dorado, Arkansas, has contracted to construct the 70th Houdry-licensed cat-cracker, a TCC unit of 4500 bbl. fresh-feed capacity, with additional capacity for recycling. It will process sour stocks of wide boiling range, over synthetic catalyst.

Naturally, in planning this major post-war improvement, Lion considered the merits of all catalytic cracking processes. Weighing heavily in favor of TCC were:

- its demonstrated ability to handle heaviest charging stocks;
- the extremely small additional capital required for corrosion protection, assuring maximum profit from the processing of low-cost, high-sulfur crudes;
- built-in recycling, permitting variation at will of product distribution according to seasonal demands—optimum yields of motor gasoline for the warmer months, proportioned production of distillate heating oil for winter.

The small TCC unit is not an engineering "guinea pig," but a well-proved design which has been engineered from the ground up, with the same basic design features of the larger commercial TCC plants. Economics, not expediency, have guided its basic planning—have made TCC the catalytic cracking process most favored by operators of small refineries. In cost per ton of steel used in construction, in cost per barrel of high-octane gasoline produced and by other equally decisive standards, the small TCC unit will compare favorably with the catalytic cracking operations of major companies. Details will be furnished gladly to interested refiners.

HOUDRY PROCESS CORPORATION
WILMINGTON, DEL.
New York Office: 115 Broadway, New York 6

Houdry Catalytic Processes and the TCC Process are available through the following authorized firms:

E. B. BADGER & SONS CO.
Boston, Massachusetts

THE LUMMUS COMPANY
New York City, New York

BECHTEL-McCONE CORP.
Los Angeles, Calif.

HOUDRY
CATALYTIC
PROCESSES

Drying Processes

with FW designed

DOWTHERM

HIGH-TEMPERATURE LOW-PRESSURE

HEATING

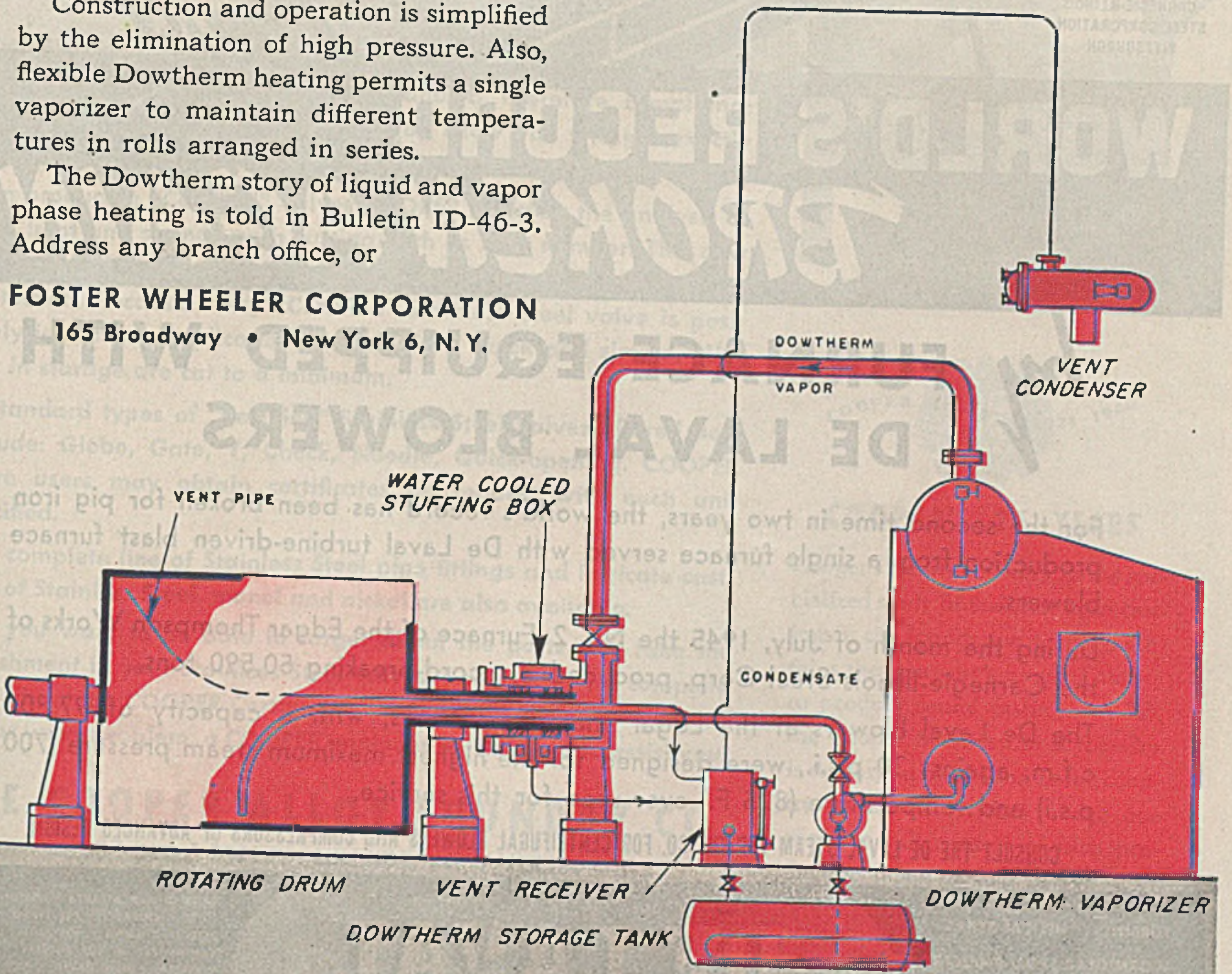
An exclusive Foster Wheeler service is design—then manufacture—of special-service heating systems. The unit illustrated shows one application of Dowtherm heating to drying rolls.

Dowtherm heating gives the unparalleled advantages of high temperature *without* high pressure. At 500 deg. F. these systems operate at atmospheric pressure, show only moderately increasing pressure up to 700 deg. F.

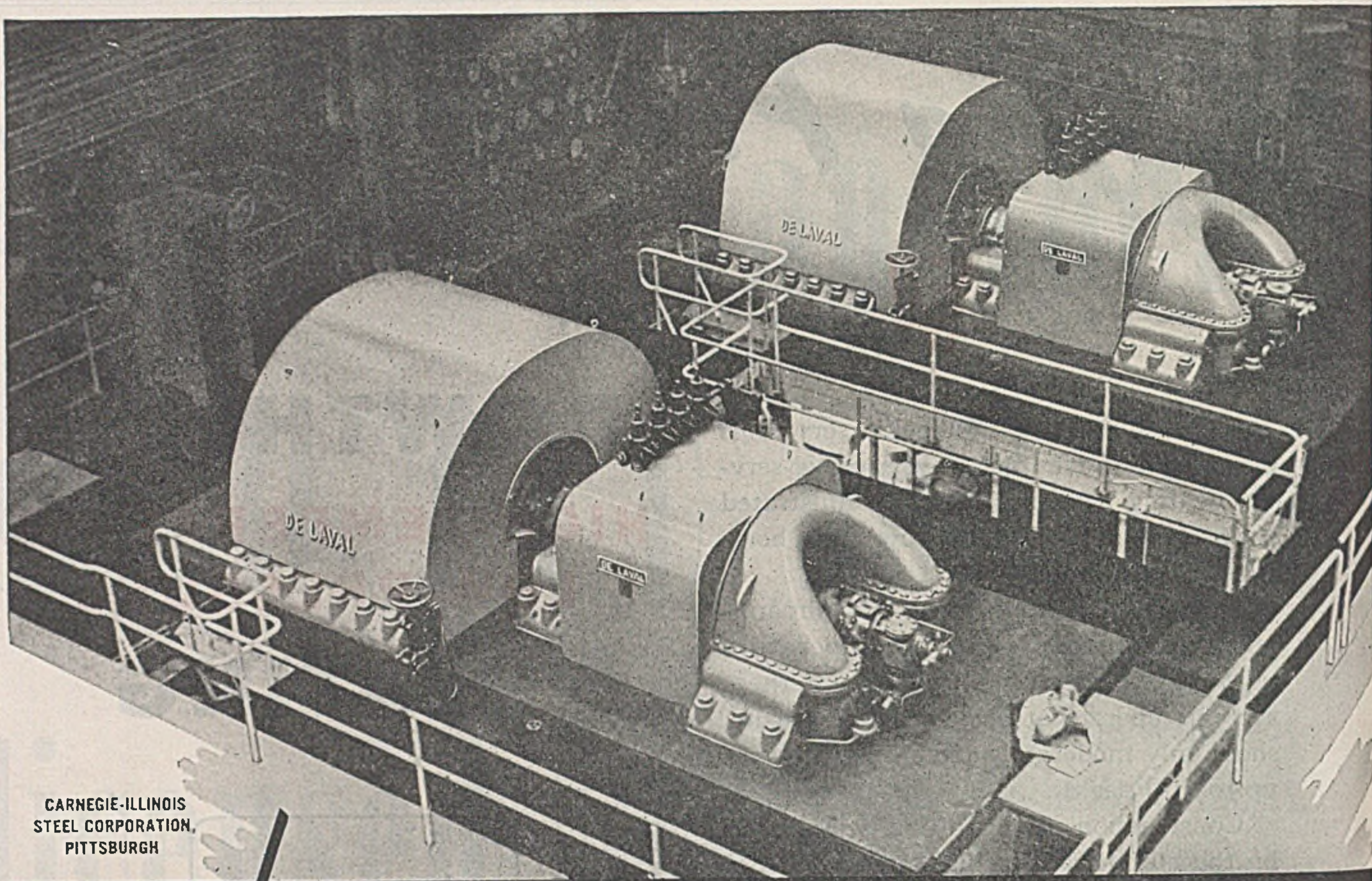
Construction and operation is simplified by the elimination of high pressure. Also, flexible Dowtherm heating permits a single vaporizer to maintain different temperatures in rolls arranged in series.

The Dowtherm story of liquid and vapor phase heating is told in Bulletin ID-46-3. Address any branch office, or

FOSTER WHEELER CORPORATION
165 Broadway • New York 6, N. Y.



FOSTER FW WHEELER


DE LAVAL
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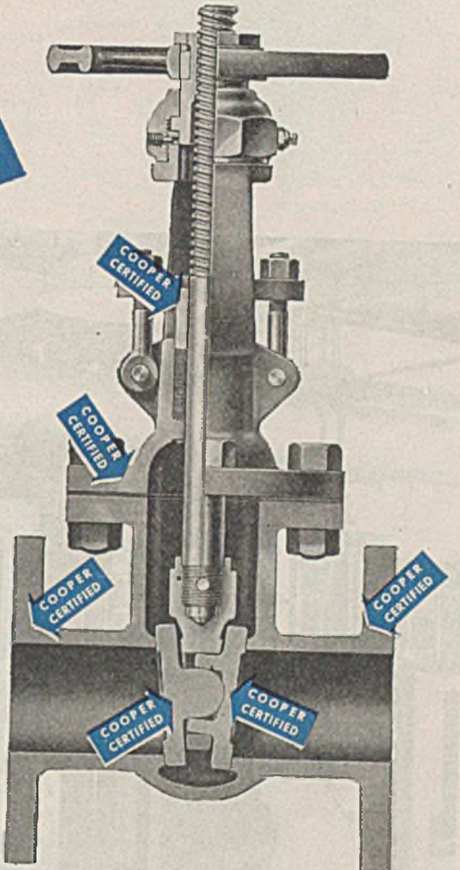
CARNEGIE-ILLINOIS
STEEL CORPORATION,
PITTSBURGH


COOPER CERTIFIED
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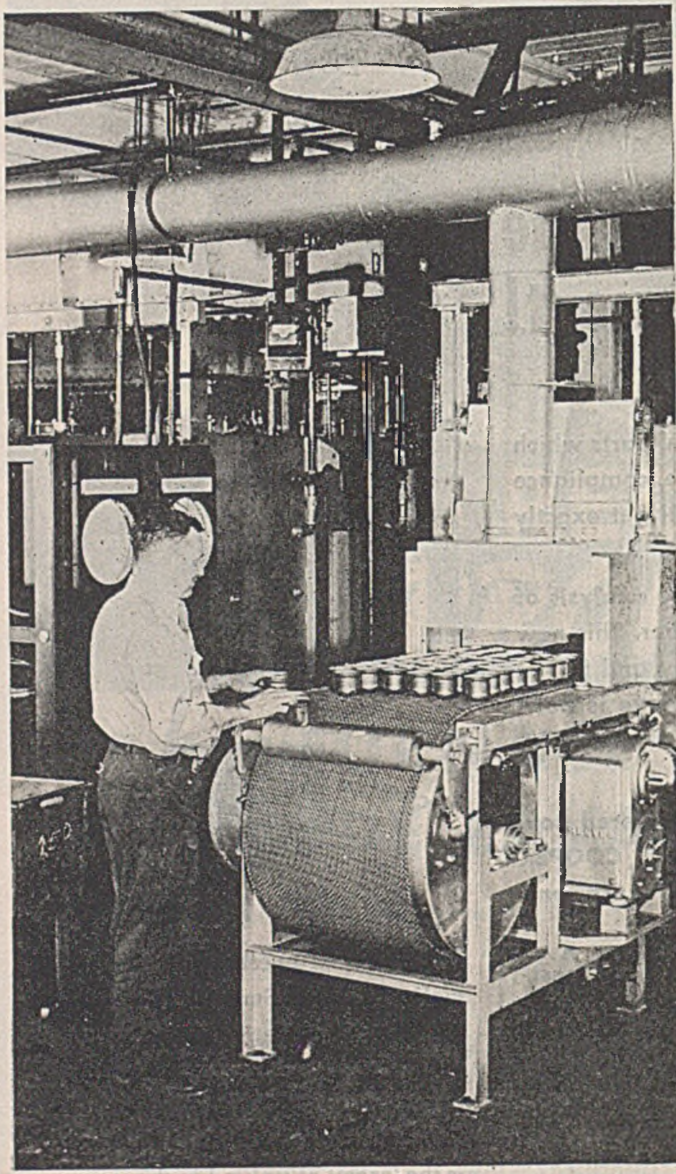
Wickwire belts handle HOT and HEAVY LOADS



Photograph Courtesy of Westinghouse Electric Corp.

Greater production—lower handling costs—more uniform quality—are a few of many reasons why Wickwire Spencer Metal Conveyor Belts are used by industry for a wide range of applications.

One such application—the bright annealing of metal parts—is shown at left. This belt, designed for operation at 1700° F., is of No. 14 gauge, 3 mesh, rod reinforced every spiral. Rod reinforcement prevents contraction in width; minimizes stretch and permits handling of heavier loads at high temperatures.

Because all Wickwire Belts are custom-engineered, you may be assured of long, dependable service. They are the accepted standard for heat treatment of metals, glass and ceramic ware, and for the processing of foods, chemicals and other materials. Belts are fabricated of any metal or alloy capable of being drawn into wire—in any length—in widths from 1" to 192"—to operate at temperatures as low as −40° F. or as high as 2100° F., and to resist corrosion, abrasion and other destructive forces.

Send for our profusely illustrated catalog showing types and advantages of numerous conveyor belt constructions. Address Mechanical Specialties Department, Wickwire Spencer Steel, Sterling St., Clinton, Mass.

WICKWIRE SPENCER METAL CONVEYOR BELTS ARE BEING USED IN

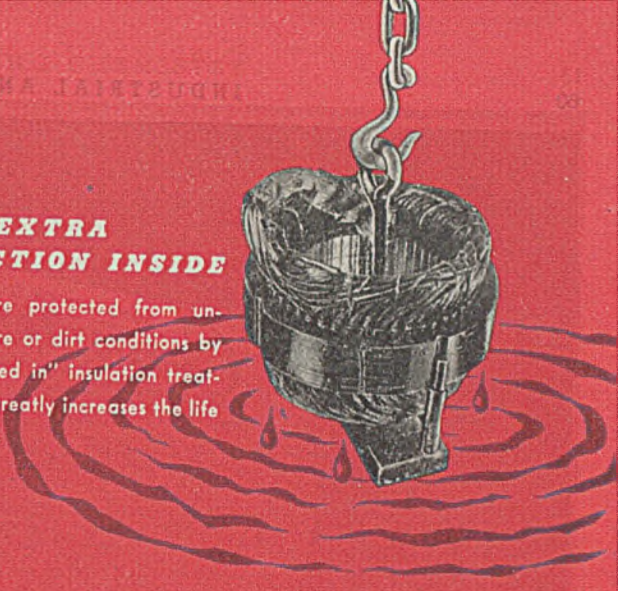
Annealing Ovens
Baking Ovens
Brazing Furnaces
Chemical Processing
Decorating Glass
Ceramic Products
Canning
Dehydrating Food
Degreasing
Frozen Foods
Hardening Furnaces
Infra-Red Drying

WICKWIRE SPENCER Steel

A DIVISION OF THE COLORADO FUEL AND IRON CORPORATION
EXECUTIVE OFFICES—500 FIFTH AVENUE, NEW YORK 18, N. Y.
Abilene (Tex.) • Boston • Buffalo • Chattanooga • Chicago • Clinton (Mass.)

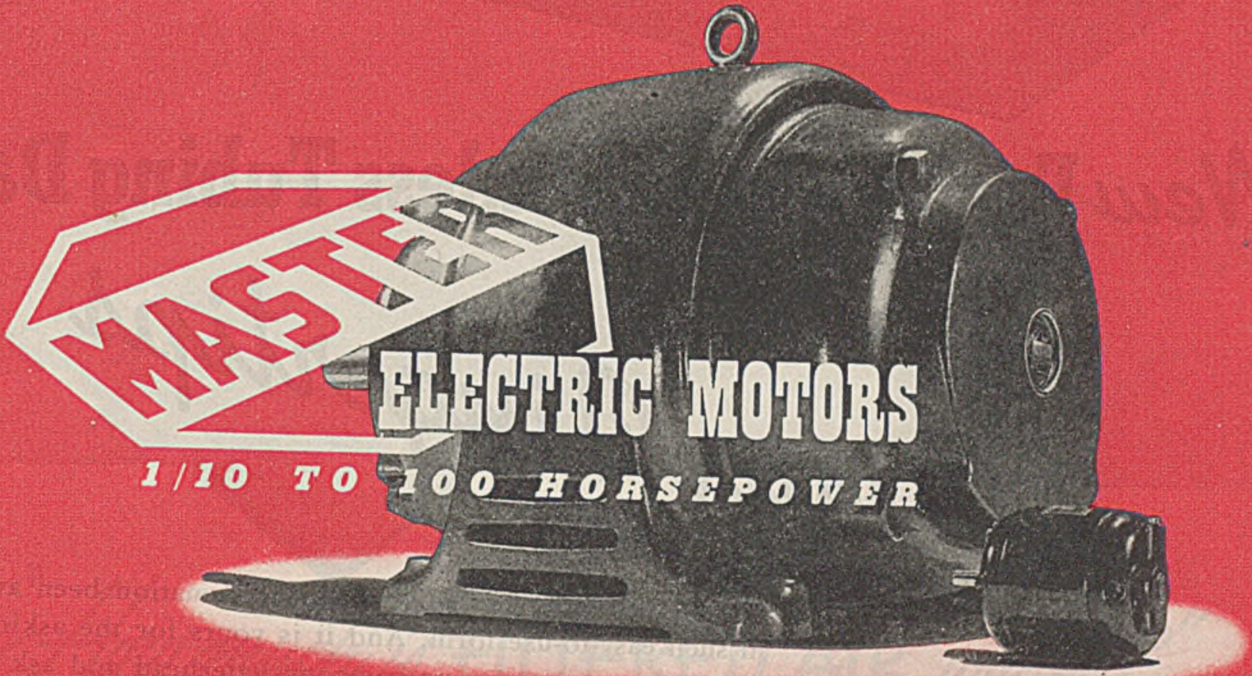
TRA PROTECTION OUTSIDE

cast iron frame and end shields are so constructed that
internal working parts of the motor are fully protected
n falling dirt or dripping liquids.



EXTRA PROTECTION INSIDE

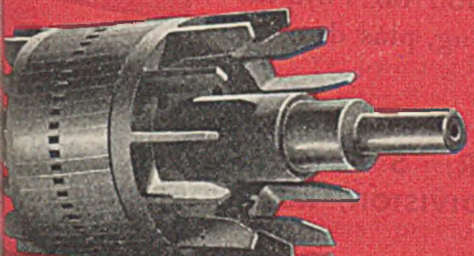
Windings are protected from unusual moisture or dirt conditions by special "baked in" insulation treatment which greatly increases the life of the motor.



ELECTRIC MOTORS

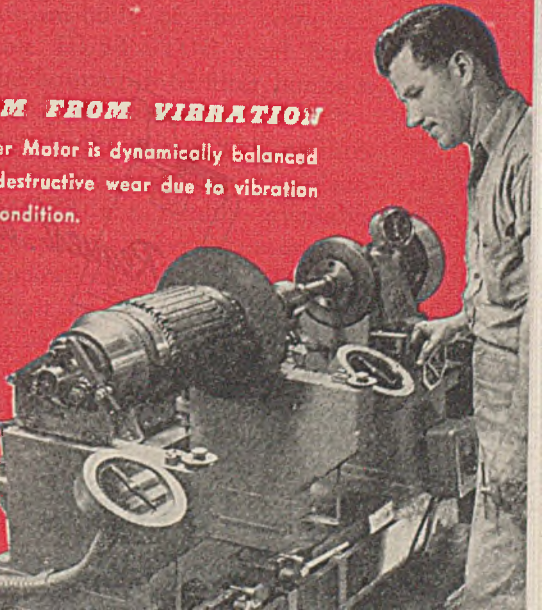
1/10 TO 100 HORSEPOWER

THE MASTER ELECTRIC COMPANY • DAYTON, OHIO



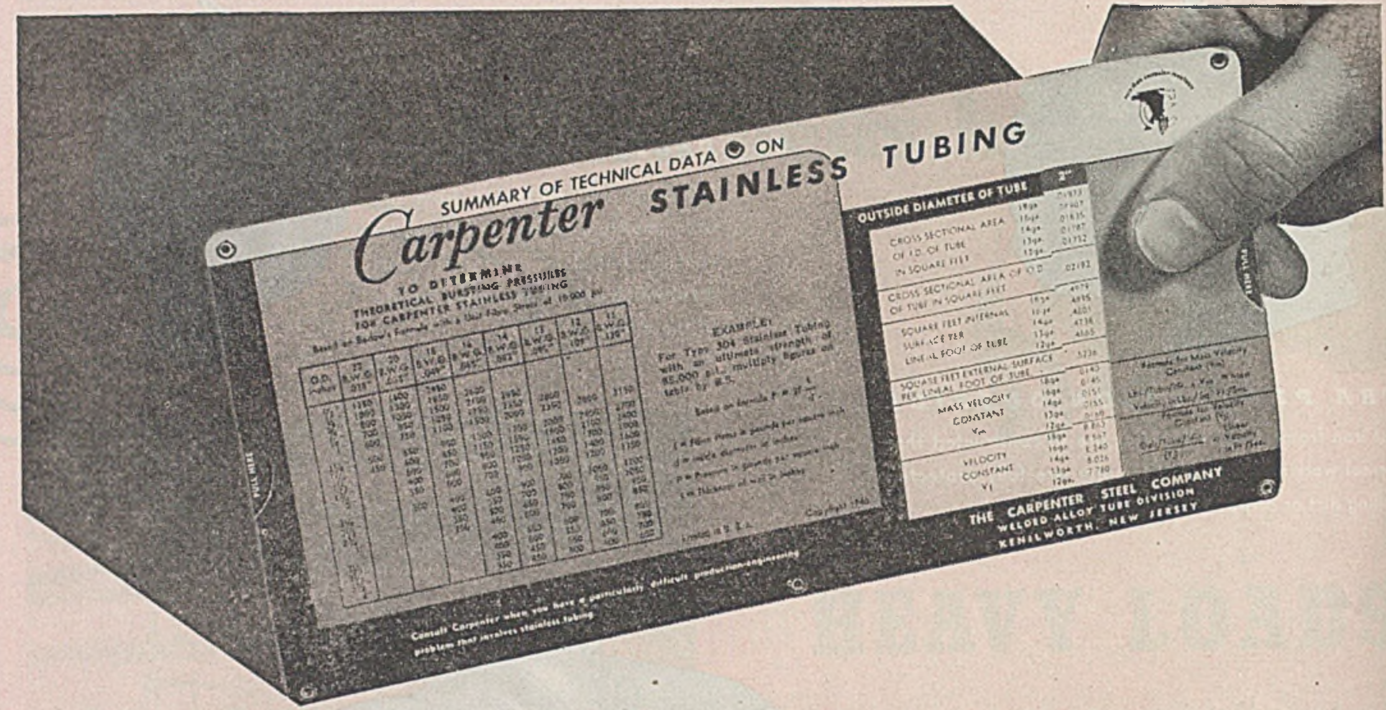
EXTRA FREEDOM FROM VIBRATION

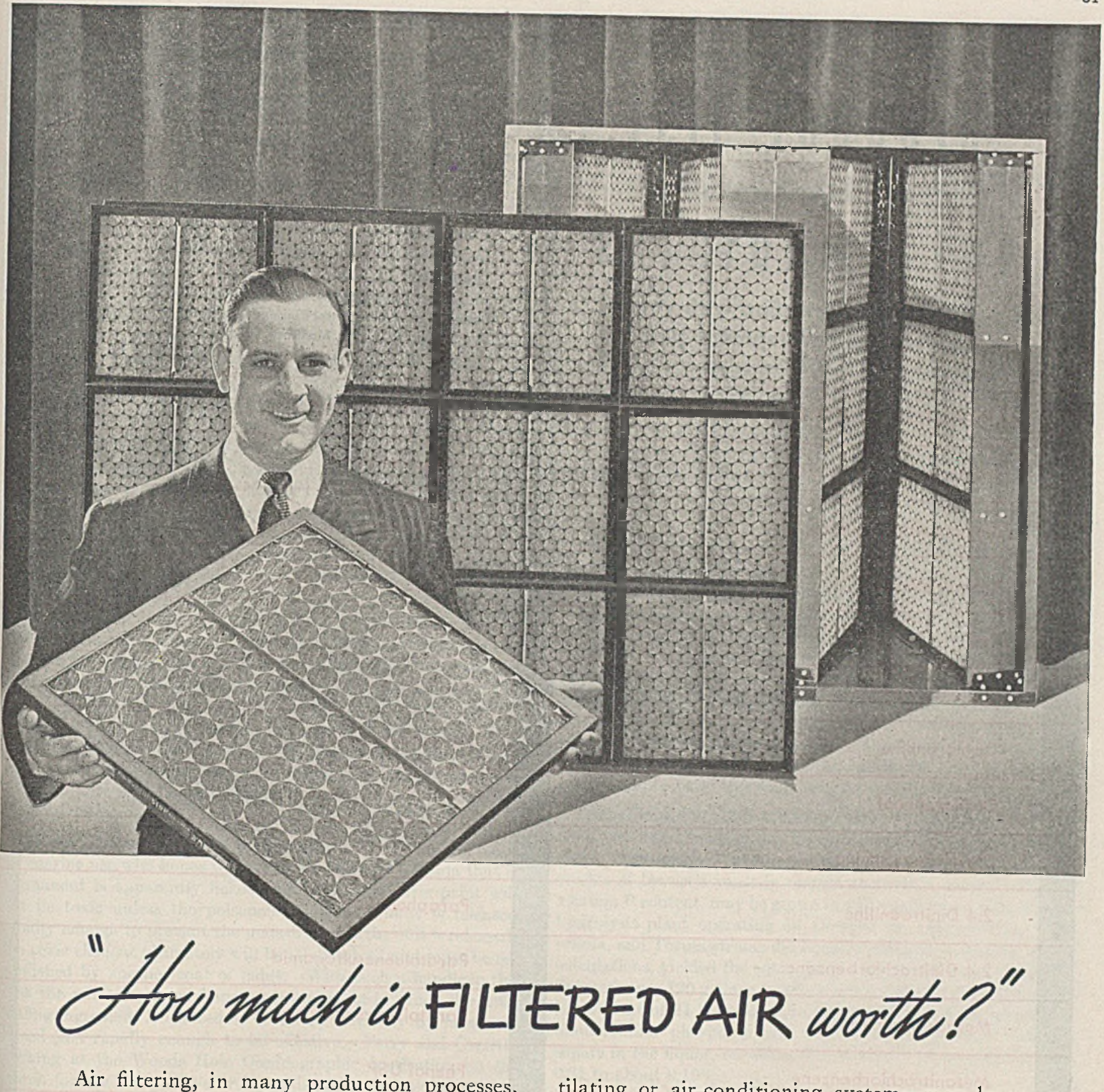
The rotor of every Master Motor is dynamically balanced to eliminate noise and destructive wear due to vibration from an out-of-balance condition.



RA RUGGED CONSTRUCTION

lly heavy alloy steel shafts and oversize bear-
dd greatly to the durability of Master Motors.
irrel Cage motors the rotor windings are cast
l with the rotor laminations.


SUMMARY OF TECHNICAL DATA ON
Carpenter STAINLESS TUBING
TO DETERMINE THEORETICAL BURSTING PRESSURES FOR CARPENTER STAINLESS TUBING
OUTSIDE DIAMETER OF TUBE
MASS VELOCITY CONSTANT
VELOCITY CONSTANT
THE CARPENTER STEEL COMPANY
WELDED ALLOY TUBE DIVISION
KENILWORTH, NEW JERSEY



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- Ortho-Aminobiphenyl Technical
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- Phenol USP
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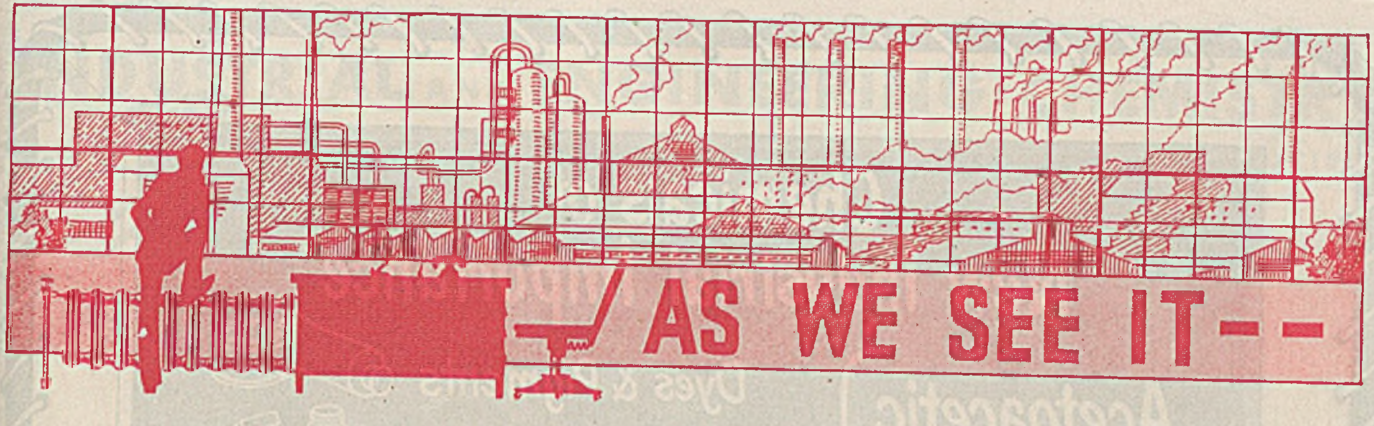


AS WE SEE IT--

Filtration Theory and Practice. Our lead-off article this month is a significant paper dealing with the mechanism of the important unit operation of filtration. Its author is B. F. Ruth, formerly at the University of Minnesota, now at Iowa State College. He has done outstanding work in this field, and his previously published work has attracted widespread attention. In this latest contribution, Carman's application of the Kozeny equation to filtration is extended and correlated to experimental results through the development of a theory of unused void volume. By this theory Ruth accounts for the actual specific filtration resistance of finely divided solids, which is higher than can be reconciled with the Kozeny equation. He describes a method for determining the unused-void factor, by permeability *vs.* mechanical compression tests on the solids to be filtered, for the practical man desiring to apply his theoretical development to actual filtration problems. The article is an unexpected dividend from our original plans for a section of filtration in the January, 1946, reviews on Unit Operations. The paper turned out to be more than just a review of a unit operation. We believe the literature has gained distinctly as a consequence, and feel quite proud of our indirect and modest part in stimulating its publication.

Deadly Compromise. The compounder of an antifouling paint for marine use who hopes to develop an effective formula that is permanent is apparently licked from the start. His paint will not be toxic unless the poisonous ingredient in it is released rapidly enough to prevent the undesired growth; if it is released, the toxic element ultimately will be all dissolved and must be replenished by another coat of paint. With such a handicap the best the paint man can hope for is a product in which the antifouling ingredient is utilized at optimum efficiency by being released just rapidly enough to be effective. Ferry and Carritt, working at the Woods Hole Oceanographic Institution on research for the Navy, have broken this rather complex situation into its elements in an organized study of the solubilities of various toxic materials commonly used in marine paints. In this first paper of a series, they record the results of that portion of their work dealing with the solubility and solution rates of cuprous oxide, a commonly used antifouling agent.

Pack-Horse Plant. The economics of transportation often makes or breaks an otherwise promising process. Many a raw material that is of good grade but occurs in widely scattered locations remains untouched because a prohibitive cost is required to collect it for treatment in a conventional large central processing plant. Low grade materials suffer the same handicap when the processing plant is some distance away. The rather unusual approach described, starting on page 576, in solving successfully a problem of this category may contain fruitful hints for the solution of other similar ones.

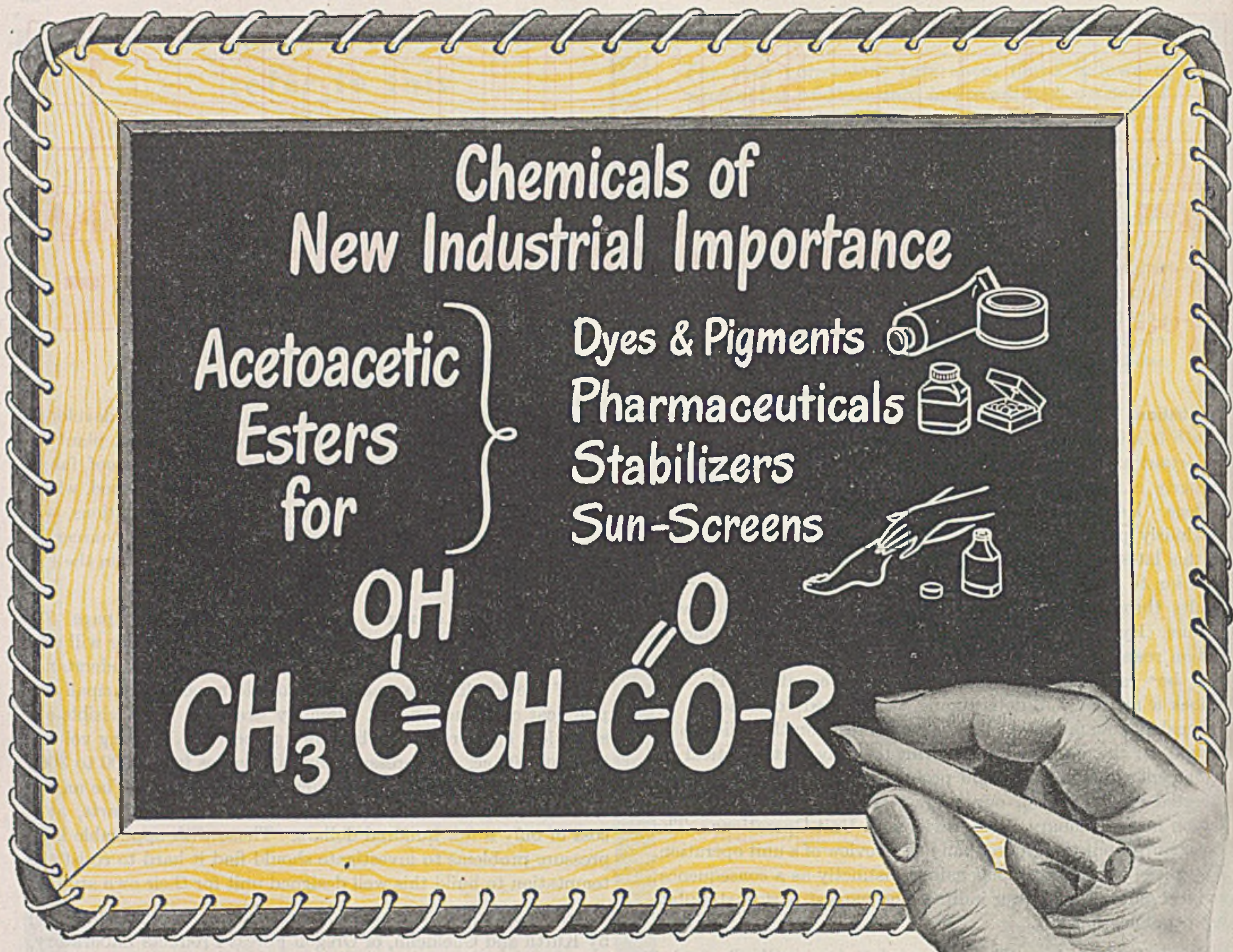
Necessity was the demanding mother of the field unit, invented at the Engineer Board's laboratory, Fort Belvoir, Va., and described by Applezweig and Ronzone for extraction of quinine from the low grade cinchona barks of South America. The process utilizes an ion exchange medium to capture and concentrate the alkaloid extract; the latter is recovered and the adsorbent is regenerated in a later stage of the cycle. Equipment developed or adapted for the plant is readily portable; the pilot plant included such items as 25-gallon, collapsible, waterproof fabric tanks. The authors believe that economies of the method, which is practical for permanent as well as portable installations, will permit continued exploitation of South American resources to compete successfully with recently renewed activities in the Far East.

Working under Pressure. In the contribution on page 572 by W. F. Caldwell, of American Cyanamid, the reader will find his ability to read blueprints more valuable than his understanding of the English language; the article consists principally of practical construction and assembly drawings for a visible-observation, high pressure, laboratory autoclave. Working volume is about 100 cc., and pressure capacity varies from 2000 to 3000 pounds per square inch, depending on temperature. The unit is constructed almost entirely from readily available parts, at a cost of only a few hundred dollars. Those with applicable high pressure problems to investigate should find it hard to resist the temptation to build this well designed unit for their own studies.

Fodder from Fir. This brief laboratory report (pages 617-619) by Kurth and Cheldelin, of Oregon Forest Products Laboratory, states that feeding yeasts, comparing favorably with the best strains of brewer's yeast in respect to protein, amino acid, and vitamin B content, may be grown in still waste liquor from a wood hydrolysis plant operating on Douglas fir. Mycotorula, Hansenula, and Torula strains did equally well and, according to our calculations, yielded the equivalent of between 3 and 4 pounds of dry yeast per 120 gallons (1000 pounds) of liquor in return for an investment of 24 hours of time and a total of 0.5 pound each of diammonium phosphate and urea. In the process, reducing sugars in the liquor, on which the yeasts fed, were lowered from 0.81 to about 0.19%.

With the Departments. Brown discusses equipment capacities and encourages intelligent deviation from the manufacturer's rated values as experience is gained in a given application; a word of caution about poorly designed equipment from inexperienced manufacturers is thrown in for good measure. Munch reviews fundamental aspects of flow measurement, briefly describes a useful handbook for practical applications, and tells about an instrument recently put on the market for automatically controlling a time *vs.* temperature rise or maintenance cycle. Murdock points out the mutual benefits to be gained by plant and community through true cooperation in the disposal of industrial wastes; examples of good and bad ways in which this problem has been dealt with in the past are recounted, and formulas are given that have proved useful for determining equitable charges when the plant wastes add to the cost of community sewage disposal. Von Pechmann explains the desirability of uniformity and proper emphasis in reporting for management, and lists suggestions for achieving that end in written reports.

The Editors


Chemicals of
New Industrial Importance
Acetoacetic Esters for
Dyes & Pigments
Pharmaceuticals
Stabilizers
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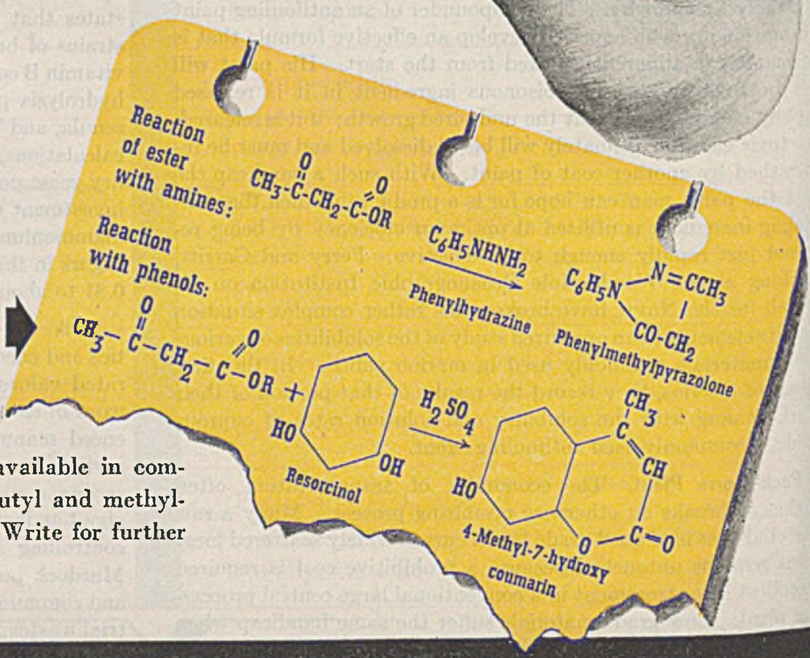
Reaction of ester with amines:
CH3-C-CH2-C-OR
C6H5NHNH2
Phenylhydrazine
C6H5N—N=CCH3
CO-CH2
Phenylmethylpyrazolone
Reaction with phenols:
CH3—C—CH2—C—OR +
H2SO4
HO
OH
Resorcinol
CH3
C
CH
HO
O—C=O
4-Methyl-7-hydroxy coumarin

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials
WALTER J. MURPHY, EDITOR

The Fallacy of Selfishness

FOR many an academic scientist, the personal satisfaction of knowing he is contributing to the world's reservoir of fundamental knowledge is a major reward for years of brain-cracking effort. Indeed, some outstanding workers forego far greater returns, as conventionally viewed, to dedicate themselves to the pursuit of truth in the shape of scientific fact.

Such a person usually measures the value of his work by the acclaim and interest that follow its publication in the scientific literature. Through the collective response of others in related fields, he gains a perspective on his labors that he could never get unaided. Frequently, he is thus shown new avenues of investigation and is inspired to resume his voluntary travail with freshened insight and renewed vigor.

Publication is an indispensable pivot-point in the spontaneous cycle of accomplishment, recognition, and satisfaction that comprise the main lure of academic research. Fortunately, the research worker knows that for all permanent purposes his work is good only to the precise extent that his report of it is good. As a practical matter, therefore, he shapes his offering for the recordings of history with the same scrupulous care that characterized the work it describes.

The benefit of this system derives with the beautiful logic of a solution in elementary geometry. The distilled essence of the highest creative effort the world can claim is thus made common property, free to all who will equip themselves to understand. Such knowledge transcends barriers of time, language, race, and custom. Few acts have affected the destiny of human society as profoundly as the happy accident that led to the now time-honored system of universal publication of academic research findings. None has contributed more to our ability to control the physical aspects of our environment.

What of applied industrial research? An interesting comparison may be drawn.

Most of the industrial research organizations in America encourage staff members to publish information of general scientific value, even though such information may be likewise of substantial industrial interest. In fact, that additional portion of applied knowledge with broadest industrial value also is rather systematically included in the material published. Examples that come to mind are process flowsheets and fundamentals of engineering design.

We believe this state of affairs is no accident. Rather, it must have come over the years, with the discovery that the philanthropy involved in giving bona fide support to a free interchange of scientific information through the surrender of hard-won facts was outweighed many times by the value of the information published by others through the functioning of the system.

Obviously, such an informal, voluntary arrangement permits of abuses, and we are sorry there are organizations that have not thought deeply enough to understand why they should support the system from which they benefit so greatly. It must be peculiarly exasperating to some companies who are generous in their publication policies to know they have a competitor who is not publishing his research results, and who is literally riding on their backs, like the old man of the sea, in utilizing the information they present. It is a tribute to the farsightedness of the companies caught in such circumstances and to the merits of the system that they publish at all in the face of such a deterrent. That they do is accountable in part because of the other direct benefits they derive. The respect and goodwill arising from publication of significant research are enormous and are not underrated by alert executives of the top-flight organizations. One of the most fruitful dividends of an enlightened publication policy is the effect it has in attracting good research men for employment. They are drawn because well-presented research papers command their respect and arouse their interest, and because of the inherent promise that they, in turn, will receive legitimate professional recognition for achievements they may make. The corresponding negative impressions earned by organizations conspicuous in their lack of cooperation are, we suspect, far more injurious to them in the long run than any small temporary advantage they may gain by withholding information from their competitors.

Freedom of scientific interchange, flourishing in an America whose very essence might best be epitomized by the word "freedom", deserves the fundamental credit for bringing the Nation to its present preëminent position in mastery of the physical sciences. We hope this philosophy of freedom will spread, both within our own country, where much is yet to be gained, and abroad.

We feel, too, that other fields of knowledge and of human intercourse, such as politics, both here and abroad, stand to gain immeasurably from the wellsprings of strength inherent in similar free exchanges. Basically, our civilization itself is a prime example of the enlightened self-interest that we advocate. It, too, stems from the discovery that man gets more by sharing the fruits of his highest skills than by keeping them to himself at the cost of being deprived of the greater total skills of others.

Correlating Filtration Theory with Industrial Practice

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Present address,
Iowa State College, Ames, Iowa.

IN RECENT years the understanding of the basic mechanism of separation by filtration and sedimentation operations has been considerably advanced and unified. The essential similarity of the two processes is well illustrated by comparing the Kozeny equation (*7*),

$$u = \frac{p^3}{5(1-p)S^2} \frac{Pg}{\eta L(1-p)} \tag{1}$$

for linear velocity of fluid flow through a stationary bed of granular solids, with the equation of Powers (*10*),

$$u = \frac{p^3}{5(1-p)S^2} \frac{(\delta - \rho)g}{\eta} \tag{2}$$

for the velocity with which a similar bed of solids will fall through a stationary column of fluid. Carman (*5*) discussed the application of Equation 1 to filtration, and Steinour (*15*) showed that a modified form of Equation 2 is applicable to sedimentation.

The application of Equation 1 to filtration is more apparent when written in the form,

$$\frac{dV}{d\theta} = \left[\frac{p^3}{(1-p)K'S^2}\right] \frac{A^2\delta Pg}{\eta W} = \frac{A^2P'}{\alpha_p \eta W} \tag{3}$$

where the term in brackets is the specific permeability of unit volume of solids, and α_p is a specific filtration resistance per unit weight. If it is assumed that the porosity, p, is a function of pressure stress only, it follows that the average resistance, α, of a filter cake is determined solely by the upper limit of pressure stress—that is, the filtration pressure. This provides a theoretical basis for the experimentally observed fact that the time-volume discharge curve of a constant pressure filtration is a portion of a more or less perfect parabola, regardless of the nature of the substance filtered. Actually, a short interval of time is required for a bed of solids in compression to attain a new equilibrium void volume each time the pressure is increased. As a result, the average values of specific filtration resistance in various methods of testing diverge to some extent as filtration pressure increases. This is fairly unimportant, however, since tests at constant gradients of volume-time, pressure-time, or pressure-volume are easily carried out if more complete data are desired.

The failure of filtration equations and theory to be more useful in industrial practice arises, not so much from inability to correlate resistances in various methods of testing more precisely, as from inability of industry to control the properties that determine specific filtration resistance to a degree sufficient to make the application of mathematical analysis worth while. Without such control the design and selection of filters are necessarily based largely upon rule-of-thumb estimates intended to provide for the least favorable conditions likely to be encountered.

Of the numerous reasons that might be advanced for the failure of industry to exercise a better control over variable filtration behavior, perhaps the most important has been the lack of suitable methods of detecting and measuring variations in prefilt properties as these are influenced by changes in processing conditions. If adequate methods were made available, it is possible that a day-to-day correlation of prefilt properties with prefilt history might furnish information that would eventually lead to better control, and with it a narrowing of the present gap between theory and practice.

This paper briefly reviews research and ideas that appear to offer a clue to the interpretation of variable filtration behavior; it also discusses means of quantitatively evaluating the factors responsible. The material presented has been gathering dust in the author's files for nearly a decade; during that time any claim to the importance which might have accompanied earlier publication has been lost. Nevertheless, it is felt that certain phases are still capable of contributing to the rapprochement of science and practice, and are worthy of being placed on record.

SPECIFIC FILTRATION RESISTANCE

At an early date (*13*) attention was drawn to the possibility of predicting filtration resistance from a knowledge of cake porosity and of average particle size and shape. This observation was based upon experiments in which the permeabilities of beds of glass spheres and screened minerals were correlated by means of:

$$\frac{dV}{d\theta} = \frac{v^2\delta f^2R^2}{K'''} \frac{A^2Pg}{\eta W} \tag{4}$$

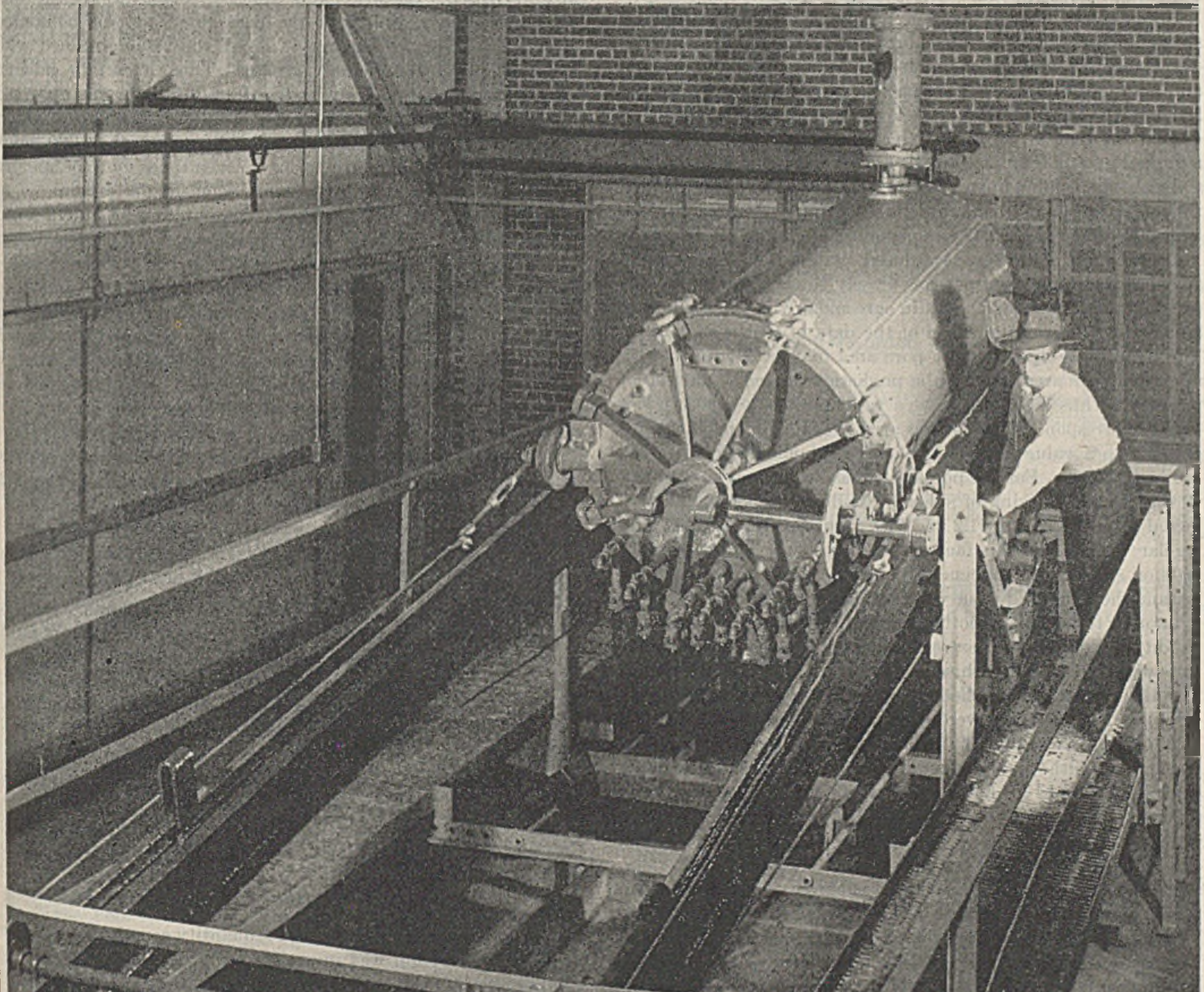
where f was a shape or surface factor defined as the ratio of the surface area of unit volume of spheres passed and retained by a given pair of standard screens, to the surface area of unit volume of irregularly shaped particles passed and retained by the same pair of screens. Average particle diameter was taken as the square root of the harmonic mean of the aperture areas of any two screens used to prepare a given sample. For two successive perfect screens of the standard screen scale series, this is a diameter 1.155 times the opening width of the screen on which the sample is retained.

Equation 4 is a simplified and approximate form of the more accurate expression

$$\frac{dV}{d\theta} = \frac{v^3\delta^2f^2R^2}{(v + 1/\delta)^2\,(18\epsilon)} \frac{A^2Pg}{\eta W} \tag{5}$$

obtained (*8, 12*) by expressing capillary radius and length in the Poiseuille equation in terms of the properties of a bed of uniformly sized spheres, in a manner similar to that employed by Fair and Hatch (*6*). In this derivation ϵ occurs as the ratio of the average to the effective cross section of the pores, a quantity to be deter-

The specific filtration resistance of finely divided solids and chemical precipitates is generally greater than can be accounted for on the basis of the Kozeny equation. A modification is proposed in which abnormal resistance to passage of liquids is explained by the assumption that a portion of the measured void volume is unused or "dead". A method is described for experimentally distinguishing the resistance contribution of "dead" void volume from that of particle size and shape by means of permeability tests on solids subjected to increasing degrees of mechanical compression. Affording a separate quantitative measure of each factor, permeability-compression testing appears to provide a means of correlating day-to-day and batch-to-batch variations in filtration resistance with prefilt history. It is thought that such data might lead to a better control of optimum filtering properties in industrial practice. Evidence is presented for believing that electrokinetic phenomena play an important role in determining filtration behavior. The hypothesis of dead void volume is shown to have physical basis as a region adjoining the capillary wall in which electro-osmosis, induced by streaming potential generation, opposes the flow caused by hydrostatic pressure difference. The phenomenon is somewhat analogous to the electromotive force of polarization encountered in the operation of electrolytic cells.∼∼The picture shows a Kelly filter press used by Aluminum Company of America for separating red mud from sodium aluminate liquor.



mined by experimental tests. The essential similarity of Equation 5 and the Kozeny equation is easily shown by replacing the group, $\nu^3\delta/(\nu + 1/\delta)^2$, with the equivalent group, $p^3/1 - p$, noting that the definition of surface factor permits $3/S$ to be substituted for fR, where S is the surface of unit volume of solids.

Equation 4 results from observing that the square of specific void volume is an approximately linear function of $\nu^3\delta/(\nu + 1/\delta)^2$ over a considerable range of porosity, a substitution equivalent to replacing $p^3/K'(1 - p)$ in the Kozeny equation with $p^2/K''(1 - p)^2$. Using a value of $K'' = 4K'$ (exact at a porosity of 50%), the simplified expression is in error by less than 10% between porosities of 35 and 65%.

The author and C. L. Meyette subjected Equation 5 to an exhaustive series of tests in which the factor 18ϵ was determined, using $^1/_8$-inch ball bearings and screened glass spheres between the sizes of 28 and 65 mesh (*8*). The mean value of a large number of such tests was 41.9 ± 0.75, an average deviation of 1.8%.

Utilizing the average value of 18ϵ found in tests on spheres, surface factors were determined for ten different crushed minerals over the size range 28 to 200 mesh and between the maximum and minimum porosity limits obtainable without the application of mechanical pressure. While surface factor generally decreased several per cent as porosity decreased from maximum to minimum values (thereby appearing to confirm a belief that 18ϵ was a variable depending upon porosity), the average values were extremely constant and characteristic of the mineral tested, ranging from 0.86 for galena to 0.47 for magnesite.

Considerable interest was aroused by the fact that 41.9/18 gives a value for ϵ corresponding closely to the ratio of average to minimum pore area, a result in agreement with the findings of Smith (*14*) in his examination of the data of Green and Ampt. The hypothesis that effective pore area may be identified with minimum pore area permits the prediction of ϵ as a function of porosity. Thus 18ϵ should have a value of 39.9 at a porosity of 47.6% (corresponding to spheres arranged in cubic packing), increasing to a value of 50 for spheres in rhombohedral packing (porosity 26%). For the porosity values which can be attained in the random packing of spheres (42 down to 38%), the predicted values of 18ϵ are 41.2 and 42.7, respectively. Although no regular variation of this factor with porosity was detectable in tests on spheres, the agreement between the experimental average and the computed value was considered noteworthy.

In order to test the hypothesis and at the same time verify the validity of Equation 5 at extreme ranges of porosity, permeability tests were carried out with some 8000 $^1/_8$-inch steel ball bearings in both cubic and rhombohedral packing arrangements (*9*). Two carefully machined cells were employed; one provided a channel 1.25 inches square and 8.00 inches long, and the other was 6.00 inches long with a parallelogram-shaped cross section forming angles of 60° and 120° between sides 1.43 inches in length. Each cell was tested in an empty and a fully packed condition, after which corrections for flow through the side-wall channels and corners were determined by tests carried out upon single rows, single layers, and multiple layers of spheres. The cell designed for cubic packing was also tested in rhombohedral packing after blocking off the exceptionally large passages formed at the two vertical side walls by alternate layers of balls. It was because of some doubt as to the validity of the correction for wall flow in this case that rhombohedral packing was later tested in the 60° cell. The results obtained were:

Packing	p	18ϵ
Cubic	0.476	39.65
Rhombohedral in 90° cell	0.26	42.2
Rhombohedral in 60° cell	0.26	44.4

Although the accuracy of the experimental work leading to these results was unquestioned, some doubt existed as to whether the relatively simple method employed in correcting for side-wall flow was adequate. For this reason the results were considered inconclusive, neither verifying nor disproving the hypothesis. They did, however, furnish reason to believe that Equation 5 with a K constant of 41.9 in place of the variable quantity 18ϵ was sufficiently valid over wide ranges of porosity.

To compare the preceding value of K with the constant in the Kozeny equation, $(3/S)^2$ may be substituted for f^2R^2 in Equation 5. This yields a value for K' of (41.9/9) or 4.65, some 7% smaller than the commonly accepted value of 5.

APPLICATION TO CHEMICAL PRECIPITATES AND PARTICLES IN SUBSIEVE SIZE RANGE

When Equations 4 and 5 were applied to chemical precipitates and finely ground mineral particles sized by sedimentation, the correlation of permeability with particle size as determined by microscopic measurement presented difficulties in that the value obtained for shape factor was not only smaller than expected, but in the case of ground minerals became smaller as particle size decreased. Suspicion was aroused, moreover, by the fact that, when permeability to the passage of air was compared with permeability to passage of liquid, the value obtained with air was always considerably greater. Thus, a certain calcium carbonate precipitate employed in test filtrations was observed to be two to three times more permeable to air than to water. Samples of silica and magnesite ground for more than 200 hours in a ball mill were found to be six or seven times more permeable to passage of air than to water. Some doubt existed as to whether average particle size as computed from microscopic measurements corresponded very closely to the size which might have been ascribed to particle beds had it been possible to subject them to a standard screen analysis. Nevertheless, values of f computed from air permeabilities were usually in sufficiently good agreement with values of f obtained from liquid flow permeabilities in the screen size range of particle size to indicate that flow of liquids through small capillaries must be subject to a retarding force not encountered with gases, a factor for which Equations 4 and 5 make no allowance.

Equations 4 and 5 can be made applicable to flow of liquids as well as gases if it is assumed that for liquids a portion of the void volume is not available for flow. Equation 4 then becomes

$$\frac{dV}{d\theta} = \frac{(\nu - \nu_0)^2\delta f^2R^2}{K'''}\,\frac{A^2Pg}{\eta W} \tag{6}$$

where ν_0 represents the useless or "dead" volume. Such a hypothesis was regarded as likely since it was corroborated by the behavior of precipitates tested under increasing pressure heads and by filter cakes analyzed for their moisture contents. The porosity variation from front to back of a single filter cake, as well as the variation of average porosity of entire cakes deposited at a series of constant pressures, was far too small to explain the variation in specific resistance with filtration pressure on the basis of Equations 4 or 5. On the other hand, it was possible to explain the observed variation by assuming that $1/\alpha_p$ was proportional to $(\nu - \nu_0)^2$ rather than ν^2 alone.

MEASUREMENT OF UNUSED VOID VOLUME

The problem as to whether the ν_0 quantity constituted a real or apparent correction was investigated by observing the permeability of a constant weight of filter solids while varying the void volume. This was done by subjecting the solids to pressure stresses mechanically applied in a small filter, one septum of which was a piston actuated by a load table resembling a large dead-weight gage tester. Clear fluid that had long been in contact with the solids to be tested was conducted to the face of the movable head or piston under a constant head of a few feet of fluid; at the same time the solids were subjected to uniform compression at pressures increasing from 0.25 to 70 pounds per square inch. The permeability of the compressed solids was determined by timing the discharge of fluid from the bottom septum into a microburet over short periods. A dial gage reading to 0.001 inch permitted measurement of the descent of the piston and subsequent computation of the volume of the cell at each pressure load station. The weight and density of the solids were determined by weighing the compressed cake before and after drying.

The data were customarily treated by plotting the square root of the rate of flow against specific void volume. Such plots were straight lines which, when extrapolated to zero rate of flow, cut the void volume axis at values of ν_0 varying with the nature and condition of the solids tested. Values of fR and f computed from Equation 6 by utilizing the ν_0 correction obtained in this manner gave much more reasonable surface factors when correlated with average particle size determined by microscopic measurements.

PERMEABILITY-COMPRESSION TESTING

Application to Prefilt Control. Whatever the cause of the dead void volume correction, it is clearly a factor capable of producing wide fluctuations in specific filtration resistance among prefilts identical as to average particle size and shape. The simple expedient of decreasing void volume during permeability measurements provides a means of distinguishing the effect of dead volume from that of particle size and at the same time provides a quantitative measure of each. By writing Equation 4 in the form,

$$\frac{dV}{d\theta} = \frac{(\nu - \nu_0)^2}{K''S^2} \frac{A^2\delta\, Pg}{\eta\, W} \tag{7}$$

where K'' has a value of about $(4 \times 41.9/9)$ or 18.6, it provides a measure of the physical properties of prefilt solids in terms of specific surface. If it is assumed that ν_0 depends upon some property of the prefilt fluid proportional to specific surface, ν_0 may be replaced by $d'S$, which affords a measure of this property in terms of an apparent film thickness, d'.

Method of Securing Test Filtration Data. From a theoretical point of view at least, permeability tests under mechanical compression provide an ideal means of obtaining test filtration data. This is because a single test carried out under easily controlled conditions supplies the complete equilibrium differential relation between specific filtration resistance, α_p, and pressure stress, from which the relation between average resistance, α, and filtration pressure can be obtained by integration. To obtain the same information by ordinary testing methods would require a multiple number of tests and the expenditure of much more time and labor. To secure it with the same accuracy would require a combination of technique, skill, and good fortune that is practically impossible to attain.

The same data might also be used to predict the time-volume-pressure relations to be expected in other methods of testing (constant gradients of volume-time, pressure-time, and pressure-volume) if equilibrium void volume were attained instantaneously. Actually, increasing pressure during a filtration causes it to proceed as if somewhat less than the predicted resistance were being offered to flow of fluid. The reason becomes obvious when the behavior of irregular-shaped granular solids in compression is studied. Whether the solids are wet or dry, a considerable time is required before sufficient resistance to crushing develops to halt the downward movement of the piston. In the case of a wet chemical precipitate the viscous resistance offered by a fluid while being forced out of a cake by a large pressure load suddenly applied develops a hydrostatic pressure, the initial value of which approaches closely that of the load intensity. Since the sum of hydrostatic pressure and the mechanical stress on the solids must at all times be equal to the load intensity, it is apparent that some time must elapse before the mechanical stress on the solids can rise to full value.

The difficulties usually encountered when attempts are made to perform constant-weight-of-solids testing in ordinary filter presses are absent in this method. The cake cannot develop cracks or pull away from the side walls. The fluid used may be filtrate, and thus any changes in ionic equilibria are avoided. The total volume of fluid passed through the cake may be kept quite small, which avoids the increase in resistance that often occurs when clear fluid is passed through a membrane.

The following data were obtained in a test carried out on November 14, 1933:

Material. Calcium carbonate slurry was taken from a large stock supply used over a period of years in test filtrations; it was originally prepared by hot reaction of lime and soda ash, followed by leaching until free of sodium hydroxide: approximate age at time of test, four years; average density of solids, 2.85 grams/cc.; particle form, mixture of aragonite and calcite; average size of most numerous particle, about 2.6×10^{-4} cm. In four years the specific filtration resistance of this material had decreased to about 75% of the original. This decrease was believed due to the practice of returning accumulations of dried filter cake and slurry samples to the original supply at the end of a series of tests.

Additional Data. Diameter of permeability-compression cell, 5.21 cm.; area, 21.30 sq. cm.

Temperature of fluid passing through compressed solids, 24.2° C.; density assumed to be 1.00 gram/cc.; viscosity assumed to be that of water, 0.915 centipoise.

Weight of wet cake removed from cell, 81.600 grams.

Weight of dried cake 45.003 grams; computed volume of solids, 15.79 cc.

Compressed volume of wet cake computed from density of water and calcium carbonate, 52.39 cc.

Volume decrease during test: $21.30 \times 0.3078 \times 2.54 = 16.65$ cc.

Initial volume of cake at start of test: $52.39 + 16.65 = 69.04$ cc.

Void volume per cc. of solid as a function of piston descent:

$$\frac{(69.04 - 15.79) - 21.30 \times 2.54D}{15.79} = 3.376 - 3.428D$$

where D = descent of the piston, inches

The fluid head producing flow decreased several centimeters during each test as a result of the rise of liquid level in the microburet. The arithmetic mean head effective during each test period is reported in Table I.

Treatment of Data. The square root of the flow rate, in (cc./sec.) per cm. of fluid head, is plotted against specific void volume in Figure 1. The slope of the plot is 0.00486, and the dead void volume intercept at zero rate of flow is 0.92 cc./cc. of solid.

Apparent specific surface is given by rearrangement of Equation 7:

$$S = \frac{(\nu - \nu_0)\, A}{\sqrt{dV/d\theta\, \Delta H}} \sqrt{\frac{\delta g \rho}{K''\eta W}} = \frac{21.30}{0.00486} \sqrt{\frac{2.85 \times 980.6 \times 1.00}{18.6 \times 0.00915 \times 45.00}}$$

$$= 83{,}800 \text{ sq. cm./cc. of solid}$$

Apparent thickness of film corresponding to dead void volume is:

$$d' = \nu_0/S = 0.92/83{,}800 = 1.098 \times 10^{-5} \text{ cm.}$$

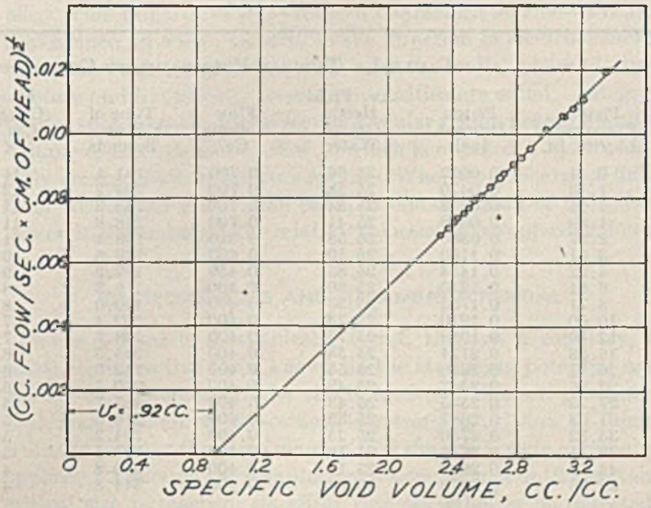


Figure 1. Method of Determining Dead Void Volume in a Permeability-Compression Test

The shape factor is:

$$f = \frac{3}{SR} = \frac{3 \times 2}{83{,}800 \times 0.00026} = 0.275$$

Specific Resistance. The specific filtration resistance of a mass of granular solids is defined by the equation:

$$\alpha = P' \bigg/ \frac{\eta dV\ W}{A\ d\theta\ A} \tag{8}$$

The resistance of either a differential amount of solids or of a larger amount in uniform compression is distinguished from average resistance by writing α_p instead of α.

The nature of α_p as a function of void volume and particle size or specific surface becomes evident upon rearrangement of Equations 6 and 7:

$$\alpha_p = \frac{K'''}{(\nu - \nu_0)^2 \delta f^2 R^2 g_c} = \frac{K'' S^2}{(\nu - \nu_0)^2 \delta g_c} \tag{9}$$

If time is expressed in hours, conveniently small numerical values of α and α_p result, either with metric or English units. If consistent English units are employed, the dimensions of specific resistance are hr.^{2} × lb. force/(lb. mass)^2, or if the distinction between mass pounds and force pounds is ignored, simply hr.^{2}/lb.

Values of α_p in English units may be obtained from the data of Table I by introducing the proper conversion factors. Utilizing flow rates,

$$\alpha_p = \frac{(21.30)^2 \times 1.00}{(dV/d\theta\,\Delta H) \times 0.00915 \times 45.00} \left(\frac{453.6 \times g}{3600^2 \times g_c}\right) = \frac{0.0386}{(dV/d\theta\,\Delta H)}$$

Using void volumes, α_p is given by

$$\alpha_p = \left(\frac{83{,}800}{\nu - 0.92}\right)^2 \frac{18.6}{2.85 \times 980.6} \left(\frac{453.6 \times g}{3600^2 \times g_c}\right) = \frac{1635}{(\nu - 0.92)^2}$$

Values of α_p computed from flow rates are listed in the last column of Table I; as curve *A* of Figure 2, they are shown plotted against the mechanical pressure stress in pounds per square inch.

Prediction of Average Filtration Resistance. During the separation of a finely divided solid from a fluid by filtration, the pressure stress P_s responsible for void volume reduction arises from the cumulative drag of the fluid on the capillary walls. Since this stress increases in the direction of filtrate flow, α_p also increases in the same direction. The over-all or average value of α can be obtained by writing Equation 8 for a differential amount of solids and integrating between the pressure stress limits at the faces of the cake. In the absence of any appreciable resistance to fluid flow through filtrate and slurry conduits, the sum of hydrostatic pressure of the fluid and mechanical pressure stress on the solids is equal to the filtration pressure. For this reason dP_s may be substituted for $-dP'$, giving for the expression to be integrated:

$$\int_0^{P_s} \frac{dP_s}{\alpha_p} = \frac{\eta dV}{A^2 d\theta} \int_0^W dW = \frac{\eta W dV}{A^2 d\theta} \tag{10}$$

Average specific filtration resistance is then given by:

$$\alpha = P' \bigg/ \int_0^{P_s} dP_s/\alpha_p \tag{11}$$

The left-hand side of Equation 10 was integrated numerically in the present instance, employing Simpson's rule and values of α_p read from curve *A* of Figure 2. Values of α as given by Equation 11 are shown as curve *B* in Figure 2, where they are plotted against a filtration pressure equal to the upper limit of pressure stress on the solids.

Relation between Specific Resistance and Filtration Pressure. A complete and accurate relation between void volume and pressure stress cannot, in general, be secured in any single equation simple enough to permit formal integration of Equation 10. However, the relation between $1/(\nu - \nu_0)^2$ and the square root of pressure stress is so nearly linear above some small critical pressure (usually less than 5 pounds/square inch) that no great error results from assuming that the relation is linear over the entire pressure range. This permits the expression of α_p as

$$\alpha_p = \frac{K'' S^2}{(\nu - \nu_0)^2 \delta g_c} = \alpha_0(1 + \beta \sqrt{P_s}) \tag{12}$$

for a wide range of materials of low and medium compressibility.

Integration of Equation 10 with α_p expressed in this form yields for average filtration resistance

$$\alpha = \frac{0.5\ \beta^2 P'}{\beta\sqrt{P'} - \ln(1 + \beta\sqrt{P'})} \tag{13}$$

If β is not too large, this rather cumbersome expression can be approximated with very good accuracy by another equation similar to 12 but with different coefficients.

Application of the foregoing generalization to the data of Table I results in

$$\alpha_p = 230(1 + 0.02935\ \sqrt{P_s}) \tag{14}$$

for the relation between specific resistance and uniform pressure stress. The integrated expression for average α as a function of filtration pressure becomes:

$$\alpha = \frac{3.377\sqrt{P'}}{1 - (78.4/\sqrt{P'}) \log (1 + 0.02935\sqrt{P'})} \tag{15}$$

Values of α computed from Equation 15 yield a very slightly curved line when plotted against the square root of pressure. A straight line having the equation

$$\alpha = 233\ (1 + 0.01736\sqrt{P'}) \tag{16}$$

gives values agreeing with those of Equation 15, with a maximum error of about 1%.

Comparison of Predicted Filtration Resistance with Test Filtration Data. Values of α, as found in a typical series of constant pressure filtrations upon the same material at an earlier date, are plotted as curve *C* of Figure 2. Inasmuch as the time-volume discharge data utilized are easily accessible (*2*), they need not be given here. It will be noted that, although the test filtration results are well fitted by an equation of the same form, they are 10 to 15% higher. Since other permeability-compression tests made upon this same calcium carbonate slurry yielded results agreeing well with those of Table I, the writer is inclined to believe that the difference is primarily the result of a continued decrease in compressibility accompanying the aging of the precipitate between the time of the filtration tests and the permeability-compression tests.

Comparative Permeability to Flow of Liquid and Gas. A dry powdered sample of the same carbonate precipitate

Table I. Typical Permeability-Compression Test

Piston Pressure[a], Lb./Sq. In.	Piston Descent, Inch	Av. Fluid Head, Cm. of Water	Flow Volume, Cc.	Time of Flow, Seconds	Flow Rate (Cc./Sec.) per Cm. Head × 10⁶	Sp. Void Volume, Cc./Cc. Solid	α_p, Hr.^{2}/Lb.
0.41	0.0052	25.66	0.700	191.1	14.27	3.358	271
1.13	0.0470	25.58	0.700	224.2	12.20	3.214	317
1.51	0.0658	25.53	0.700	235.3	11.65	3.150	331
1.89	0.0818	25.41	0.700	248.8	11.06	3.096	354
2.27	0.0860	26.58	0.320	108.4	11.10	3.081	352
3.01	0.1160	26.10	0.400	149.6	10.24	2.977	377
4.92	0.1453	25.85	0.450	192.2	9.06	2.877	426
6.81	0.1610	25.90	0.400	179.8	8.59	2.823	450
8.71	0.1752	25.83	0.400	190.0	8.15	2.773	474
10.60	0.1910	25.78	0.400	202.4	7.665	2.720	504
12.49	0.1988	25.73	0.400	208.7	7.45	2.693	518
16.38	0.2174	25.58	0.400	225.5	6.94	2.630	556
20.17	0.2320	25.53	0.400	242.0	6.47	2.580	597
23.96	0.2443	25.48	0.400	250.7	6.26	2.537	617
27.75	0.2555	25.43	0.400	265.7	5.92	2.500	652
31.53	0.2647	25.35	0.400	278.5	5.665	2.468	682
35.32	0.2750	25.25	0.400	294.2	5.38	2.432	718
39.11	0.2813	25.16	0.400	303.1	5.245	2.410	736
44.79	0.2938	25.11	0.400	319.8	4.98	2.368	776
52.36	0.3078	25.03	0.400	344.8	4.635	2.320	833

[a] Half the hydrostatic pressure drop through the cake (0.18 pound/square inch) has been added to the mechanical pressure computed from the sum of the known weights of the piston, load table, and gage testing weights.

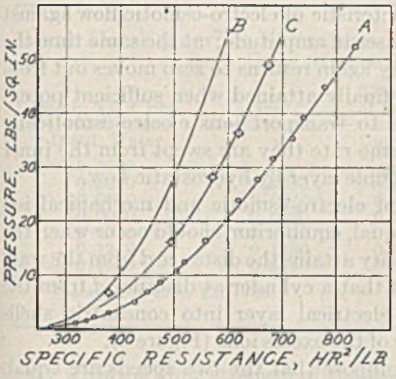


Figure 2. Comparison of Specific Filtration Resistance as Found in a Series of Constant Pressure Filtrations with the Behavior Predicted from a Permeability-Compression Test

(weight, 9.254 grams) was tamped tightly into a glass tube to form a column 6.6 cm. in length and 1.63 sq. cm. in area. The permeability was determined at a constant void volume of 2.31 cc./cc. of solid with both air and water. The specific permeability was computed in each case, using Equation 4. The permeability obtained with air was 3.07 times larger than the value found with water, a ratio which can be explained if the permeability to flow of water is computed using Equation 6 and a "dead" void volume of 0.993 cc./cc. of solid.

DEAD VOID VOLUME CONSIDERED AS ELECTROKINETIC PHENOMENON

It is possible to advance a number of explanations for the appearance of the ν_0 quantity in the expression for specific permeability when particle size becomes small: Among these are the possibilities (1) it might represent void volume occluded in crystal agglomerates, and thus be physically incapable of sharing in the passage of fluid; (2) it might be due to decrease in particle size by crushing, followed by plugging of the voids with debris; (3) it might represent the volume of a strongly adsorbed layer of fluid; or (4) it might be a phenomenon of electrokinetic origin.

Although it is possible that all four of these factors contribute to some extent, it seems unlikely that the first three can be responsible for more than a minor share. Thus, although adsorption undoubtedly plays a part, it is difficult to believe that adsorption forces can act through the relatively great distances (up to several hundred molecular diameters) sometimes needed to explain the magnitude of ν_0. On the other hand, it is quite easy to explain both the magnitude and variable nature of the ν_0 quantity from an electrokinetic point of view.

The idea that a considerable part of the resistance to fluid flow in filtration may be electrokinetic in origin is not new, having been suggested by the author a number of years ago (*11*). According to well established principles, the interface between a solid and a liquid is the seat of a double electrical layer in which ions of one kind (usually the negative) are adsorbed and tightly held at the solid surface. The removal of one kind of ion leaves an excess of the other kind in solution. These arrange themselves in a diffuse layer in which the excess of concentration of the second kind over the first diminishes from a maximum at the wall to zero at an outer boundary extending to an indefinite distance, *m*, from the surface. Theory provides no measure of *m*, but it does afford a good idea of the distance *d* between the center of gravity of the charges in the diffuse layer and that of those adsorbed on the surface. This is given by the Debye-Hückel equation

$$d = \sqrt{\frac{1000\ DRT}{8\pi e^2 N^2 \mu}} \tag{17}$$

in terms of fundamental constants, temperature, and ionic strength μ. For any particular solvent and temperature the distance *d* depends only upon ionic strength. Thus for water at 25° C., *d* is given by $3.05 \times 10^{-8}/\sqrt{\mu}$. For a 10^{-5} molar concentration of a univalent electrolyte, it is a length of nearly 10^{-5} cm., decreasing to 10^{-7} cm. for a 0.1 *M* solution (*4*). Since ionic strength increases as the square of ion valence, the value of *d* is much less for equimolar solutions of multivalent ions.

In the discussion to follow it will be convenient to regard *m* as a distance perhaps three or four times larger than *d*. In a capillary tube of radius *r* (large in comparison to *d*), $r - m$ is the radius of an electrically neutral cylinder containing equal numbers of positive and negative ions. It is surrounded by an annular sheath of thickness *m*, composed of two concentric cylinders of thicknesses *d* and $m - d$, each containing equal numbers of the excess kind of ion. Because the expression "thickness of the double electrical layer" is ordinarily understood to refer to distance *d* only, that portion of the double electrical layer lying between *d* and *m* will be referred to as the inner or diffuse region.

MECHANISM OF ELECTRO-OSMOSIS

The electric potential between the charges adsorbed at a surface and the double electrical layer (the zeta potential) gives rise to the well known electrokinetic phenomena of electro-osmosis and streaming potential when the surface encloses the fluid (as does a capillary tube), and to cataphoresis and sedimentation potential when the surface is that of discrete particles free to move in a surrounding fluid.

If an electric potential is applied to fluid at the ends of a system of capillary tubes, ionic migration will take place as in an electrolytic cell, each ion dragging with it an atmosphere of associated fluid molecules. In the central core of the tube the frictional effect of equal numbers of countermigrating ions is largely neutralized, but in the diffuse double layer the excess of positive over negative ions (assuming it is the negative ion that is adsorbed) will result in an unbalanced force on the fluid. This may be regarded as equivalent to a hydrostatic pressure of variable intensity, decreasing from a maximum at the wall to zero at the inner boundary of the double layer. In the absence of any ordinary hydrostatic pressure difference, the fluid movement initiated by this electrically generated pressure will be resisted by the forces of viscous shear in the same manner as if the pressure were applied mechanically. If a pressure distribution between the wall and the inner boundary *m* is assumed, the velocity profile of the resulting flow may be secured by a simple graphical integration of the basic equation relating pressure, viscosity, and rate of fluid shear. When this is done, velocity increases from zero through the double layer to reach a flat maximum extending from *m* to the axis of the tube. This makes apparent how the entire body of fluid can be pulled along by a force exerted within the confines of a narrow sheath or skin to produce the familiar phenomenon of electro-osmotic flow.

If electro-osmosis is opposed by hydrostatic pressure, the flat central portion of the velocity profile is depressed to form a parabola. This imparts to the profile a characteristic sine-wavelike appearance, in which velocity in the direction of electro-osmosis passes through maxima at points near the walls, where electro-osmotic and hydrostatic pressure intensities are equal. Integration of such a profile yields for the annular region near the wall a volume of electro-osmotic flow to which is opposed a hydrostatically created flow in the core region. Whether discharge of fluid from the capillary will take place in one direction or the other is seen to depend upon the relative volumes of the opposing flows.

ELECTRO-OSMOSIS AND STREAMING POTENTIAL

When a fluid is mechanically forced through a capillary, a small electromotive force known as the streaming potential can usually be detected. Under the influence of this self-generated potential, a small electro-osmotically transported flow of liquid will take place in the same manner as if the e.m.f. were externally applied. Although the retardation of flow is small until a certain critical size is reached, its effect can nevertheless be detected. Abramson (*1*) showed that in a certain case it amounted to 10%

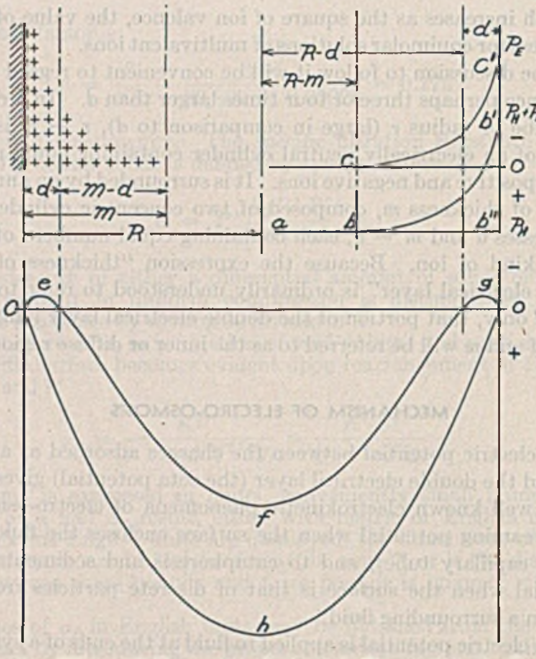


Figure 3. Effect of Streaming Potential Generation in Retarding Flow of Liquids through Small Capillaries

Top Left. Capillary wall with ions of one kind (assumed to be the negative) adsorbed in a stationary layer, leaving excess positive ions arranged in a diffuse mobile layer extending to distance *m* from the wall; *d*, distance to center of gravity of double electrical layer. Annular shells of thickness *d* and $m-d$ thus contain equal numbers of excess positive ions.

Top Right. *abb*″, initially uniform hydrostatic pressure gradient P_H producing downward flow of fluid; in the absence of streaming potential, velocity distribution would assume the parabolic profile *oho*. Curve *cc*′, assumed equilibrium distribution of electro-osmotic pressure intensity, P_E, opposing hydrostatic pressure; caused by upward streaming of fluid under the influence of potential generated by ejecting excess ions from the capillary outlet. Curve *abb*′, distribution of net pressure gradient acting after the ratio E/P has become constant.

Bottom. *oefgo*, velocity profile obtained by numerical integration of equation,

$$du = \frac{(P_H + P_E)rdr}{2\,\eta\,1}$$

taking values of $P_H + P_E$ from curve *abb*′. The ratio of P_E to P_H has been adjusted by trial and error to yield a profile in which absolute velocity passes through zero at distance *d* from the wall. Upward streaming of fluid in shell *d* then carries positive ions back toward the inlet at the same rate that ions in shell $m-d$ are swept to the outlet; thus, electric neutrality of the system and a constant ratio of E/P are preserved. Volume rate of flow corresponding to profile *oefgo* is 37% of that given by profile *oho*. Since the initial rate of flow will correspond closely to distribution *oho*, a reduction in flow rate upward of 60% may be expected to take place during the time E/P builds up to a maximum value.

in a capillary 1×10^{-4} cm. in radius, increasing rapidly for capillaries of smaller size.

A qualitative explanation of the phenomenon follows: When fluid starts to flow through a capillary, the velocity distribution profile near the wall is at first substantially parabolic in the direction of flow. Since no potential difference exists to cause migration of ions, fluid movement in the double electrical layer is without restraint. This results, however, in discharging a portion of the double layer from the end of the capillary, whereupon a small potential difference between the ends of the capillary immediately appears. Under the influence of this small e.m.f. positive ions adjacent to the wall at once begin to move toward the inlet end of the capillary. As the excess of positive ions in the effluent continues to increase, the potential becomes larger and the electro-osmotic flow greater. With an increasing electro-osmotic pressure opposing the mechanically applied pressure, fluid motion in the outer part of the double electrical layer adjoining the wall is first halted and then reversed in direction. The sine-wavelike profile characteristic of electro-osmotic flow against hydrostatic pressure increases in amplitude; at the same time the null point at which velocity again returns to zero moves out from the wall. Equilibrium is finally attained when sufficient potential difference is built up to transport ions electro-osmotically back to the inlet at the same rate they are swept from the inner portion of the electrical double layer by hydrostatic flow.

If the average speeds of electro-osmotic and mechanical ion transport are considered equal, equilibrium should occur when the null point of absolute velocity attains the distance *d* from the wall. This follows from the fact that a cylinder at distance *d* from the wall divides the double electrical layer into concentric shells containing equal numbers of the excess ions (Figure 3).

There is no reason to suppose that the two speeds are equal. Nevertheless, it seems reasonable to assume that the actual distance at which absolute velocity of flow changes direction must bear a close and constant proportionality to *d* as given by the Debye-Hückel equation, provided total thickness *m* of double electrical layer is less than the radius of the capillary.

APPLICATION TO EXPERIMENTAL OBSERVATIONS

The foregoing mechanism provides a simple qualitative explanation for a number of well known phenomena. Thus geologists have long been aware that seepage of water through mineral cleavage planes takes place much more slowly than would be expected on the basis of Poiseuille's law. Terzaghi (*16*) found that the apparent viscosity of water increased abruptly to many times its normal value when made to flow between parallel planes spaced less than 10^{-5} cm. apart.

The fact that continued passage of clear water through almost any type of fine-pored membrane is accompanied by a gradual increase in resistance is a matter of common experience and has been reported many times in the literature. In making streaming potential measurements, it is sometimes necessary to wait for periods of 15 to 24 hours before the ratio E/P (developed potential to hydrostatic pressure head) becomes constant. Both of these phenomena appear to have a reasonable explanation in the fact that growth of the electro-osmotic flow region proceeds from a thickness of zero to an equilibrium value, at a rate depending upon the extent to which the rate of mechanical transport exceeds that of electro-osmotic transport. If these rates are nearly equal, it is conceivable that fairly long periods of time might elapse before an equilibrium potential would be reached. The gradual increase in resistance that simultaneously takes place is explained by the fact that, as electro-osmotic velocity increases, the absolute velocity of flow throughout the central region of the capillary is correspondingly decreased.

If the foregoing hypothesis is correct, it would be expected that, upon interrupting flow of fluid through a capillary, the difference in ion concentration at the two ends would cause electro-osmosis to continue until the potential disappeared; or if flow were started again, that the resistance upon resuming flow would be less than it had been when flow was stopped. Such behavior was actually observed by Bishop, Urban, and White (*3*) who found that, when the pressure producing flow of a dilute potassium chloride solution through a cellophane membrane was reduced to zero, a backward flow of fluid took place for a short time.

If the ionic strength of the fluid flowing through a blocked membrane were suddenly increased, the flow would be expected to increase because of a collapse of the double electrical layer from its original thickness to the smaller value corresponding to a greater ionic strength. Such a phenomenon was actually observed (*3*) when thorium ions were added to a solution which had passed through a cellophane membrane until the resistance had increased to some ten times the initial value. When a thorium salt was added, the flow increased almost to the original rate.

For the same reason it would be expected that the extent to which membranes are blocked by the passage of fluid should

TABLE II. EFFECT ON FILTRATION RESISTANCE OF INCREASING IONIC STRENGTH OF FILTRATE[a]

Mole NaCl per 1000 Grams Distd. Water	Ionic Strength, μ	Thickness of Double Layer d, Cm. × 10^6	Filtration Resistance, Hr.^{2}/Lb.
0.0000	....	....	507
0.0020	0.0020	0.678	398
0.0040	0.0040	0.480	363
0.0080	0.0080	0.339	370
0.0320	0.0320	0.169	309
0.1280	0.1280	0.0848	227
0.5120	0.5120	0.0424	215

[a] Tests made Dec. 23, 1936.

vary with the ionic strength of the solution passed through. The same workers cite tests in which the resistance of a membrane to the passage of a univalent salt solution was observed to increase many fold, whereas little or no resistance increase was observed when an equal volume of a thorium salt of the same molar concentration was passed through a similar membrane.

EVIDENCE OF ELECTROKINETIC PHENOMENA IN FILTRATION PROCESSES

The gradual increase in resistance exhibited by filter cakes when being washed would seem to be an obvious example of electrokinetics. Another phenomenon, the electrokinetic origin of which is perhaps not so apparent, is the increase in specific resistance observed when increasingly dilute suspensions of an inert material are filtered at the same constant pressure. The author at one time ascribed this effect to the almost universal presence of unsuspected resistance-offering impurities in the liquids used to make up test filtration suspensions (*11*); however, this hypothesis has since been discarded in favor of an electrokinetic explanation. If the same hydrostatic pressure difference is employed to force liquid through long and short capillary tubes of the same diameter (that is, thick and thin filter cakes), the greater volume rate of flow through the shorter capillaries will generate a correspondingly larger streaming potential gradient and diaphragm current. Since an increase in current flow corresponds to a higher electro-endosmotic pressure intensity opposing the applied hydrostatic pressure difference, the ratio of volume rate of flow through the two lengths of capillaries will in general be less than the expected ratio—that is, the inverse ratio of their lengths. Hence, when the data are interpreted on the basis of resistance to fluid flow per unit length (or weight of solids), the specific resistance appears to increase with decreasing capillary length (or prefilt concentration).

The effect of changing the ionic strength is easily demonstrated by laboratory experiment. Thus the author observed that the specific resistance of a Filter-Cel suspension made up with distilled water decreased rapidly with successive additions of increasing amounts of sodium chloride, until at a 0.5 *M* concentration the resistance was only 40% of the original value. Such an experiment affords an explanation of failures to secure exact checks when testing newly prepared batches of Filter-Cel over a period of time; even the small amount of solute present in ordinary tap water will lower the resistance to a value considerably less than that in distilled water.

A series of identical suspensions were made of 41.4 grams of Filter-Cel per 1000 grams of distilled water. Reserving one batch as a control, weighed quantities of sodium chloride were added to the remainder to secure the solution molalities shown in Table II. Constant pressure filtrations at pressures between 24.6 and 25.0 pounds/square inch were carried out at 23° C. in a plate-and-frame filter press to a cake thickness of 2.0 cm. on a filtering area of 440 sq. cm. The time-volume discharge data were recorded automatically by means of an electrical time-marking clock. Filtration resistance decreased with increasing salt concentration, as Table II shows. In computing ionic strength and thickness of the double layer, it has been assumed (without proof) that the dry Filter-Cel contributed no solute ions to the prefilts.

CONCLUSIONS

It is difficult to avoid the conclusion that electrokinetic phenomena play a large part in the success or failure of filtration as a method of separation. Thus the question as to how particles so much smaller than the openings of a filter septum manage to become entangled in such a way as to block it early in the initial stages of filtration may well have an electrokinetic answer. On the other hand, the difficulty of securing a clear filtrate, or even of initiating the arrest of colloidal particles when prepared with a large excess of one of the reagents may also have a similar explanation. In filtration tests carried out for long periods on a material such as ferric hydroxide, the time-volume discharge curves depart from parabolic form in both the early and late stages of the filtration in a characteristic manner. This behavior, unintelligible from any other point of view, appears to have a reasonable explanation when regarded as an electrokinetic phenomenon.

NOMENCLATURE

A = area of particle bed, sq. cm.
α = av. specific filtration resistance (weight basis) of a filter cake subjected to nonuniform pressure stress, hr.^{2} × lb. force./(lb. mass)^2
α_p = specific resistance (weight basis) of a particle bed subjected to uniform pressure stress, hr.^{2} × lb. force/(lb. mass)^2
d' = apparent film thickness, cm.
δ = density of granular solids, grams/cc. of solid
ϵ = ratio of average to effective cross section of pore formed by a unit cell of eight contacting spheres
f = surface or shape factor, no units
η = fluid viscosity in poises, grams mass/cm. × sec.
g = local value of gravitational acceleration, cm./sec.^{2} or ft./sec.^{2}
g_c = dimensional constant in Newton's law, 980.665 (gram mass × cm.)/(gram force × sec.^{2}) or 32.1740 (lb. mass × ft.)/(lb. force × sec.^{2})
ΔH = fluid head, cm.
K, K', K'', K''' = constants (41.9, 4.65, 18.6, and 168, respectively)
L = depth of particle bed, cm.
P = hydrostatic pressure difference, grams mass/sq. cm.
P' = hydrostatic pressure difference, lb. force/sq. ft.
p = packing porosity, cc. of void volume/cc. of total volume
ρ = fluid density, grams/cc.
R = average radius of spheres or particles, cm.
S = specific surface, sq. cm./cc. of solid
u = linear velocity of fluid flow, cm./sec.
$dV/d\theta$ = volume rate of flow, cc./sec.
ν = specific void volume, cc./cc. of solid
ν_0 = dead void volume, cc./cc. of solid
v = void volume per unit weight of solids, cc./gram
W = weight of particle bed, grams

LITERATURE CITED

(1) Abramson, H. A., *J. Gen. Physiol.*, 15, 279 (1932).
(2) Badger, W. L., and McCabe, W. L., "Elements of Chemical Engineering", 2nd ed., p. 509, New York, McGraw-Hill Book Co., 1936.
(3) Bishop, G. H., Urban, F., and White, H. E., *J. Phys. Chem.*, 35, 137 (1931).
(4) Bull, H. B., "Physical Biochemistry", p. 181, New York, John Wiley & Sons, 1943.
(5) Carman, P. C., *Trans. Inst. Chem. Engrs.* (London), 16, 168 (1938).
(6) Fair, G. M., and Hatch, L. P., *J. Am. Water Works Assoc.*, 25, 1551 (1933).
(7) Kozeny, J., *Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse*, Abt. IIa, 136, 271 (1927).
(8) Meyette, C. L., M. S. thesis, Univ. of Minn., 1933.
(9) Meyette, C. L., unpublished report, 1935.
(10) Powers, T. C., Research Lab., Portland Cement Assoc., *Bull.* 2 (1939).
(11) Ruth, B. F., IND. ENG. CHEM., 27, 808, 812 (1935).
(12) Ruth, B. F., Ph.D. thesis, Univ. of Minn., 1931.
(13) Ruth, B. F., Montonna, R. E., and Montillon, G. H., IND. ENG. CHEM., 23, 850 (1931).
(14) Smith, W. O., *Physics*, 3, 139 (1932).
(15) Steinour, H. H., IND. ENG. CHEM., 36, 618, 840, 901 (1944).
(16) Terzaghi, K., *Z. angew. Math. Mech.*, 4, 107 (1924).

Autoclave for Visual Observation of High Pressure Reactions

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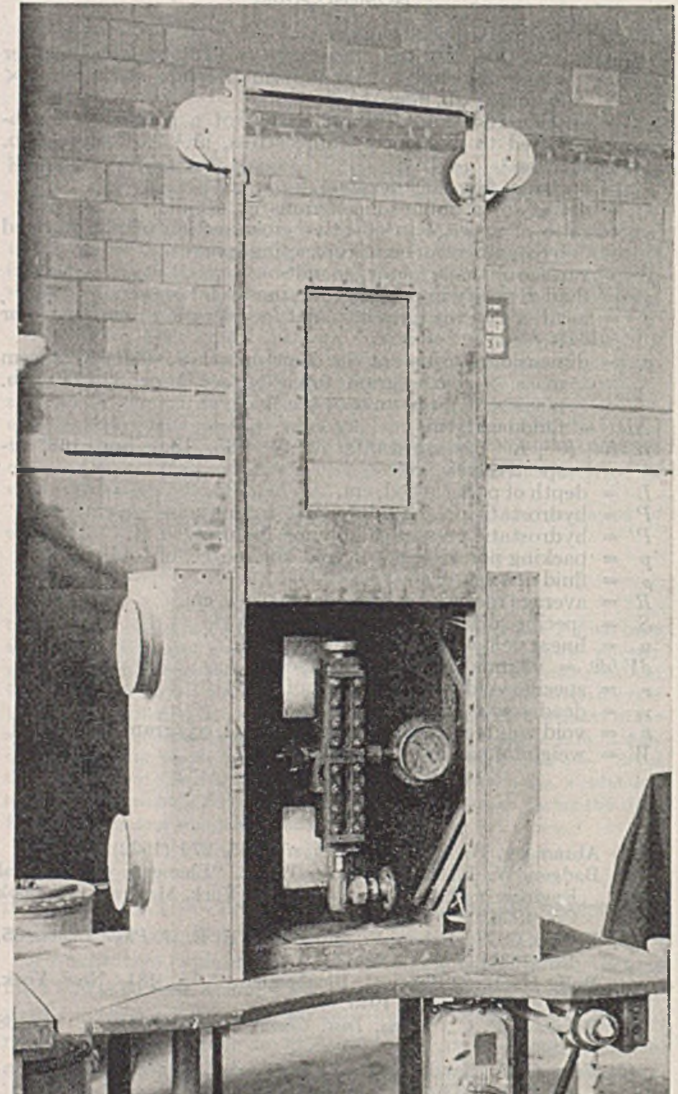

Photograph of Visual Autoclave

The trend toward high pressure and high temperatu chemical reactions has necessitated the development experimental apparatus which will permit visual observ tion of conditions during the entire operation. Th equipment described indicates how this result is achiev by means of a rotating Jerguson gage with clear glass o two sides through which light may pass. It is housed an insulated casing, provided with strip heaters for raisi the temperature and with glass windows for viewing th temperature and pressure gage. Besides serving as miniature autoclave, it may be used for determining solu bilities in solvents which are volatile at atmospheric pre sure and the temperatures obtained. It also permits th determination of solution densities under varying cond tions of temperature and pressure.

IN RECENT years research on chemical reactions involvi higher pressures and temperatures has created a demar on the chemical engineer to produce a vessel in which these rea tions can be observed by the eyes as they progress to completio A search of the literature on the subject brought to light sever ingenious arrangements of sight glasses which seemed practic for viewing portions of the operations. None of them, howeve met the drastic requirements of members of our High Pressu Division who demanded sight through all of the liquid content as well as a view of the top of the liquid with any solid matte contained in it.

In the petroleum industry many liquid level gages have bee used for pressures running to 105 kg. per sq. cm. (1500 pound per square inch) and temperatures of several hundred degre Fahrenheit. The Jerguson Gage and Valve Company helped i working out a gage which the author could adapt to the require ments.

Figure 1 shows the experimental high pressure gage, having a over-all length of 16 inches. The chamber is made of type 31 stainless steel, with tempered glass sight glasses on both sides t permit the passage of light with an unobstructed view of prac tically the entire contents. This stainless steel chamber is tappe at each end for 1.27 cm. (0.5 inch) N.P.T. (national pipe thread and one end takes a 1.27-cm. XH pipe nipple connected to a gat valve at the discharge end (Figure 2), specially machined fo quick connection and disconnection of the charging bomb Figure 3 shows the bomb, which is also used for receiving th contents of the autoclave when the reaction is completed.

In the opposite end of the chamber is screwed a Westo thermometer having a 6-inch stem and a range of 0° to 300° C The long stem assures ample contact with the liquid contents and therefore, accurate immersion temperatures. On the sides of th chamber at the center are two 6.4-mm. (0.25-inch) N.P.T taps. One is for a pressure gage, and the opposite one is for a explosion disk. Although this disk ruptures at a pressure appre ciably higher than the maximum operating pressure, it is con sidered more reliable than a safety valve which might fail t function if solids blocked the operating mechanism. There were also space limitations which led to the selection of the explosio disk for this operation.

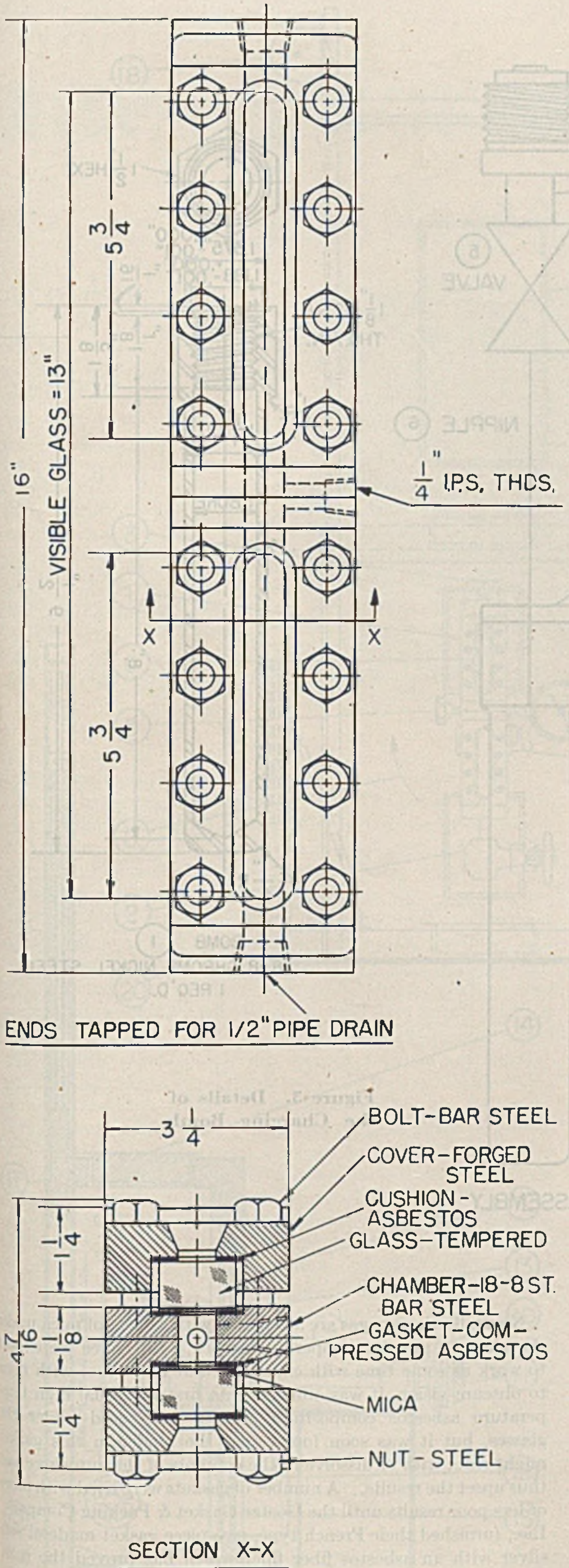

Figure 1. Autoclave (Dimensions in Inches)

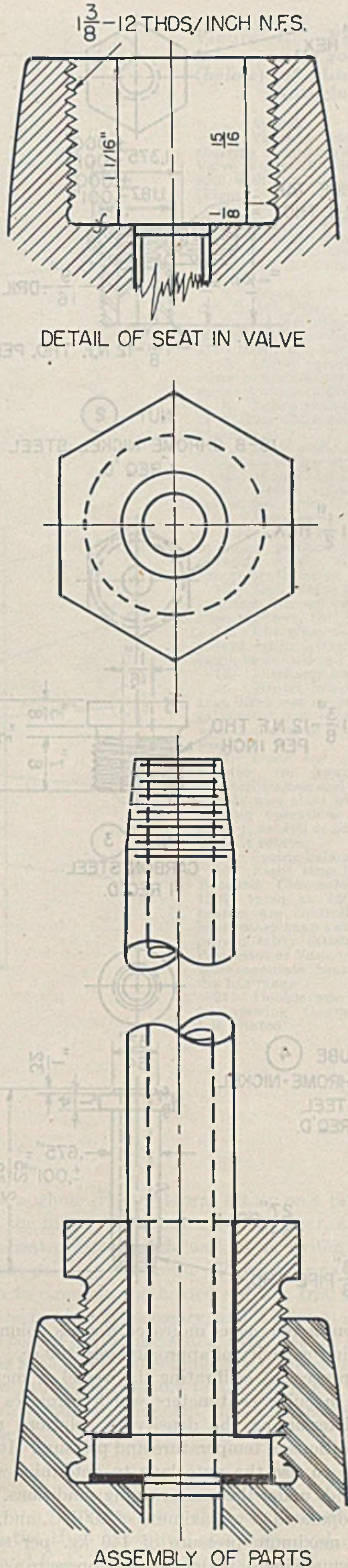

Figure 2. Charging Bomb Connection

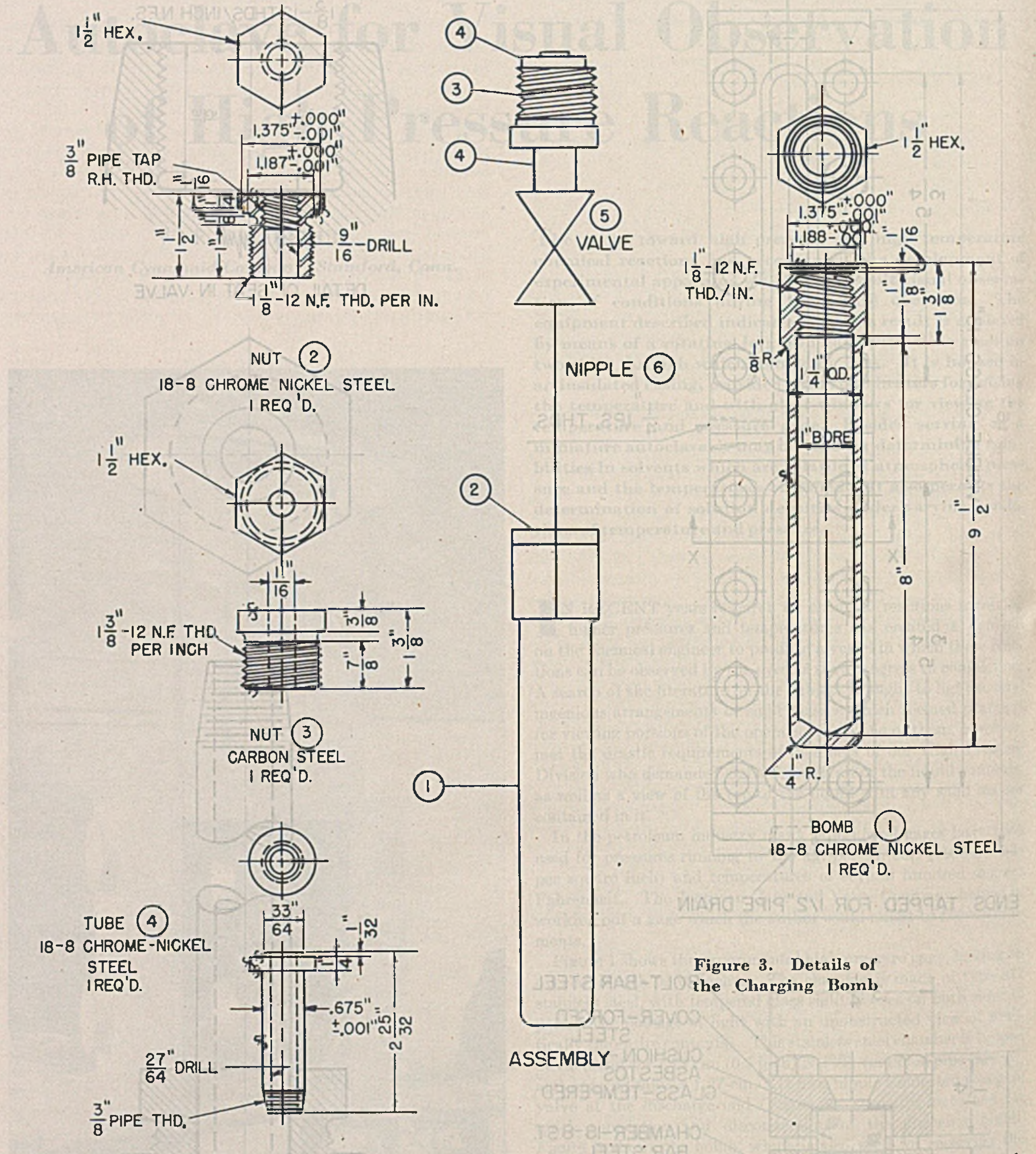

Figure 3. Details of the Charging Bomb

Calibration of the vessel indicated a gross volume of 135 cc., and a working capacity of approximately 100 cc. Incidentally, during the process of calibrating the vessel, a metal scale was marked off in cubic centimeters which furnishes an excellent means of determining the density of solutions under widely varying conditions of temperature and pressure. It is, of course, also possible to use the autoclave to determine solubilities of solids in liquids under the same varying conditions.

The unit operates at a maximum of 200° C. and, at this temperature, a maximum pressure of 140 kg. per sq. cm. (2000 pounds per square inch), with increasing pressure as the temperature diminishes until 210 kg. (3000 pounds) is reached at 20° C.

Normally these gages are assembled with a sheet of mica under the glass to prevent temperature shock. But since we expect to work at some time with chemicals that may react with mica to obscure vision, it was omitted. At first the usual high temperature asbestos composition gaskets were used under the glasses, but it was soon found that the binder in this gasket might react with or dissolve in the contents of the autoclave and thus upset the results. A number of gaskets were tried with more or less poor results until the Goetze Gasket & Packing Company, Inc., furnished their French type, two-piece gasket made of soft silver with an asbestos fiber filler which has proved the most satisfactory so far.

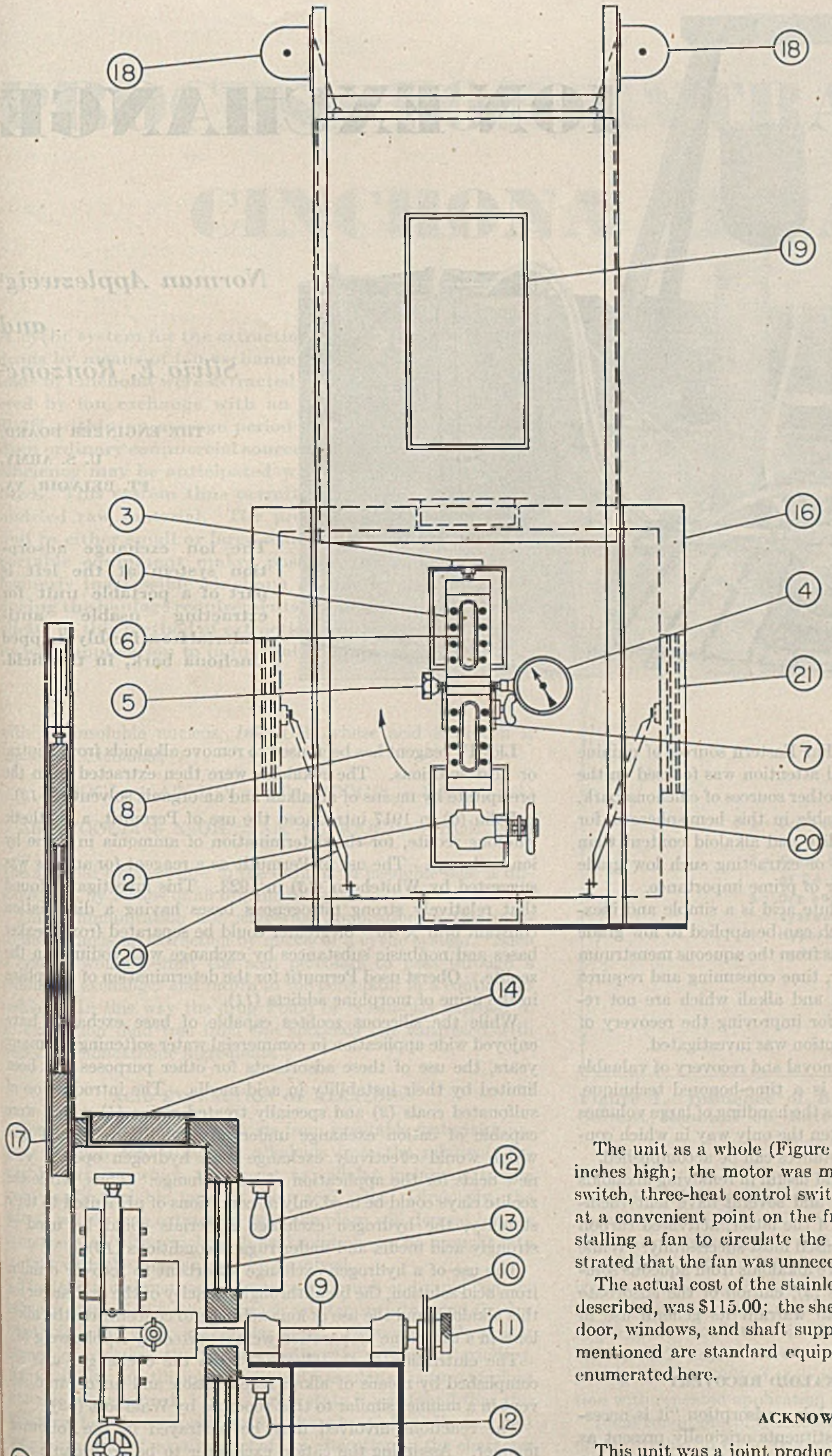

Figure 4. Front View (*above*) and Cross Section (*below*) of Housing and Autoclave

1. Autoclave
2. Valve for charging and discharging autoclave (Chapman Valve & Manufacturing Co., List 990) with specially machined end (Figure 2)
3. Thermometer (Weston Electrical Instrument Company)
4. Pressure gage of range selected for operation in hand so as to secure most accurate pressure indication
5. Safety head with explosion disk (Black, Sivalls & Bryson)
6. Sight glasses on both sides of autoclave, totaling $^{3}/_{8}$ inch × $11\,^{1}/_{2}$ inches on each side
7. Clamp operated by thumbscrew to permit easy insertion and removal of autoclave 1
8. Arrow indicating direction of rotation which serves to agitate contents of 1
9. Shaft attached to clamp 7, imparting rotary motion to autoclave 1 at rate of 8 r.p.m.
10. Roller chain sprocket driven from gear-head motor
11. Knurled nut to loosen 10 so that autoclave 1 may be set in exact position for attaching charging bomb (Figure 3) to charge or discharge 1
12. Light bulbs providing illumination through two double wire glass windows, 13
14. Charging hole cover removed when attaching charging bomb to autoclave 1
15. Discharge hole cover
16. Heater housing of No. 16 gage black iron inside, No. 24 gage galvanized iron outside, insulated with 2 inches of granulated rock wool
17. Door for closing heater housing 16, hung on spring counterbalances and provided with double wire glass window, 19, for viewing operations within autoclave 1, as well as pressure gage 4, while it rotates
18. Spring balance for door 17
20. Eight strip heaters (E. L. Wiegand Chromalox, No. S.E. 1202) rated at 250 watts each; heaters are controlled by three-heat rotary snap switch which has proved fairly satisfactory, but a Powerstat or Variac would provide more accurate heat control over the full range
21. Double wire glass window for viewing thermometer 3 as 1 is rotated

The unit as a whole (Figure 4) was set up on a pipe stand, 32 inches high; the motor was mounted at the rear, and the light switch, three-heat control switch, and motor switch were placed at a convenient point on the front. Provision was made for installing a fan to circulate the heated air, but trial runs demonstrated that the fan was unnecessary, and it was not installed.

The actual cost of the stainless steel gage, less the attachments described, was $115.00; the sheet metal heater housing with base, door, windows, and shaft support totaled $116.00. The fittings mentioned are standard equipment, and their costs will not be enumerated here.

ACKNOWLEDGMENT

This unit was a joint product of the Development Engineering Division and the High Pressure Laboratory, and credit is due J. H. Paden and K. C. Martin, who supplied helpful suggestions and, finally, the energy and will power so necessary to make a new and unusual piece of equipment function successfully.

ION EXCHANGE

Norman Applezweig[1]

and

Silvio E. Ronzone[2]

THE ENGINEER BOARD,
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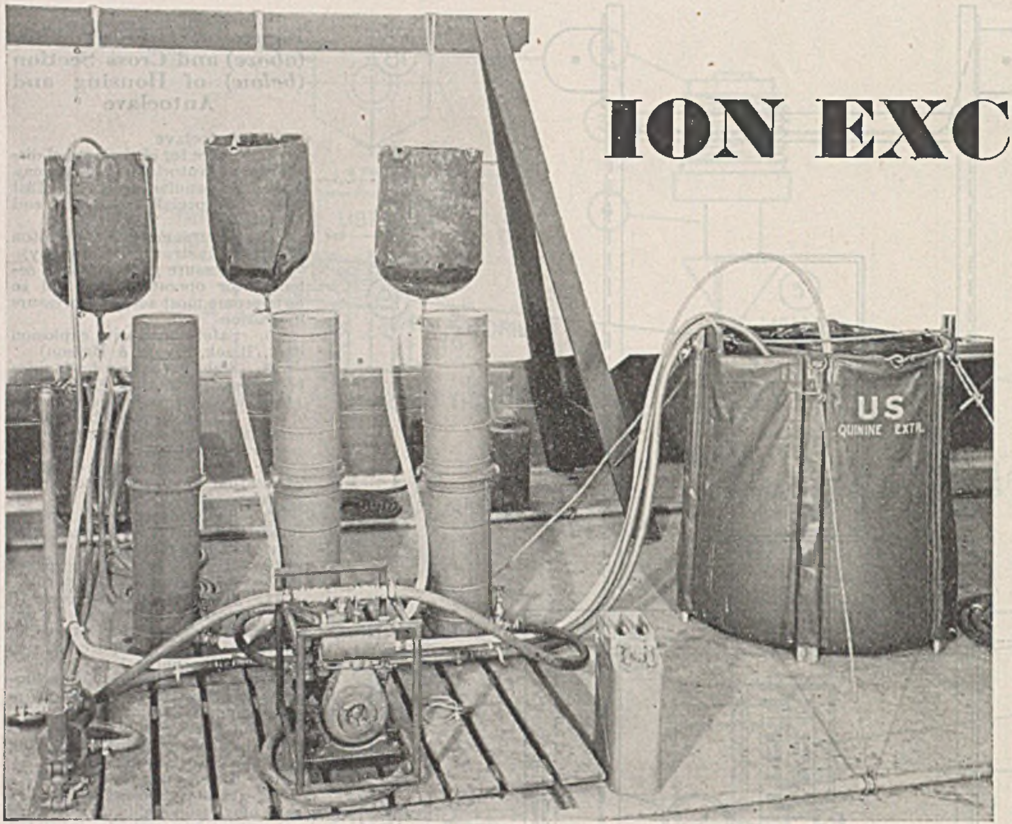
FT. BELVOIR, VA.



The ion exchange adsorption system at the left is part of a portable unit for extracting usable antimalarial from freshly stripped cinchona bark, in the field.

FOLLOWING the loss of the Far Eastern sources of quinine and its raw materials, critical attention was focused on the utilization of South American and other sources of cinchona bark. Unfortunately, the material available in this hemisphere is for the most part much lower in quality and alkaloid content than the East Indian bark. The cost of extracting such low grade bark consequently became a factor of prime importance.

The leaching of cinchona by dilute acid is a simple and inexpensive method of extraction which can be applied to low grade bark (*8*). Recovery of the alkaloids from the aqueous menstruum by alkali precipitation is, however, time consuming and requires relatively large quantities of acid and alkali which are not recoverable. As a possible means for improving the recovery of alkaloids from acid solution, adsorption was investigated.

The use of adsorbents for the removal and recovery of valuable ingredients from dilute solutions is a time-honored technique. It has the advantage that it permits the handling of large volumes of material economically and is often the only way in which concentration of easily destroyed substances can be accomplished.

Many adsorbents have been found useful in removing alkaloids from solution in organic solvents and several have lent themselves to use in aqueous media. Of the latter, activated carbon and the activated clays have been used most successfully. While activated carbon will readily remove alkaloids from aqueous solutions under almost any conditions (*4*), elution of the adsorbate has not proved efficient enough to warrant its general use in alkaloid recovery.

ION EXCHANGE IN ALKALOID RECOVERY

Myers (*9*) suggested that in studying adsorption "it is necessary to analyze for all of the constituents originally present as well as those that may be formed by ion exchange, to determine whether the process is 'physical' adsorption or an ion exchange reaction". The adsorption of alkaloids by clays capable of base exchange might be attributed to a chemical reaction between the "cationic" alkaloid and the insoluble macromolecular acid clay. Lloyd's reagent has been used to remove alkaloids from neutral or acid solutions. The alkaloids were then extracted from the precipitate by means of an alkali and an organic solvent (*7, 12*).

Folin (*6*) in 1917 introduced the use of Permutit, a synthetic siliceous zeolite, for the determination of ammonia in urine by ion exchange. The use of Permutit as a reagent for amines was suggested by Whitehorn (*13*) in 1923. This investigator found that relatively strong nitrogenous bases having a dissociation constant of 5×10^{-9} or greater could be separated from weaker bases and nonbasic substances by exchange with sodium on the zeolite. Oberst used Permutit for the determination of morphine in the urine of morphine addicts (*11*).

While the siliceous zeolites capable of base exchange have enjoyed wide application in commercial water softening for many years, the use of these adsorbents for other purposes has been limited by their instability in acid media. The introduction of sulfonated coals (*2*) and specially treated resins (*1*) which were capable of cation exchange under any conditions of pH and which would effectively exchange with hydrogen opened vast new fields for the application of ion exchange. Thus, while the zeolite clays could be used only at conditions of pH suited to their stability, the hydrogen exchange materials could be used in strongly acid media and under rugged conditions (*10*).

The use of a hydrogen exchange adsorbent to recover quinine from acid solution, the breakthrough capacity of the exchanger for this alkaloid, and the use of ion exchange to concentrate the alkaloids in a totaquine preparation were reported by Applezweig (*3*).

The elutriation of the alkaloids from the exchanger was accomplished by means of alkali regeneration and an organic solvent in a manner similar to that reported by Waldbott (*12*).

The reactions involved may be portrayed in the following manner. Assuming the cation exchanger to be an organic acid

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PROCESS FOR EXTRACTING CINCHONA ALKALOIDS

A cyclic system for the extraction of alkaloids from crude drugs by means of ion exchange has been devised. Alkaloids of cinchona were extracted by dilute acid and recovered by ion exchange with an over-all average yield of 81.2% within an average period of 82 hours. Dried bark from ordinary commercial sources was used. Even greater efficiency may be anticipated when undried bark is utilized. This system thus permits the use of either dry or undried raw material. The process lends itself equally well to either small or large scale operations. The use of portable equipment makes possible the exploitation of formerly inaccessible cinchona stands by drastically reducing the haulage requirements. The economy and simplicity of this method of extraction would seem to forecast its wide application to industrial alkaloid recovery.

with an insoluble nucleus, *In*COOH, whose acid hydrogen is capable of exchange,

$$\mathrm{HOOC}In + \mathrm{Alk{\cdot}H'X} \rightleftharpoons \mathrm{Alk{\cdot}H'OOC}In + \mathrm{HX} \qquad (1)$$

$$\mathrm{Alk{\cdot}H'OOC}In + \mathrm{NaOH} \rightleftharpoons \underline{\mathrm{Alk}} + \mathrm{NaOOC}In + \mathrm{HOH} \qquad (2)$$

The alkaloid which is now in the form of an insoluble base is dissolved out by means of an organic solvent.

This communication also suggested application of this technique to cinchona extraction by means of a cyclic system. Such a system would permit the acid percolate to pass through a column of exchanger and return to the percolator in a continuous fashion. In this way the drug would be constantly exposed to an extraction fluid free from the alkaloids but saturated with respect to noncationic ingredients.

ACID EXTRACTION OF ALKALOIDS

The acid extraction of alkaloids from vegetable material functions through converting the alkaloids from the relatively insoluble form in which they exist as cellular inclusions to the more readily soluble form of their acid salts. Obviously, the rate at which such extraction can take place will depend largely upon the ease with which fresh acid solution can be brought into contact with the substance to be dissolved.

The traditional method of securing thorough and rapid contact between extraction media and such substances is to grind the dry vegetable material to subcellular sizes. However, with a view toward eliminating the tedious and costly process of grinding, the possibility of utilizing the natural vascular structure of plant material was explored. In the dried state it was found that this structure had been considerably altered. Cell walls had lost their permeability, as a result both of alteration in the character of the wall itself and the fact that the cellular contents, gums, resin, etc., had been deposited on the walls in the form of a varnishlike coating. An attempt to treat chips of dry bark by maceration with repeated changes of dilute acid produced an extraction of only 50% of the available alkaloids in 8 days (curve 1, Figure 1).

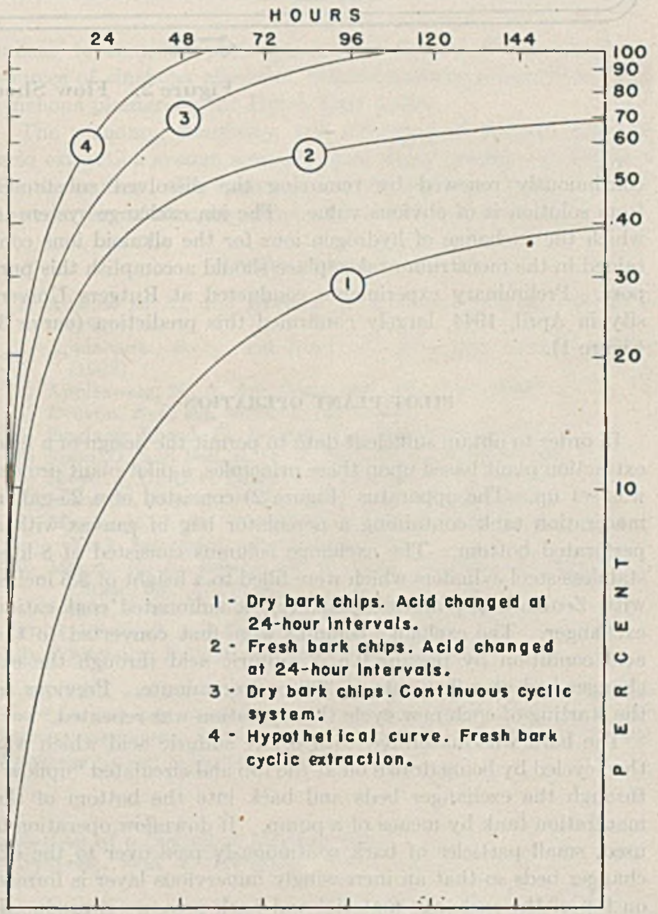


Figure 1. Influence of Bark Condition and Rate of Solvent Renewal on Rate of Extraction of Alkaloids

On the other hand, the vascular structure of fresh or even badly wilted plant material is found to be not seriously impaired. This is demonstrated by the fact that the turgidity of the cell structure of wilted plants can be restored by a period of soaking in water. Experiments conducted in South America on cinchona bark, harvested 2 days before maceration was started, yielded an average of over 60% of their total alkaloids in 4 days of maceration with repeated application of dilute acid (curve 2, Figure 1).

Ideal conditions of extraction would be obtained if a constant flow of fresh acid could be brought in contact with the plant material. To accomplish this purpose by repeated applications of new lots of acid as described above would not be feasible because of the large quantities of chemicals involved. The application of a continuous cyclic system in which the acid concentration is

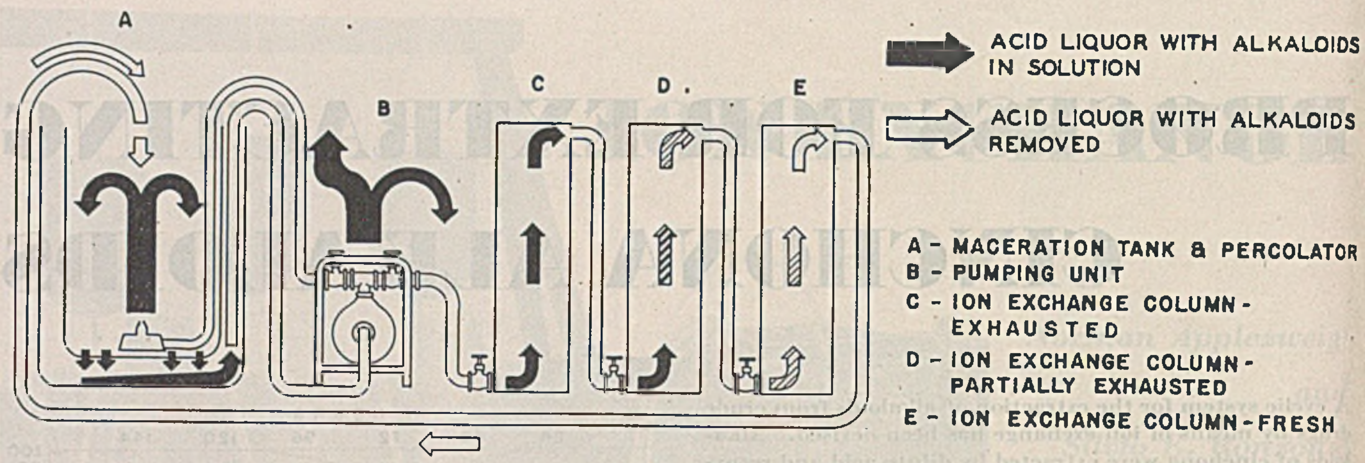


Figure 2. Flow Sheet of Pilot Plant Extraction

continuously renewed by removing the dissolved substances from solution is of obvious value. The ion exchange system in which the exchange of hydrogen ions for the alkaloid ions contained in the menstruum takes place should accomplish this purpose. Preliminary experiments conducted at Rutgers University in April, 1944, largely confirmed this prediction (curve 3, Figure 1).

PILOT PLANT OPERATION

In order to obtain sufficient data to permit the design of a field extraction plant based upon these principles, a pilot plant project was set up. The apparatus (Figure 2) consisted of a 25-gallon maceration tank containing a percolator bag of canvas with a perforated bottom. The exchange columns consisted of 8-liter stainless steel cylinders which were filled to a height of 8.5 inches with ZeoKarb (Permutit Company), a sulfonated coal cation exchanger. The exchange columns were first converted to the acid condition by passing 0.5 *N* sulfuric acid through the exchanger bed at a flow rate of 300 cc. per minute. Previous to the starting of each new cycle this operation was repeated.

The bark was macerated with 0.1 *N* sulfuric acid which was then cycled by being drawn off at the top and circulated "upflow" through the exchanger beds and back into the bottom of the maceration tank by means of a pump. If downflow operation is used, small particles of bark continuously pass over to the exchanger beds so that an increasingly impervious layer is formed on top of the exchange material and back pressure is produced. If a line filter is used to prevent particles from passing into the exchange columns, pressure soon builds up in the filter. To avoid the added weight in power plant and other equipment necessary for operation under pressure, upflow circulation was employed throughout the system. Pieces of bark drawn from the maceration tank passed harmlessly through the entire system and returned to the tank.

Sufficient bed capacity was provided to permit effective exchange in spite of any channeling which might result from upflow operation. Circulation was started with three columns in the line, the first being removed when saturated and a fourth added when necessary.

When the cycles were completed, or a column was filled to capacity as determined by a Mayers test of the influent and effluent, regeneration of the exchanger was undertaken. This was accomplished by treating each column with 12 liters of 0.5 *N* sodium hydroxide. The hydroxide was passed through the columns very slowly (less than 300 cc. per minute). This regeneration was followed by a fast rinse for a few minutes with water for the purpose of removing excess alkali which would be concentrated in the subsequent distillation. The water rinse also performed the function of removing a great deal of coloring matter which is released by the alkali regeneration. This coloring matter consists almost wholly of materials extracted from the cinchona bark, and assay showed that it contained only a small amount of alkaloid. Such alkaloid as was found in samples of colored solids recovered from rinse water would easily be accounted for by the water solubility of the basic alkaloids. In this connection, it is desirable to continue the water rinse no longer than is necessary to prevent any harmful accumulation of alkali in the end product. Prolonged washing could remove a significant portion of the basic alkaloids.

Following the alkali regeneration, the exchanger was stripped of its alkaloid content by displacing the aqueous contents of the bed with 3 liters of alcohol, cycling 8 liters of alcohol for 2 hours, and finally displacing with 3 liters of alcohol which was, in turn, displaced by water. The first 2 liters of water were collected for the purpose of salvaging the alcohol content.

After the alkali regeneration and water rinse no trace of the freed alkaloids could be detected within the bed or upon the surface of the granules of ion exchanger. It is apparent that the alkaloid is very finely dispersed and still in close contact with the ion exchanger. The aqueous alcoholic solution of alkaloids was then treated further by distillation to remove the alcohol and the resulting heavy concentrate evaporated to dryness. The residue was weighed and assayed for total alkaloid content.

As Table I shows, over-all average yield of alkaloids was 81.2% in an average maceration period of 82 hours. Ion exchange functioned as a recovery system with an average efficiency of 98.6%. The solid material thus produced varied in alkaloid content from 40 to over 80% and in color from light pink to very dark red, depending upon the nature and quantity of the nonalkaloidal constituents. Since one of the principal objectives of the research program was to develop a usable antimalarial, totaquine, further rectification seemed necessary.

TABLE I. ALKALOID YIELD FROM ION EXCHANGE PROCESS

Expt. No.	Total Time, Hr.		Total Alkaloid Extd., %[a]	Efficiency of Recovery, %[b]	Over-all Recovery, %[c]
	Maceration	Circulation			
1	76	20	..	..	63
2	76	20	64	100	76
3	76	20	90	96	86
4[d]	100	20	93	96	100
Av.	82	20	82.3	98.6	81.2

[a] Computed on basis of total alkaloid content of spent bark.

[b] Percentage of extracted alkaloids recovered.

[c] Computed on basis of total alkaloid content of original bark.

[d] The high recovery in expt. 4 is explained by the fact that complete recovery is not achieved within each cycle and residues accumulate on the exchanger which appear in subsequent cycles.

For this purpose the crude alkaloid concentrate was dissolved, to saturation, in 1 *N* hydrochloric acid. The saturated solution was carefully adjusted by the addition of alkali to a pH of 6.5. At this point much of the coloring matter and other extraneous material was precipitated and removed on a filter. The pH was further adjusted by the same means to the point where a heavy white floc appeared. This precipitate was removed on a filter and constituted the rectified totaquine (Table II).

Table II. Rectification of Crude Alkaloid Concentrate

Process No.	1[a]	2[b]	3[c]
Wt. crude material, g.	50.0115	50.0447	50.0028
Wt. alkaloid in crude material, g.	39.1038	38.0986	38.0971
Total solids recovered, g.	31.0396	32.1166	26.5680
Wt. of alkaloid recovered, g.	29.3635	29.6468	24.5435
Wt. of alkaloid remaining in soln., g.	8.7403	8.4518	13.5536
Recovery, %	77.06	78.71	64.42
Total alkaloids in:			
Crude totaquine, %	76.19	76.19	76.19
Rectified totaquine, %	94.60	92.31	92.38
Ash from rectified totaquine, %	5.38	4.15	8.25

[a] Cold process, precipitated from H_2SO_4 at pH 9 by NaOH, total volume 3000 cc.

[b] Cold process, precipitated from HCl at pH 9 by NH_4OH, total volume 3000 cc.

[c] Hot process, precipitated from hot (80° to 90° C.) HCl at pH 9 by NaOH, total volume 3000 cc.

Even under close laboratory control, approximately 20% of the alkaloids remained in solution in spite of adjustment of pH (Table I). Computations involving the solubilities of the natural basic alkaloids indicate that losses of this magnitude are to be expected. To recover this valuable material, the ion exchange unit was again brought into use. The alkaloid-bearing liquor was merely reacidified by the addition of a small quantity of concentrated acid and then circulated through the ion exchange columns; the residual liquor, stripped of its alkaloids, was run to waste.

By this means totaquine can be produced which conforms to specifications for the product in so far as purity is concerned. The proportions of the various crystallizable alkaloids will naturally depend upon their proportions in the original bark.

DISCUSSION

That acid extraction is an economical method for cinchona alkaloid production was demonstrated by Marañon and coworkers (*8*). The adaptation of acid extraction to field production units by the Engineer Board research group of the Army has further extended the usefulness and economy of this method by permitting the utilization of fresh bark and thus avoiding the losses and much of the expense due to drying, grinding, and shipping.

The application of ion exchange to the acid extraction system brings its over-all efficiency and economy to a point where it can compare favorably with any of the commercial methods now in use. The quantity of chemicals and the bulk of equipment are considerably lower than the original acid extraction–alkali precipitation system (*5*). The process therefore lends itself as well to small scale field production as to use in large scale permanent installations.

Since field production will permit the exploitation of formerly inaccessible stands of cinchona, it should be possible by this means to continue profitable exploitation of South America's sources of cinchona alkaloids, despite postwar competition from cinchona planters in the Dutch East Indies.

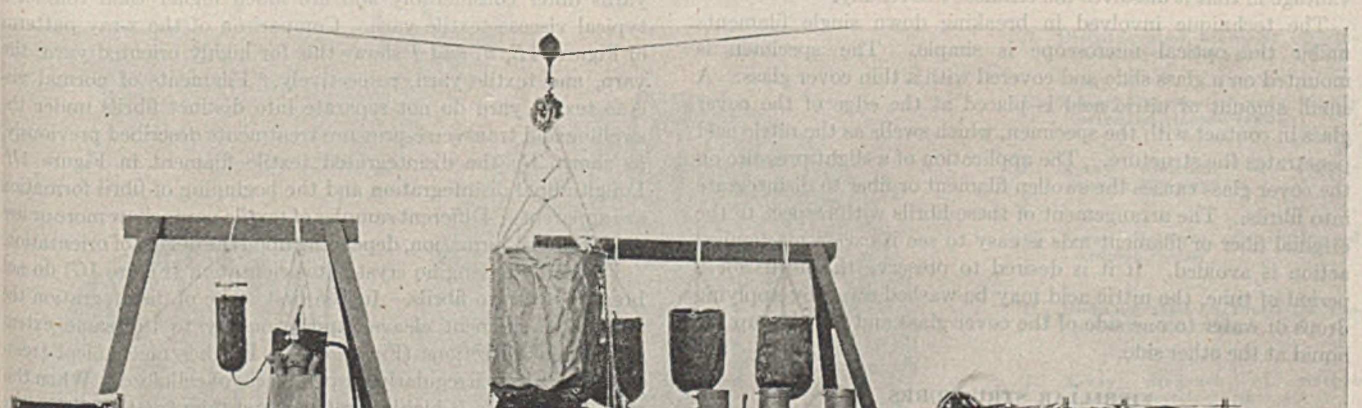
The economy, simplicity, and efficiency of the ion exchange acid extraction system seems to open many possible applications for the process. Ion exchange has already been found useful in the recovery of atropine, scopolamine, and morphine (*3*).

LITERATURE CITED

(1) Adams, B. A., and Holmes, E. L., *J. Soc. Chem. Ind.*, 54, 1 (1935).
(2) Applebaum, S. S., and Riley, R., Ind. Eng. Chem., 30, 80 (1938).
(3) Applezweig, N., *J. Am. Chem. Soc.*, 66, 1990 (1944).
(4) Drevon, *Bull. soc. chim.*, 7, 732 (1940).
(5) Engineer Board, Ft. Belvoir, Va., *Rept.* 940 (1945).
(6) Folin, O., and Bell, R. D., *J. Biol. Chem.*, 29, 329 (1917).
(7) Lloyd, J. U., U. S. Patent 1,300,747 (April 15, 1919).
(8) Marañon, J., *et al.*, *Philippine J. Sci.*, 56, 242 (1935).
(9) Myers, R. J., in "Advances in Colloid Science", Vol. I, New York, Interscience Publishers, 1942.
(10) Myers, R. J., Eastes, R. W., and Urquhart, D., Ind. Eng. Chem., 33, 1270 (1941).
(11) Oberst, F. W., *J. Lab. Clin. Med.*, 24, 318 (1938).
(12) Waldbott, *J. Am. Chem. Soc.*, 27, 8 (1905).
(13) Whitehorn, J. C., *J. Biol. Chem.*, 56, 751 (1923).

Data, charts, and illustrations from the laboratory reports of the Engineer Board are used with permission of the Chief of Engineers, U. S. Army. Preliminary experiments in this investigation were carried out at Rutgers University College of Pharmacy, Newark, N. J.

Portable Quinine Extraction Unit, Consisting of a Series of Maceration Tanks, an Ion Exchange Adsorption System, and a Distilling Unit



Fibrillar Structure of Rayon Fibers

L. M. WELCH AND W. E. ROSEVEARE
E. I. du Pont de Nemours & Company, Inc., Richmond, Va.

H. MARK
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A method has been developed for breaking down rayon filaments into fibrils which may be seen with the optical microscope. Photomicrographs and x-ray diffraction patterns illustrate the differences in the structure of rayon filaments having various degrees of crystallite orientation. The fibrillar structures of highly oriented rayons are compared to those of cotton linters and ramie.

FIBERS of natural cellulose are known to break down into fibrils under the action of chemical agents or by mechanical disintegration (*3*, *6*, *7*). In studying the action of swelling agents on rayon with the optical microscope, it was found that certain types of rayon filaments break down into fibrils similar in appearance to those of the natural fibers, except for the spiral arrangement found in the latter. Similar fibrillar structures in Lilienfeld and other high-tenacity cellulose yarn have been described (*3*, *10*). Formerly, fibrillar structures were believed to exist only in natural fibers (*8*). A method of fibrillation and its application to various cellulosic fibers are described in this paper.

Several swelling agents—cuprammonium, sodium hydroxide, and sulfuric acid—which have been used (*2*, *6*) in studying the fibrillar structures of natural cellulose fibers, may be used in breaking down rayon filaments; however, the tendency for complete solution with these reagents led to the trial of other swelling agents. Seventy per cent nitric acid was found to be very satisfactory. This solution does not nitrate at room temperature but forms an addition compound (*5*) with cellulose and has an advantage in that it dissolves the cellulose less readily.

The technique involved in breaking down single filaments under the optical microscope is simple. The specimen is mounted on a glass slide and covered with a thin cover glass. A small amount of nitric acid is placed at the edge of the cover glass in contact with the specimen, which swells as the nitric acid penetrates the structure. The application of a slight pressure on the cover glass causes the swollen filament or fiber to disintegrate into fibrils. The arrangement of these fibrils with respect to the original fiber or filament axis is easy to see if excess mechanical action is avoided. If it is desired to preserve the fibrils for a period of time, the nitric acid may be washed away by applying drops of water to one side of the cover glass and blotting up the liquid at the other side.

FIBRILLAR STRUCTURES

The use of this technique on rayon fibers has shown differences in the structure of the following rayons having varying orientations: very highly oriented viscose and saponified acetate yarns, highly oriented viscose tire yarn, viscose textile yarn, and unoriented viscose yarn, having tenacities about 5, 5, 3.7, 1.8, and 1.0 gram per denier, respectively.

Figure 1*A* is a single filament of a highly oriented viscose rayon swollen in 70% nitric acid. This filament shows a longitudinal split with fibrils crossing from one side to the other before receiving any mechanical treatment. The application of pressure disintegrates the filament further and reveals clearly the fibrillar structure, as shown in Figure 1*B*. In this fiber the fibrils are oriented approximately parallel to the filament axis.

Filaments of high-tenacity saponified cellulose acetate yarns, as well as those of highly oriented viscose rayons, are characterized by spontaneous splitting when swollen in 70% nitric acid. In the initial stages of disintegration under the application of low pressures, the fibrils appear to be oriented parallel to the fiber axis. The principal difference between these two types is the fewer crossovers of the fibrils in the saponified cellulose acetate filaments, indicating a higher orientation of fibrils in the latter case. Figure 1*C* shows a single filament of a high-tenacity saponified cellulose acetate yarn broken down into fibrils.

Figure 1*D* shows the fibrillar structure of a viscose yarn for tire cords (*1*) having a degree of orientation somewhat lower than that for the two samples mentioned previously. Filaments of the tire yarn do not split spontaneously on swelling, but rather the fibrils tend to stick together. With the application of pressure the swollen filament first separates into comparatively large filamentlike structures, which can be divided further into fibrils. On the other hand, filaments of the more highly oriented viscose and the saponified cellulose acetate yarns break down into fibrils of fairly uniform size, in the first stage of mechanical disintegration.

The crystallite orientations of the above-mentioned viscose yarns differ considerably and are much higher than that of a typical viscose textile yarn. Comparison of the x-ray patterns of Figures 1*E*, *F*, and *I* shows this for highly oriented yarn, tire yarn, and textile yarn, respectively. Filaments of normal viscose textile yarn do not separate into distinct fibrils under the swelling and transverse-pressure treatments described previously, as shown by the disintegrated textile filament in Figure 1*H*. Longitudinal disintegration and the beginning of fibril formation are apparent. Different samples of textile yarns show more or less distinct fibril formation, depending upon the degree of orientation.

Filaments having no crystallite orientation (Figure 1*G*) do not break down into fibrils. In the first stage of disintegration the unoriented filament cleaves approximately to the same extent in different directions (Figure 1*K*). Further mechanical treatment gives only irregularly shaped pieces of cellulose. When this regenerated yarn is highly stretched and then treated with nitric acid, the filament tends to break longitudinally, and the beginning of fibril formation is apparent (Figure 1*J*).

The same viscose and spinning bath conditions were used in spinning the filaments shown in Figures 1*B* and *K*. Therefore, the differences in breakdown structures of these filaments are attributed to the different stretching treatments of the extruded filaments. A comparison of the x-ray diffraction patterns and

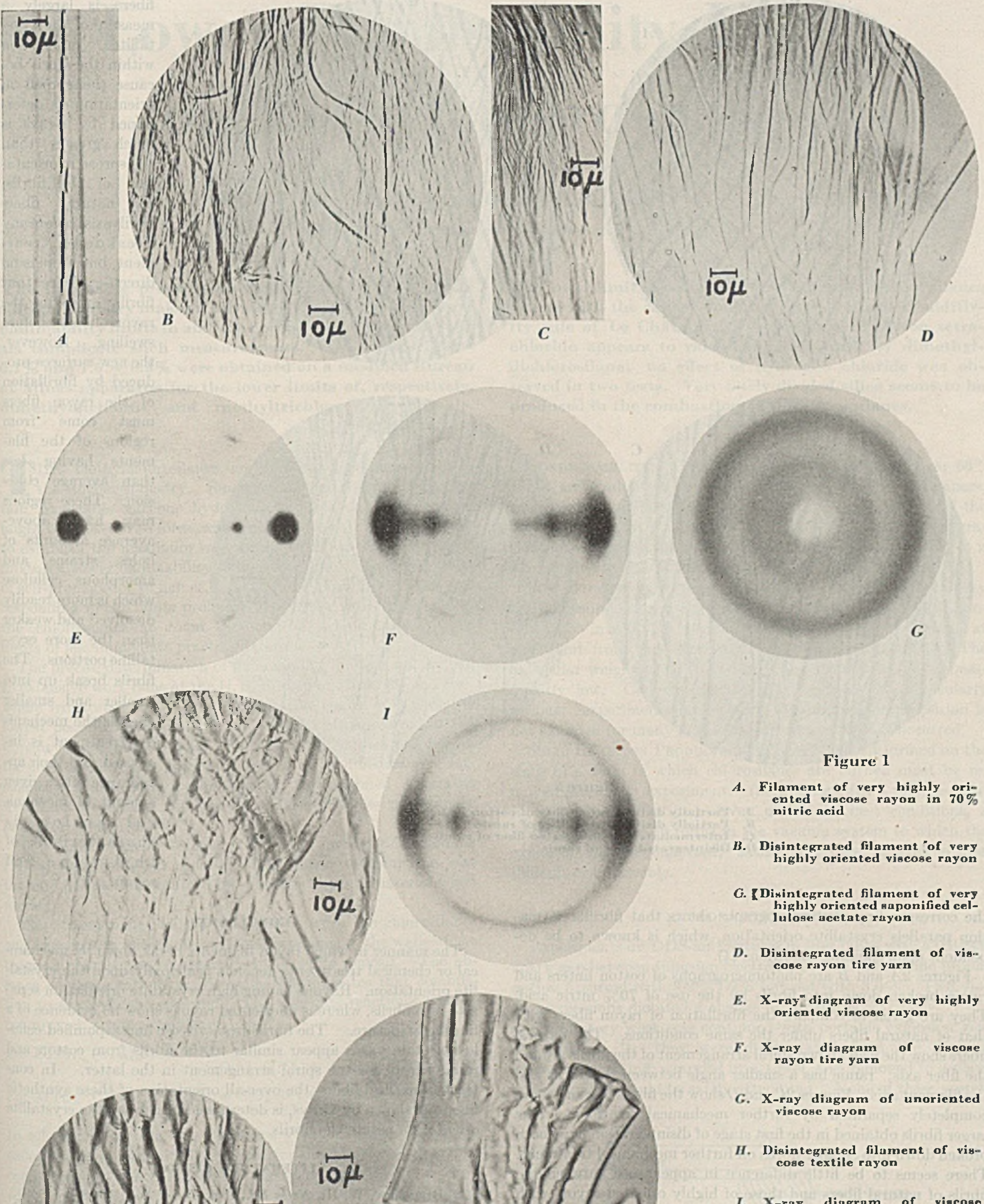

Figure 1

A. Filament of very highly oriented viscose rayon in 70% nitric acid

B. Disintegrated filament of very highly oriented viscose rayon

C. Disintegrated filament of very highly oriented saponified cellulose acetate rayon

D. Disintegrated filament of viscose rayon tire yarn

E. X-ray diagram of very highly oriented viscose rayon

F. X-ray diagram of viscose rayon tire yarn

G. X-ray diagram of unoriented viscose rayon

H. Disintegrated filament of viscose textile rayon

I. X-ray diagram of viscose rayon textile yarn

J. Filament of unoriented viscose rayon after stretching and partial disintegration

K. Partially disintegrated filament of unoriented viscose rayon

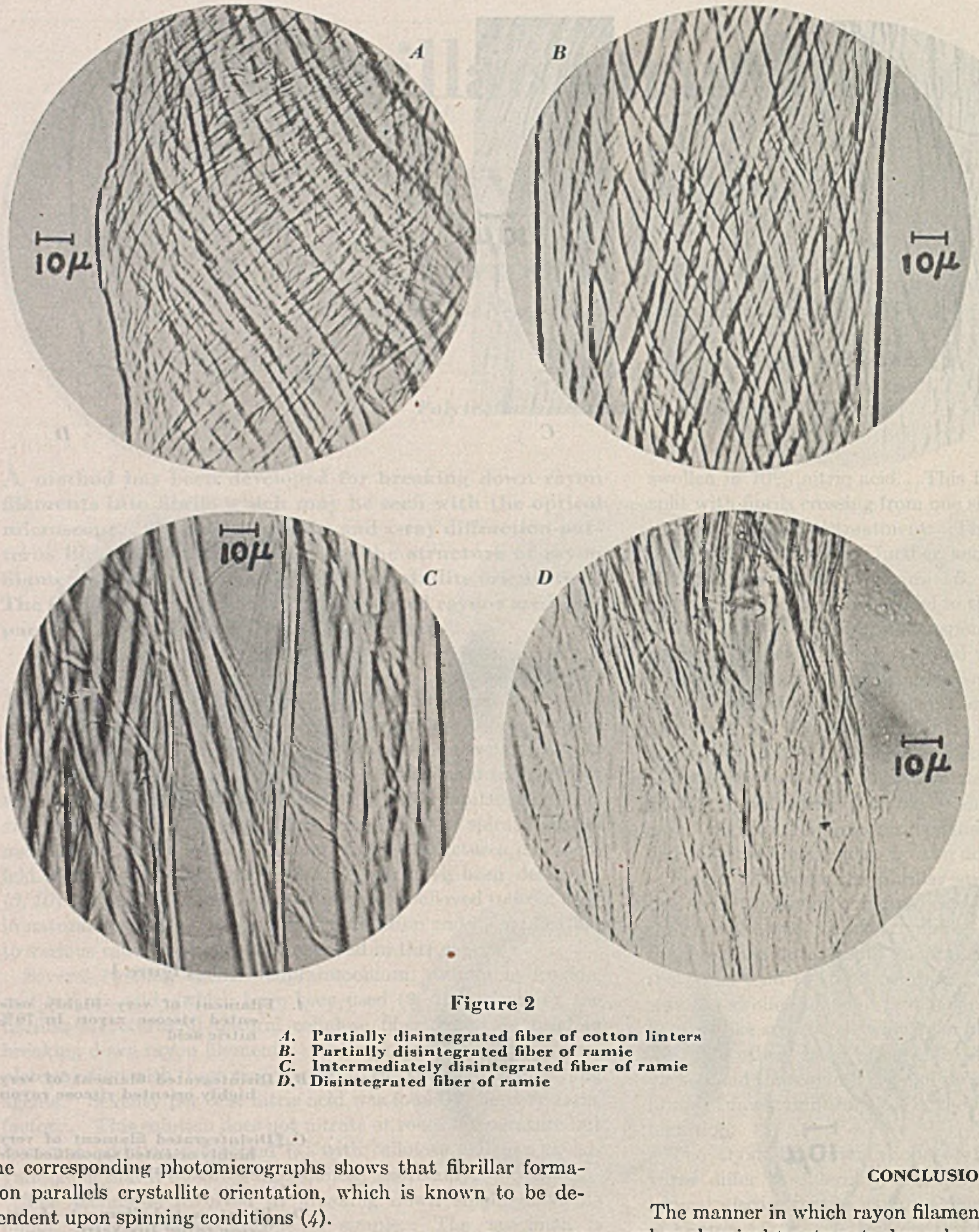

Figure 2

A. **Partially disintegrated fiber of cotton linters**
B. **Partially disintegrated fiber of ramie**
C. **Intermediately disintegrated fiber of ramie**
D. **Disintegrated fiber of ramie**

the corresponding photomicrographs shows that fibrillar formation parallels crystallite orientation, which is known to be dependent upon spinning conditions (*4*).

Figures 2*A* and *B* are photomicrographs of cotton linters and ramie broken down into fibrils by the use of 70% nitric acid. They are given to compare the fibrillation of rayon fibers with that of natural fibers under the same conditions. The natural fibers show the well known spiral arrangement of the fibrils around the fiber axis; ramie has a smaller angle between the fibrils and the filament axis. Figures 2*C* and *D* show the fibrils of ramie more completely separated by further mechanical treatment. The larger fibrils obtained in the first stage of disintegration have been broken down into smaller fibrils on further mechanical treatment. There seems to be little difference in appearance between the fibrils of natural fibers and those of highly oriented rayon, with the exception of orientation (Figures 1*B* and 2*D*).

The orientation observed by means of x-rays in the highly oriented viscose fibers is comparable with that observed in ramie fibers. The crystallite orientation within a fibril of natural cellulose is thought to be almost completely parallel to the axis of the fibril, so that the over-all crystallite orientation of natural fibers is determined by the fibrillar orientation (*9*). On the other hand the over-all orientation of the crystallites in these synthetic fibers is largely a measure of the crystallite orientation within the fibril because the spread in orientation as determined by x-rays is much greater than the spread in orientation of the fibrils. In natural fibers fibrils exist before any breakdown treatment, but there is no direct evidence that fibrils exist in the rayon fibers before swelling. However, the new surfaces produced by fibrillation of the rayon fibers must come from regions of the filaments having less than average cohesion. These regions may have above-average amounts of holes, strains, and amorphous cellulose which is more readily dissolved and weaker than the more crystalline portions. The fibrils break up into smaller and smaller ones as the mechanical treatment is increased, but their appearance with a given amount of mechanical action is characteristic of the type of rayon.

CONCLUSION

The manner in which rayon filaments break down by mechanical or chemical treatments depends principally upon the crystallite orientation. Rayons having high crystallite orientation separate into fibrils, whereas unoriented rayons show no evidence of a fibrillar structure. The fibrils from viscose and saponified cellulose acetate yarns appear similar to the fibrils from cotton and ramie except for the spiral arrangement in the latter. In contrast to natural fibers, the over-all orientation of these synthetic fibers, as shown by x-rays, is determined largely by the crystallite orientation within the fibrils.

LITERATURE CITED

(1) Bradshaw, W. H., *News Ed., Am. Chem. Soc.*, 18, 814 (1940).
(2) Denham, H. J., Shirley Inst. Mem., 2, 61 (1923).
(3) Eisenhut, O., and Kuhn, E., *Angew. Chem.*, 55, 198 (1942).
(4) Krebs, G., *Kolloid-Z.*, 98, 200 (1942).
(5) Meyer, K. H., "Natural and Synthetic High Polymers", New York, Interscience Publishers, 1942.
(6) Pennetier, G., *Bull. soc. ind. Rouen*, 1883, 235.
(7) Rollins, M. O., *Textile Research*, 15, 65 (1945).
(8) Schwarz, E. R., *Ibid.*, 13, No. 4, 4 (1943).
(9) Sisson, W. A., *Contrib. Boyce Thompson Inst.*, 9, 239 (1938).
(10) Wallner, L., *Melliand Textilber.*, 23, 261 (1942).

Lower Flammability Limits of Methylchlorosilanes

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The increasing prominence of the chlorosilanes in the silicone industry makes it advisable to measure their lower flammability limits in air. The properties of these materials complicate such measurements. The values 3.4 ± 0.1% and 7.6 ± 0.3% were obtained on a modified Bureau of Mines apparatus for the lower limits of, respectively, dimethyldichloro- and methyltrichlorosilane in air. The lower limit measured for one mixture of these silanes agreed with the value calculated by the reciprocal additivity rule of Le Châtelier. The presence of silicon tetrachloride appears to raise the lower limit of dimethyldichlorosilane; no effect of hydrogen chloride was observed in two tests. Very finely divided silica seems to be produced in the combustion of the chlorosilanes.

THE methylchlorosilanes are important intermediates in the silicone industry. Since these volatile compounds contain oxidizable carbon, hydrogen, and silicon, their vapors might be expected to form explosive mixtures with air. In order to establish the maximum safe concentration in certain of these mixtures, lower flammability limits (more precisely, lower limits of self-propagation of flames, *3*) have been determined. The corresponding upper limits probably exceed the vapor pressures of the chlorosilanes at room temperature, which makes these limits of less immediate practical interest.

The precise determination of flammability limits is not simple, as extensive work done at the U. S. Bureau of Mines (*2*) and elsewhere will testify. The only conservative course is to seek the lowest possible lower limit, which the apparatus evolved at the bureau is designed to yield. Because of difficulties peculiar to the chlorosilanes, this apparatus had to be modified to give satisfactory results. Determinations on the modified apparatus were time consuming, and it proved advisable to design a simpler setup for exploratory work.

The dimethyldichlorosilane (DDS) and methyltrichlorosilane (MTS) were of good quality. The silicon tetrachloride was the middle fraction obtained by distilling the C.P. material when needed.

The stoichiometry of the reactions between the chlorosilanes and oxygen was not studied. In all experiments the walls of the reaction chamber were covered with a white deposit. The absence of discolorations in these deposits indicates that combustion to silica always occurred. The following reactions, though not proved, are reasonable:

$$\text{For DDS:}\quad (CH_3)_2SiCl_2 + 4O_2 = SiO_2 + 2CO_2 + 2HCl + 2H_2O \qquad (1)$$

$$\text{For MTS:}\quad CH_3SiCl_3 + 2O_2 = SiO_2 + CO_2 + 3HCl \qquad (2)$$

In all except one or two preliminary experiments, enough oxygen was initially present for the complete combustion of the chlorosilanes according to these equations.

The following properties of the chlorosilanes make it unusually difficult to measure the lower flammability limits of their mixtures with air:

REACTIVITY. The chlorosilanes react readily with water; other materials, such as paper and rubber, deteriorate in their presence. Stopcocks, lubricated or not, are liable to freeze if their bearing surfaces are exposed to chlorosilane vapors.

CONDENSABILITY. DDS boils near 70° C.; MTS, near 66°. When air is admitted to vertical tubes containing their vapors, condensation by compression is likely to occur, especially if the tube is narrow or contains only chlorosilanes near their saturation pressures, and if air is admitted suddenly from the top in a stream directed down the axis of the tube.

LOW DIFFUSIVITY. A precise determination of flammability limits presupposes thorough mixing; for example, the MTS concentration in an 8% mixture of that substance must not differ at any point from this over-all value by more than 0.1%. The molecular weight of MTS is 149.5, and its diffusivity is consequently low. Condensation of MTS is therefore particularly serious; experiments have shown that uniform composition is not attained for many hours, once condensation has occurred.

SOLID REACTION PRODUCTS. The white deposit formed on the walls of a tube in which chlorosilanes are burned must be removed after each experiment. (Scrubbing with a toluene-saturated cloth is effective.) Even under the best conditions, a white film eventually forms in the vacuum system to which the explosion tube is connected; satisfactory glass blowing is then difficult or impossible.

EXPLORATORY WORK

Experiments on DDS-air mixtures in liter bulbs with a 0.3-cm. spark gap between tungsten electrodes showed that flame propagation occurred with 3.2% DDS but not with 3.0%. Two violent explosions dictated a change of apparatus.

Exploratory work was continued with portable explosion vessels (Figure 1); they were disconnected from the vacuum system after filling, wrapped in a towel, and removed to a place where ignition could be safely attempted. None of these vessels

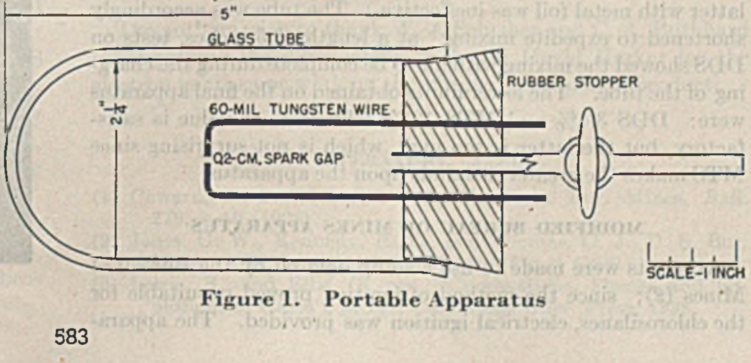

Figure 1. Portable Apparatus

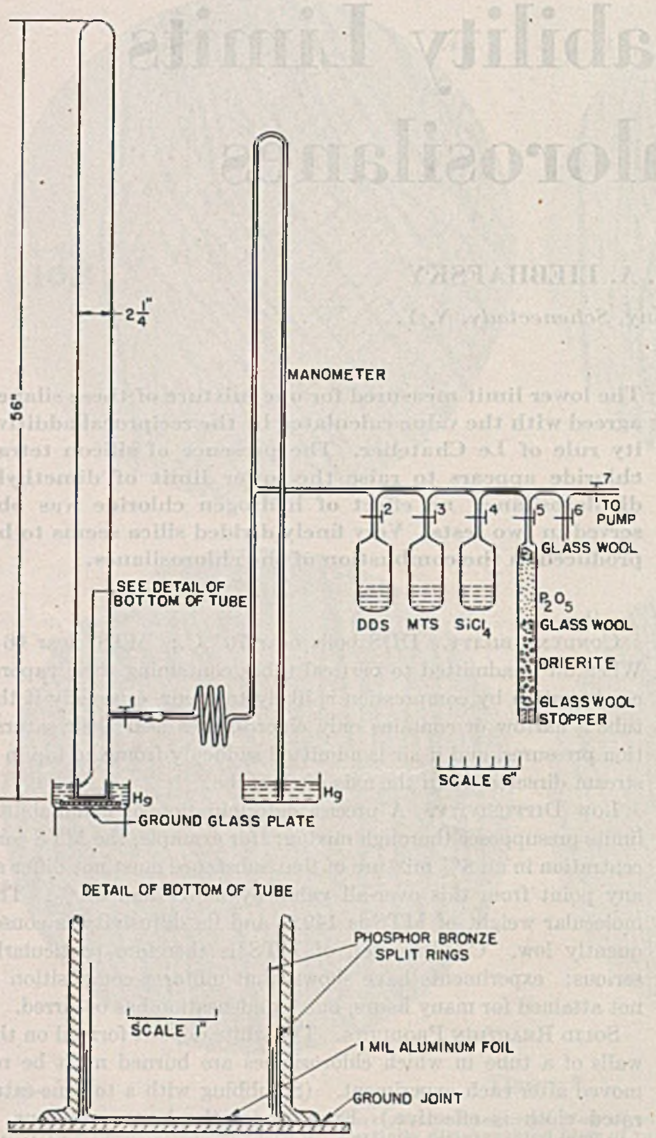

Figure 2. Diagram of Modified Bureau of Mines Apparatus

TABLE I. CHARGING OF TUBE (FIGURE 2) WITH KNOWN DDS-MTS-AIR MIXTURE

Operation No.	Open Stopcocks	Closed Stopcocks	Operation
1	1, 7	2, 3, 4, 5, 6	Pump out
2[a]	2, 7	1, 3, 4, 5, 6	Pump out
3[a]	3, 7	1, 2, 4, 5, 6	Pump out
4	1, 2, 3, 7	4, 5, 6	Finish pumping down
5[b]	1, 2, 3	4, 5, 6, 7	Determine leak rate over 5 min.
6	1, 2, 3, 7	4, 5, 6	Pump down again; read manometer (equals barometric pressure)
7[b]	1, 3	2, 4, 5, 6, 7	Remove cooling mixture from DDS and MTS reservoirs; warm MTS reservoir to desired pressure; apply leak correction from operation 5; MTS now in tube
8	7	1, 2, 3, 4, 5, 6	Pump down
9	2	1, 3, 4, 5, 6, 7	Warm DDS reservoir to a pressure greater than MTS pressure in tube
10	1, 2	3, 4, 5, 6, 7	Admit DDS to tube to desired pressure; apply leak correction from operation 5
11	7	1, 2, 3, 4, 5, 6	Pump down
12	5	1, 2, 3, 4, 6, 7	Admit dry air to system
13	1, 5	2, 3, 4, 6, 7	Adjust stopcock 1 so that mercury in manometer rises 1 cm.; readjust to maintain this pressure difference until total pressure in explosion tube approaches atmospheric; open stopcock wide to obtain atmospheric pressure in tube
14			Close stopcock 1 and admit dry air to DDS and MTS reservoirs in turn

[a] Liquids in reservoirs are permitted to boil for purging; they are then cooled to solid CO_2–acetone temperatures as evacuation is continued.

[b] Highest leak rate observed was 0.04 cm. of Hg per minute (Table II, No. 7B); in the other tests of Tables II and III the leaks were negligible.

broke, the rubber stopper being ejected when ignition did occur; only mixtures near the flammability limit were tried.

The first portable vessels were short-necked glass bulbs. Ignition occurred in these bulbs for 4.0% DDS at diameters of 2, 3, and 5 inches, which indicates that the lower limit for DDS cannot be very sensitive to the diameter above 2 inches.

After tests with longer tubes, the apparatus of Figure 1 was finally adopted. The longer tubes gave erratic results. If ignition was attempted immediately upon removal from the vacuum system, mixing was incomplete; during a wait for complete mixing, the chlorosilane reacted with the stopper. (Protecting the latter with metal foil was ineffective.) The tube was accordingly shortened to expedite mixing; at a length of 5 inches, tests on DDS showed the mixing with air to be complete during the charging of the tube. The lower limits obtained on the final apparatus were: DDS 3.4% and MTS 10%. The former value is satisfactory, but the latter is too high, which is not surprising since MTS makes the greater demands upon the apparatus.

MODIFIED BUREAU OF MINES APPARATUS

Attempts were made to use a setup devised by the Bureau of Mines (*2*); since the method of ignition proved unsuitable for the chlorosilanes, electrical ignition was provided. The apparatus as changed gave good results with hydrogen but not with the chlorosilanes. Some of the difficulties were: (*a*) condensation invariably occurred when air was admitted, (*b*) the presence of hydrolysis products around the mouth of the tube showed that chlorosilanes began to pour out as the plate was removed prior to attempts at ignition, and (*c*) chlorosilanes were probably lost to the mercury in the pump. Further changes in the apparatus and method of ignition were made to meet these difficulties.

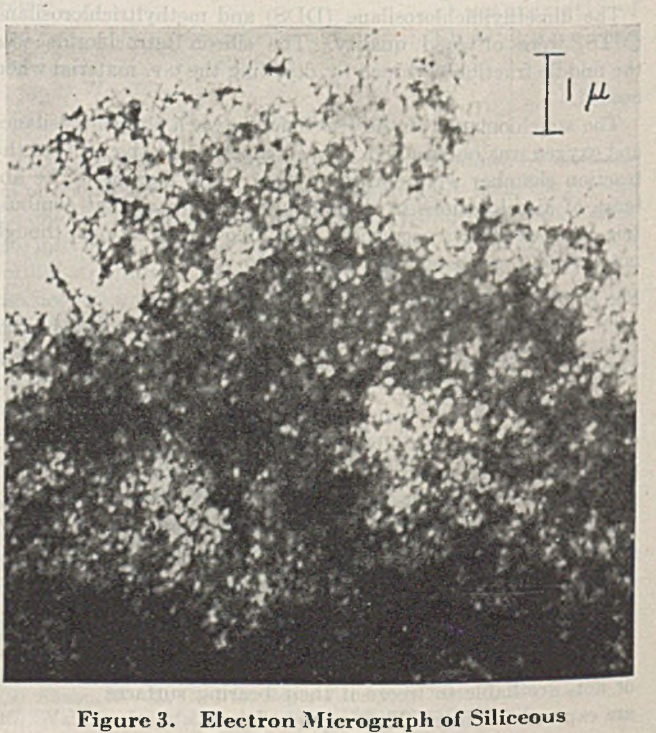

Figure 3. Electron Micrograph of Siliceous Combustion Product

Table II. Lower Flammability Limits for Chlorosilanes in Air

Chlorosilane	No.	% by Vol.	Hr. of Standing	Flame Propagation
Dimethyldichloro- (DDS)[a]	1A	3.72	40	Yes
	2A	3.45	6	Yes
	3A	3.16	16	No
	4A	3.31	6	No
	5A	3.46	16	Yes
	6A	3.32	6	No
Methyltrichloro- (MTS)[b]	1B	9.3	16	Yes
	2B	8.6	6	Yes
	3B	7.3	16	No
	4B	8.0	5	Yes
	5B	7.6	16	No
	6B	7.9	5	Yes
	7B[c]	7.8	40	No
	8B	7.8	5	No
	9B[d]	7.9	16	No
	10B	8.7	5	Yes
	11B	7.8	6	Yes
Mixt. of DDS-MTS[e]	1C	4.15	16	Yes
	2C	3.86	6	No
	3C	3.99	16	Yes
	4C	3.97	6	Yes
	5C	3.84	22	No

[a] Lower flammability limit, 3.4 ± 0.1% DDS, the mean of 3.46% (No. 5A) and 3.31% (No. 4A).

[b] Lower flammability limit, 7.6 ± 0.3% MTS (arbitrary choice).

[c] Loss of MTS probable; mercury added to give 5 cm. head near mouth of tube.

[d] Leak observed; plate reground after experiment.

[e] Chlorine, 60% by weight. Mole fractions, DDS 0.719 and MTS 0.281; lower flammability limit, 3.9% mixture.

The modified apparatus finally developed (Figure 2) differs as follows from the original: Air is admitted from the side at the bottom, instead of from the center at the top; this change eliminated condensation. Complete mixing is obtained by waiting a minimum of 5 hours instead of with a mercury pump. A 1-mil aluminum foil held between phosphor bronze split rings is added to eliminate the loss of chlorosilanes from the tube prior to ignition (Figure 2). The ignition source is a fine oxyhydrogen flame that cuts instantly through the foil, a wooden support, the vessel of mercury, and the glass plate having been removed.

The steps required to fill the tube for a run are given in Table I. Pure materials were used in all tests, and concentrations were calculated directly from the pressures measured after the admission of each component to the tube. After 5 hours or longer, ignition of the mixture was attempted in a darkened room to see whether flame propagation occurs. The tube was then dismounted, swabbed out with toluene, and set up for the next run.

The substances added to DDS (Table III) were introduced as follows: Silicon tetrachloride from a reservoir, as though a DDS-MTS mixture were being made, and hydrogen chloride from a gas cylinder through stopcock 6.

RESULTS AND DISCUSSION

Data for various chlorosilane-air mixtures are given in Table II. When flame propagation occurs in a darkened room, a dazzling white hemisphere, equator downward, moves up the tube and reaches the top in several seconds. Incandescent silicalike particles appear to be responsible for the dazzling whiteness. As the flame progresses, the walls in the burned zone become covered with a white deposit. Large white flocs of silicalike material float downward for about a minute after the flame has traveled the full length of the tube.

The flocculent material produced by the combustion of DDS was examined in the electron microscope (Figure 3). The material appears to be a loose three-dimensional network of very fine, adhering particles. The average diameter of these particles, less than 100 Å., is many times smaller than that attained by grinding silica.

In mixtures just below the flammability limit, combustion without flame propagation may occur. When this happens, only the lower portion of the tube is whitened, a reliable indication that the lower limit is near.

The value in Table II (3.4%) for the lower flammability limit of DDS is identical with that previously chosen from tests in the portable apparatus, and slightly higher than that (3.1%) obtained with the 1-liter bulb. It appears to be reliable.

The lower limit for MTS is somewhat less certain, partly because leaks occurred even after precautions had been taken. In this work a white ring formed at the periphery of the contact area between tube and glass plate (Figure 2), and this ring became progressively heavier until the plate had to be reground after run 9B (Table II) because there had been a leak. The ring contained a chlorosilane hydrolysis product; calomel was absent. (With DDS, presumably because the concentrations were lower, the ring was very faint and leakage negligible.) Nevertheless, the value 7.6 ± 0.3% seems to be sufficiently reliable for practical purposes; the higher result (10%) from the portable apparatus is untrustworthy.

According to the reciprocal additivity relationship first assumed for flammability limits by Le Châtelier (*1*), the value for the methylchlorosilane mixture of Table II should be

$$\frac{1}{(0.719/3.4\%) + (0.281/7.6\%)} = 4.0\% \qquad (3)$$

where the denominator contains the mole fraction of each silane divided by the corresponding lower limit; these mole fractions characterize the mixture containing 60% chlorine by weight. The actual result (3.9%) from Table II proves that this relationship holds for the present case. Also, the last four runs in the table show that it was possible to attain considerable precision in working with these reactive materials.

It seemed plausible that silicon tetrachloride would react with the reactive intermediates involved in the propagation of chlorosilane flames, which suggested that a small amount of this substance might significantly raise the lower flammability limit. Accordingly, five runs were carried out with silicon tetrachloride as added substance (Table III). The results do indicate a deactivating effect of the kind sought, but at silicon tetrachloride concentrations too high to be of much practical interest. The two experiments with hydrogen chloride serve as a blank, for this substance is less likely than silicon tetrachloride to react with the intermediates in question.

Table III. Effect of Added Substances on Flammability Limits of Dimethyldichlorosilane

Added Substance	Run No.	% by Volume		Time of Standing, Hours	Flame Propagation
		DDS	Added Substance		
$SiCl_4$	1	3.61	4.01	16	No
	2	3.59	1.29	16	No
	3	3.61	0.71	16	No
	4	3.59	0.19	16	Yes
	5	3.60	0.39	16	Yes
HCl	1	3.59	0.68	5	Yes
	2	3.58	3.90	16	Yes

ACKNOWLEDGMENT

The authors wish to thank W. J. Scheiber and C. A. Burkhard for supplying the pure compounds, and David Harker for the electron microscope work on the siliceous combustion product.

LITERATURE CITED

(1) Coward, H. F., and Jones, G. W., U. S. Bur. Mines, *Bull.* 279, 8-10 (1928).

(2) Jones, G. W., Kennedy, R. E., and Thomas, G. J., U. S. Bur. Mines, *Rept. Investigation* 3589; esp. Fig. 1 (1941).

(3) Lewis, B., and Elbe, G. von, "Combustions, Flames and Explosions of Gases", p. 141, Cambridge Univ. Press, 1938.

Nomograph for Formulas Containing Fractional Exponents

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The use of fractional exponents in the derivation of empirical formulas is widespread in engineering fields, especially chemical engineering, hydraulics, air conditioning, etc. Frequently empirical formulas are encountered which require the simultaneous involution of terms to fractional powers and multiplication or division of several such terms. These terms are cumbersome to handle by ordinary means, such as the log-log slide rule. A general nomograph, derived by McMillen, gives a method of simultaneous involution and multiplication of such terms. A new nomograph has been derived which accomplishes the same results and which generally requires fewer operations; hence manipulation of the chart is simpler. At the same time basic changes have been made which lead to greater accuracy of reading and interpolation of the scales and to a wider range of products. The method is illustrated by the solution of typical problems.

A CHART for the evaluation of fractional powers of terms and for the direct accumulation of a product of odd-power terms was previously prepared by McMillen[1]. The usefulness of such a chart in chemical engineering calculations, where the log-log slide rule is somewhat more cumbersome, was well presented in the article accompanying that chart.

The present chart differs from the original in two respects: First, the ratio of the moduli of the T- and P-scales, $r = 2$, is used as compared to $r = 1$ in the original chart. This provides for greater accuracy in the reading of the individual terms, wider range for the products, and a more even spread of the vertical lines of the exponent scale. Second, the revised mode of operation described provides additional range for the product scale by projection of the P-scale, extended, onto horizontal lines along the top and bottom of the chart. A range from 10^{-4} to 10^{4} is shown, although the same principle could be applied to extend the range from 10^{-12} to 10^{12} if it were advisable.

The principal deviation from the original is in the mode of operation, which will be described in detail later. In the original method the simultaneous involution and multiplication of power terms required two straight edges or two operations for each term (in certain special cases, three operations for each two terms), and the product was accumulated term by term on the P-scale. In the present method one position or operation of the straight edge is required for each term, and no product need be shown on the P-scale until the final reading.

The master chart, from which the reduction shown in Figure 1 was made, is 16 × 20 inches, exclusive of scorings and numerals. Consequently, each cycle of the T-scale is 10 inches in length, and each cycle of the P-scale is 5 inches in length. It does not follow that the scales have the accuracy of slide rule scales of corresponding length, since the latter are machine-engraved whereas the chart is entirely hand-ruled. Moreover, the chart is subject to the same possible errors of manipulation which afflict all nomographs. High accuracy of readings will be of more credit to the manipulator than to the chart.

At best the readings may be considered satisfactory for engineering calculations, where errors of 2 to 5% are allowable. The method is to be considered, in short, primarily as a time saver.

CONSTRUCTION OF CHART

Vertical Lines for Exponents. The positions of the vertical lines for exponents are determined as shown in Figure 2. Linear scales are laid off on the parallel extreme scales, using moduli in the same ratio as that to be used in laying off the logarithmic scales later; in the examples shown, this ratio is 2 to 1. A line is drawn between the zero points on the two scales and a straight edge (dotted lines) is laid from −1 on the T-scale to successive points on the P-scale. The points of intersection of the straight edge with the 0-0 line mark the abscissas of the horizontal scale, the values of these points having the same numerical value as the corresponding points on the P-scale.

This construction, as shown, gives rise to a scale which reads from right to left, a factor which facilitates the use of the chart by right-handed persons; such persons will generally operate the pivot with their right hands and thus leave the T-scale unobstructed. Left-handed persons will doubtless find a reversed chart easier to use for the same reason.

Logarithmic Scales. The T- and P-scales are logarithmic. The moduli of these scales must be in the same ratio as the linear scales used to mark off the vertical lines for exponents.

Those portions of the P-scale (10^2 to 10^1 and 10^{-2} to 10^{-4}) lying along the top and bottom edges of the chart are laid off by extending the P-scale two cycles beyond the upper and lower extremes of the chart and projecting these cycles onto the horizontal position by a straight edge laid through point 1 on the T-scale. Except for evolution, this portion of the scale may be used only in the reading of final products, not for initial terms. In other words, since it is formed by projection through the point $T = 1$, it is valid only when the straight edge lies through that point.

USE OF CHART

Involution and Evolution. The method of construction of the scale of exponents shows that the segments of the T- and P-scale intersected by two transversals crossing at point e of the exponent scale are in the relationship, $A = eB$, where A and B are linear segments of the P- and T-scales, respectively. If A and B are logarithmic segments, then $\log A = e \log B$, or $A = B^e$.

Rule 1. To raise the number, n, to the eth power, connect 1 on the P-scale with n on the T-scale. Place a pivot at the intersection of the straight edge with the vertical line for e, pivot the straight edge to 1 on the T-scale and read the answer, n^e, on the P-scale.

The example given (Figure 3) shows that $2.6^{1.75} = 5.35$. Evolution proceeds in an exactly reverse fashion, as in the same

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[1] McMillen, E. L., Ind. Eng. Chem., 30, 71 (1938).

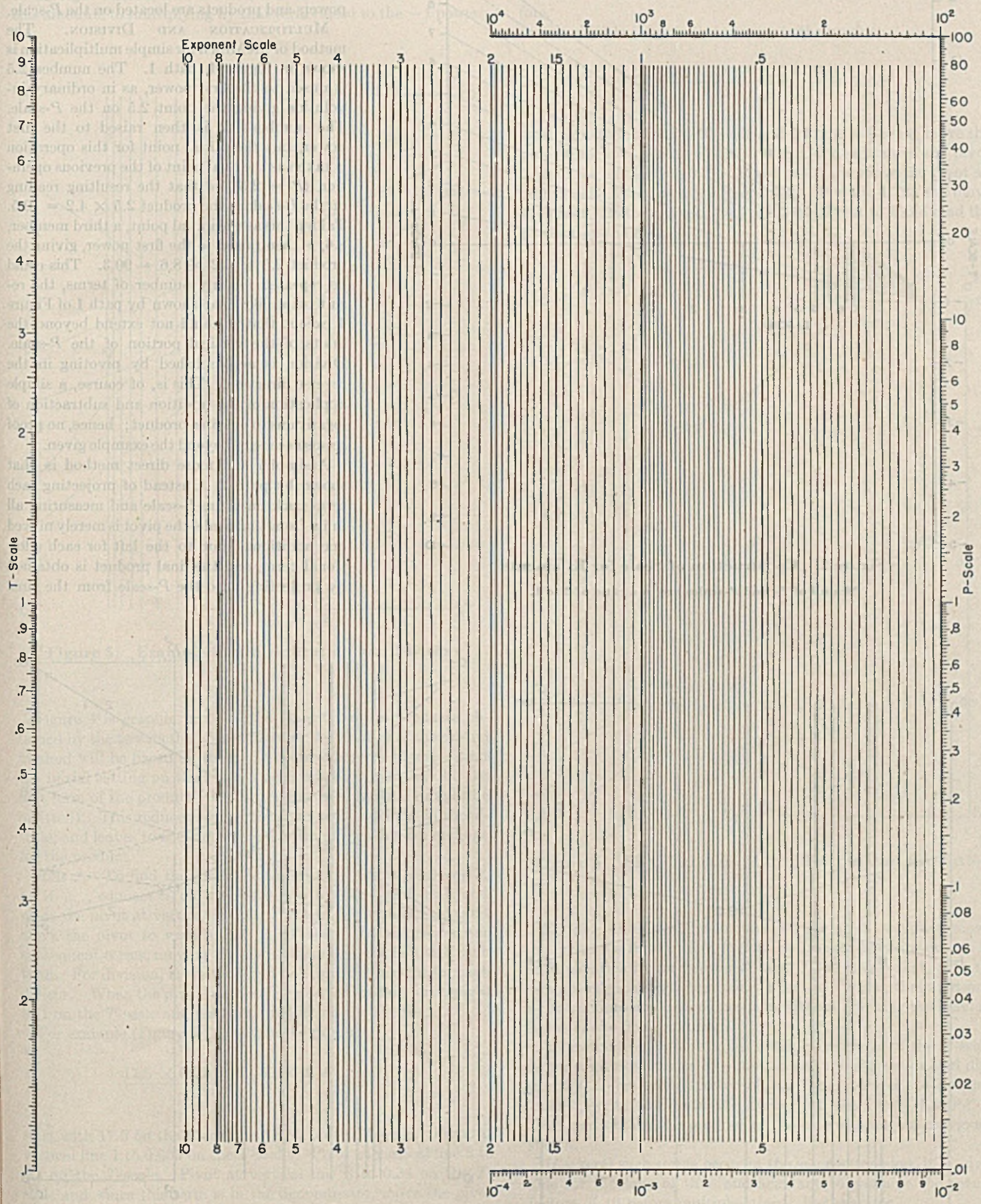

Figure 1. Chart for Formulas Involving Fractional Powers

example, $\sqrt[1.75]{5.35} = 2.6$. In both cases, as in the cases to follow, terms are located on the *T*-scale, except initial terms in multiplication; their powers and products are located on the *P*-scale.

Multiplication and Division. The method of McMillen for simple multiplication is shown in Figure 4, path 1. The number 2.5 is raised to the first power, as in ordinary involution giving the point 2.5 on the *P*-scale. The number 4.2 is then raised to the first power, but the initial point for this operation is taken as the final point of the previous operation ($P = 2.5$), so that the resulting reading on the *P*-scale is the product $2.5 \times 4.2 = 10.5$. Taking this as the initial point, a third member, 8.6, is then raised to the first power, giving the product $2.5 \times 4.2 \times 8.6 = 90.3$. This could be repeated for any number of terms, the result being like that shown by path 1 of Figure 4 except that it could not extend beyond the limits of the vertical portion of the *P*-scale. Division is accomplished by pivoting in the reverse direction. This is, of course, a simple application of the addition and subtraction of logarithms to obtain a product; hence, no proof seems necessary beyond the example given.

A simpler and more direct method is that shown by path 2. Instead of projecting each term back onto the *P*-scale and measuring all units from that scale, the pivot is merely moved one additional unit to the left for each additional term, and the final product is obtained by projecting onto the *P*-scale from the final

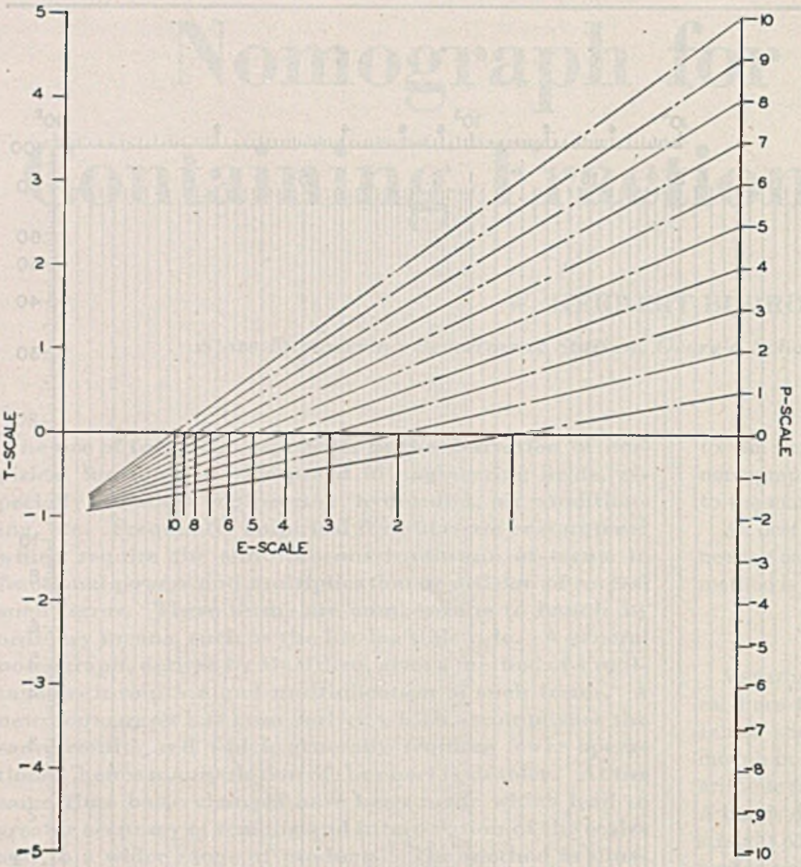

Figure 2. Construction of Scale for Exponents

Moduli of *T*- and *P*-scales are in a ratio of 2 to 1.

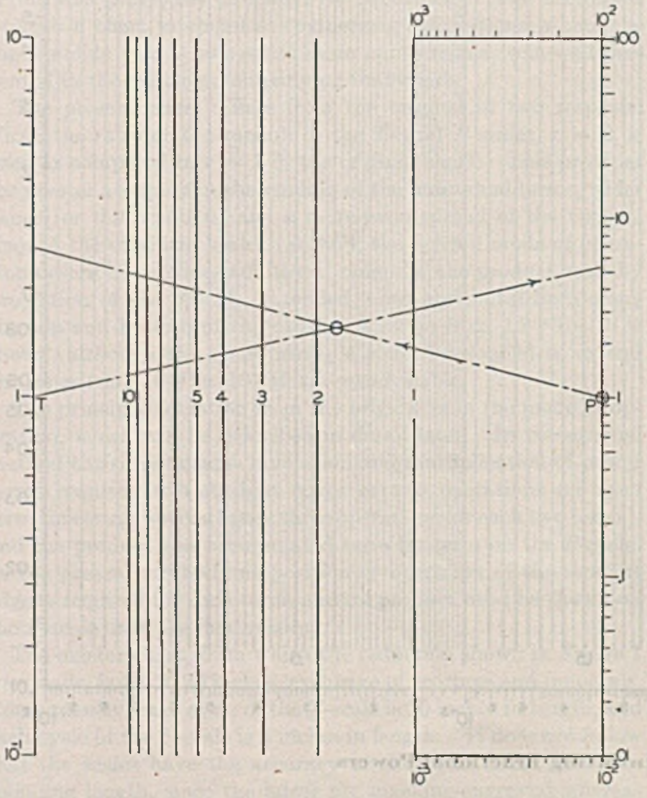

Figure 3. Involution and Evolution, Showing a Method of Obtaining Odd Powers or Roots of Any Number

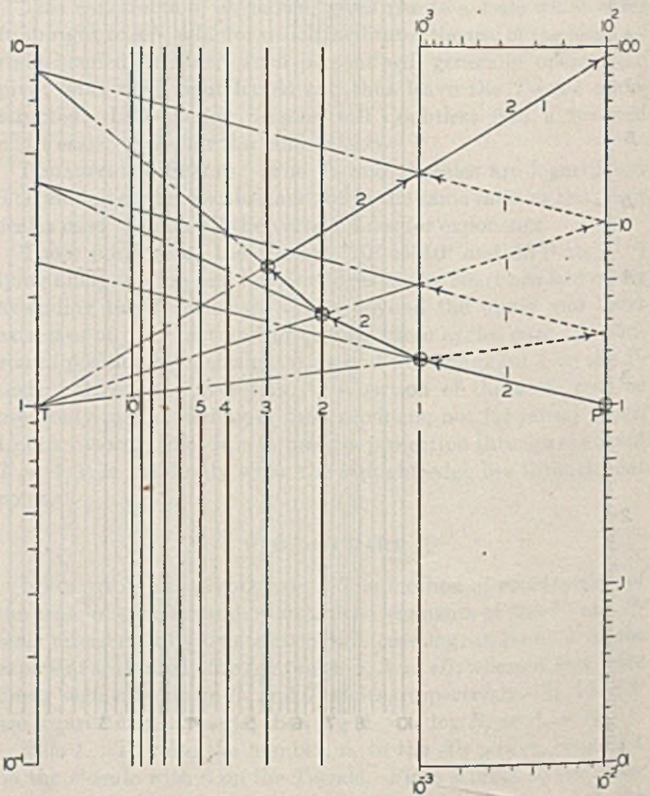

Figure 4. Two Methods of Multiplication

Path 1 shows the method of McMillen, in which a product is accumulated by adding the logarithms of the terms on the *P*-scale. Path 2 shows that the same product is obtained by accumulating the product in the "field" of exponents and projecting from the final position back onto the *P*-scale. ⊙ indicates position of pivot.

position of the pivot. The product so obtained may fall anywhere on the *P*-scale. Division is accomplished by moving the pivot to the right instead of to the left, for each term in the divisor, as this amounts to multiplying by that term raised to the −1 power.

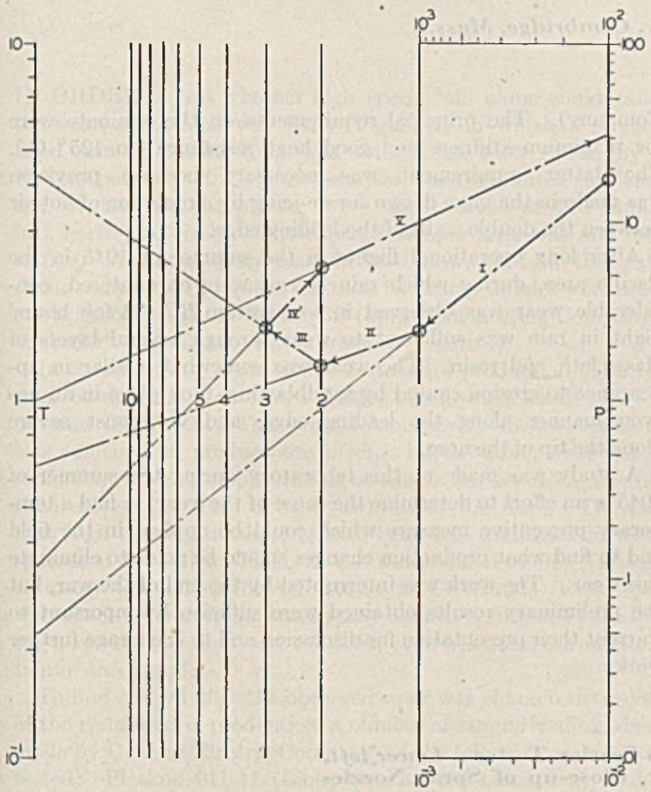

Figure 5. Example in Multiplication and Division

Figure 4 is graphic proof of the identity of the products obtained by the two methods, and proof of the validity of the second method will be based on that. It is obvious from Figure 4 that the initial setting on the *P*-scale need not be 1, but may be the first term of the product (that is, the first step in path 1 might be omitted). This reduces by one the number of settings on the *T*-scale, and leaves to the method one setting for each term and one for the product.

Rule 2. To find the product of a series of terms, $n_1 \times n_2 \times n_3 \times \ldots$, connect n_1 on the *P*-scale with n_2 on the *T*-scale and place the pivot at vertical line 1. Pivot to n_3 on the *T*-scale and move the pivot to vertical line 2. Proceed in this fashion for subsequent terms, moving the pivot one unit to the left with each term. For division, move the pivot one unit to the right for each divisor. When the pivot has been located for the last term, pivot to 1 on the *T*-scale and read the product on the *P*-scale.

For example (Figure 5), to obtain the product,

$$\frac{17.5 \times 0.22 \times 0.655 \times 4.30}{0.34} = 31.8$$

start with 17.5 on the *P*-scale and 0.22 on the *T*-scale. Pivot at vertical line 1 to 0.655 on the *T*-scale. Pivot at vertical line 2 to 4.3 on the *T*-scale. Pivot at vertical line 3 to 0.34 on the *T*-scale and, since this term is in the denominator, move the pivot back one space to vertical line 2. Pivot on this point to 1 on the *T*-scale and read the product on the *P*-scale.

Simultaneous Multiplication and Involution. The motion of the pivot by units to the left or right was for terms whose powers were +1 or −1, respectively.

Rule 3. For terms with powers other than one, move the pivot a number of spaces to the left or right corresponding to the power to which the term is to be raised. The product is obtained as before.

For example (Figure 6), to evaluate the product,

$$\frac{2.35 \times 0.018^{0.15} \times 7.6^{3.32}}{1.725^{1.25}} = 545$$

starting with 2.35 on the *P*-scale and 0.1 on the *T*-scale, move the pivot 0.15 to the left. Pivot to 0.18 and again move the pivot 0.15 to the left (i.e., to 0.3). Pivot to 7.6 and move the pivot an additional 3.32 to the left (i.e., to 3.62). Pivot to 1.725 and move the pivot 1.25 to the right (i.e., to 2.37). Pivot to 1 and read the product on the *P*-scale.

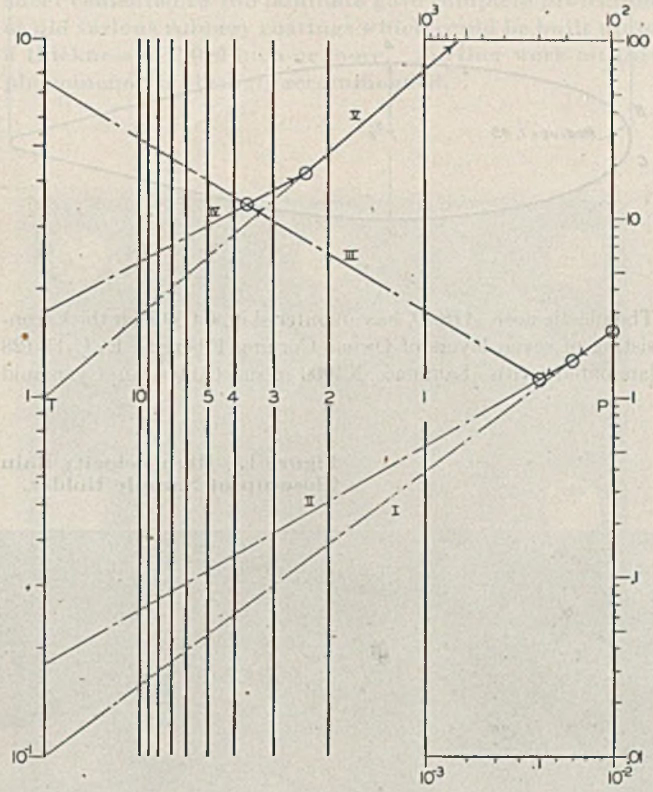

Figure 6. Simultaneous Multiplication and Involution

Notes. If, during the course of an operation, the pivot moves too far to the right or left, it may be brought back into range by multiplication by any power of one. This means that, with the straight edge laid through point 1 on the *T*-scale, the pivot may be moved into any desired position without affecting the previous terms or the final product.

To evaluate n^x, where n lies outside the range of the *T*-scale, factor n into two terms by simultaneous multiplication and division by a convenient power of 10. For example, to evaluate $1680^{0.80}$, write this term as $1.680^{0.80} \times (10^3)^{0.80} = 1.680^{0.80} \times 10^{2.40}$ and obtain the product of these two terms, as previously shown.

If several such terms occur in the same expression, it is advisable for the sake of time and accuracy to combine the several factors of 10 before multiplication. For example,

$$\begin{aligned} &7190^{0.65} \times 560^{2.10} \times 3600^{-1.10} \\ &= (7.190^{0.65} \times 10^{1.95})(5.60^{2.10} \times 10^{4.2})\ (3.600^{-1.10} \times 10^{-3.30}) \\ &= 7.190^{0.65} \times 5.60^{2.10} \times 3.600^{-1.10} \times 10^{2.85} \end{aligned}$$

HIGH SPEED RAIN ABRASION

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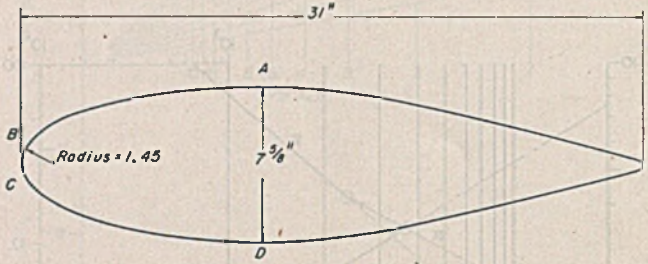
THE AN/APQ-7 (Eagle) radar bombing system developed at this laboratory employed as a housing (radome) for its scanning antenna a streamlined vane with a laminated glass cloth leading edge. The cross section of this vane is shown as follows:

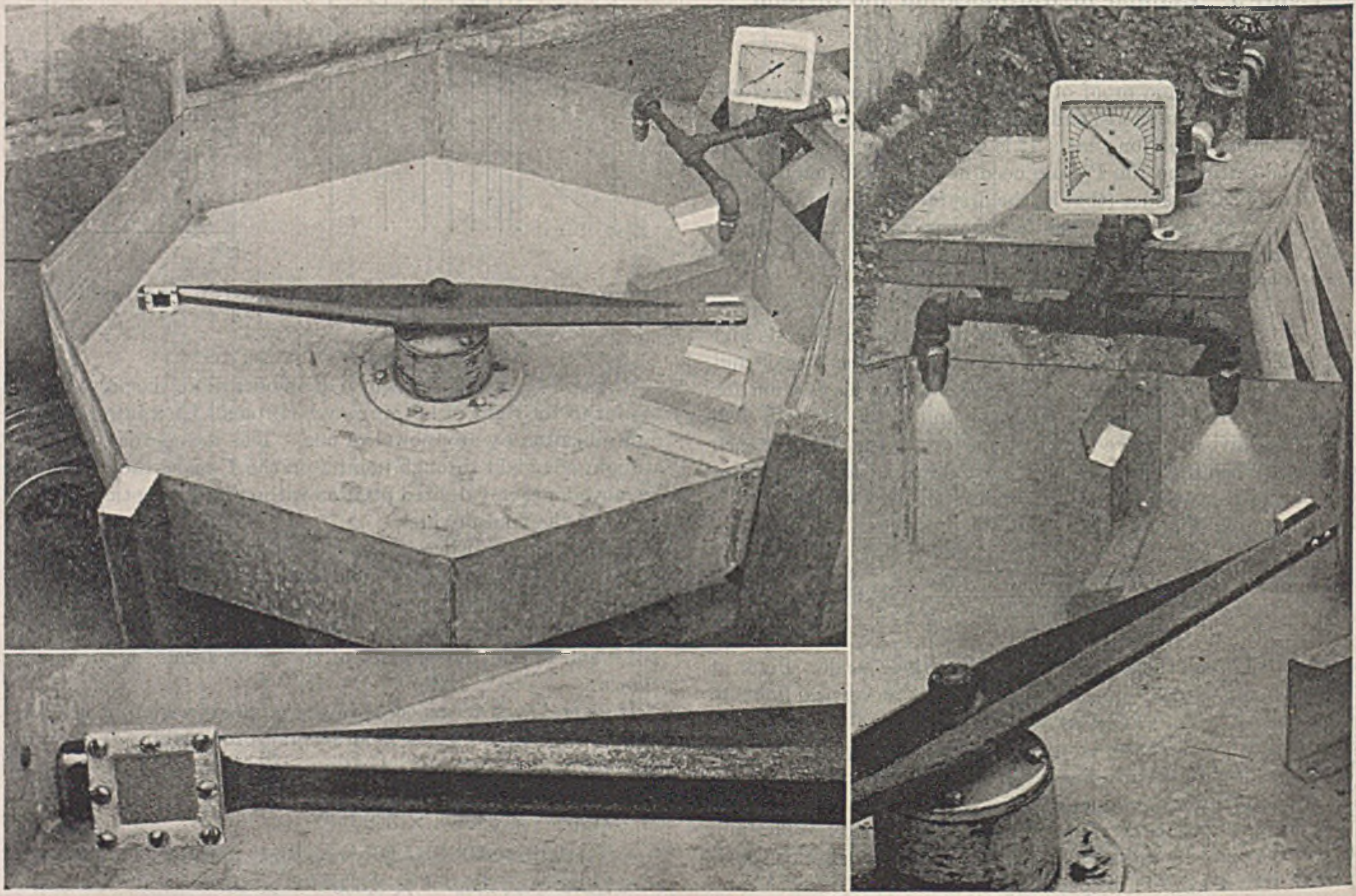


The plastic nose, *ABCD*, has an outer skin, 0.050 inch thick, consisting of seven layers of Owens Corning Fiberglas ECC-11-128 laminated with Laminac X4000 resin (American Cyanamid Company). The principal requirements on the laminate were for maximum stiffness and good heat resistance (to 125° C.). The latter requirement was necessary because provision was made in the vane design for de-icing by circulation of hot air between the double walls of the leading edge.

After long operational flights in the summer of 1945 in the Pacific area, during which rain storms were encountered, considerable wear was observed in nose section *BC*. A few hours' flight in rain was sufficient to wear through several layers of glass cloth and resin. The wear was somewhat similar in appearance to erosion caused by sandblasting, took place in an uneven manner along the leading edge, and was most severe along the tip of the nose.

A study was made at this laboratory during the summer of 1945 in an effort to determine the cause of the wear, to find a temporary preventive measure which could be applied in the field and to find what production changes should be made to eliminate this wear. The work was interrupted by the end of the war, but the preliminary results obtained were sufficiently important to warrant their presentation for discussion and to encourage further work.

Figure 1. High Velocity Rain-Drop Erosion Tester. *Lower left,* Close-up of Sample Holder. *Right,* Close-up of Spray Nozzles



OF GLASS CLOTH LAMINATES

Preliminary experiments to determine the cause of wear, observed on air-borne radar antenna housings flown at high speed through rain, were made with a testing machine which carried samples through a water spray at 260 miles per hour. The material was a glass cloth laminate designed for high stiffness and heat resistance. Laminated samples of a number of different resins were tested and showed wear. Various protective coatings were studied, as well as laminates of cotton cloth. A $^1/_{32}$-inch rubber sheet cemented to the laminate gave complete protection as did various rubbery coatings which could be built up to a thickness of 0.010 inch or more. Further work on this phenomenon is strongly recommended.

IN ORDER to test whether high speed rain alone could cause the wear, a machine was built (Figure 1) in which a streamlined arm 28 inches long was rotated at 3400 r.p.m. by a 10-horsepower motor. Two samples, one mounted at each end of the arm as shown, were thus moved at 260 m.p.h. in a horizontal circle. The exposed sample area was one inch square. A water spray was directed downward in the path of the samples. In most of the tests two spray nozzles were used, one Spraco 4B and one Spraco 5B (Spray Engineering Company), backed by 10 pounds of water pressure (Figure 1).

In the first tests, made with the standard production material, wear occurred at a rate of, roughly, one layer of cloth every 5 minutes (Figure 2). This proved conclusively that water alone was sufficient to produce the effect. Furthermore, wear was so rapid that the cause appeared to be simple impact erosion rather than erosion accelerated by hydrolysis of the resin. The fact that high speed rain alone caused wear was confirmed in tests, sponsored by Wright Field, in the wind tunnel of the National Advisory Committee for Aeronautics at Cleveland. These tests were made by blowing a water spray against a stationary leading edge, and showed that wear can occur even when there is no vibration of the sample.

To find out whether the observed wear was characteristic only of the resin used in production, a number of sample leading edges, made by General Electric Company, of the following resins, were tested: Plaskon 911-11 (Libby-Owens-Ford Glass Co.), Bakelite XRS-74 and 74A (Bakelite Corporation), Selectron 5015 (Pittsburgh Plate Glass Company), Vibron X-1302 (Naugatuck Chemical Division, U. S. Rubber Company). All showed wear. The rates of wear differed somewhat, but none could be considered satisfactory for use at high speed in rain. Samples, made under nonstandard conditions, of Bakelite resins XRS 16631 and BV 17085 (phenolic) also showed wear. As a check to determine whether conditions were too severe, a piece of Plexiglas was tested. No wear occurred.

Temporary protective measures were studied, and it was found that a $^1/_{32}$-inch sheet of rubber cemented to the laminate gave complete protection. However, such a cemented covering was not considered practical for field application. Various rubber coatings which could be painted, sprayed, or spread on the leading edge were tested, but only those which could be built up to a thickness of at least 0.010 inch gave protection. The best of these found was a Thiakol compound, 3M-EC801 (Minnesota Mining and Manufacturing Company). Thinner coatings apparently did not sufficiently absorb the shock of the impinging drops.

In attempting to find a laminate which is not subject to this type of wear, a test was made with cotton duck laminate instead of glass cloth. A distinct improvement was observed; the cloth itself never wore through although sometimes the resin chipped out around the weave. Several samples, in which only the outside layer of glass cloth was replaced by cotton duck, proved equally as good as the all-cotton samples. A number of samples made in this manner with Selectron 5015 resin showed no wear.

TWO definite conclusions can be drawn from this preliminary work. First, all materials to be used in exposed positions on high speed aircraft should be tested for resistance to rain abrasion. Second, further study, both theoretical and experimental, should be carried out on this problem. Now that this condition has been recognized, it can be expected that laminates of glass and other types of cloth can be developed which will have a satisfactory resistance to high speed rain.

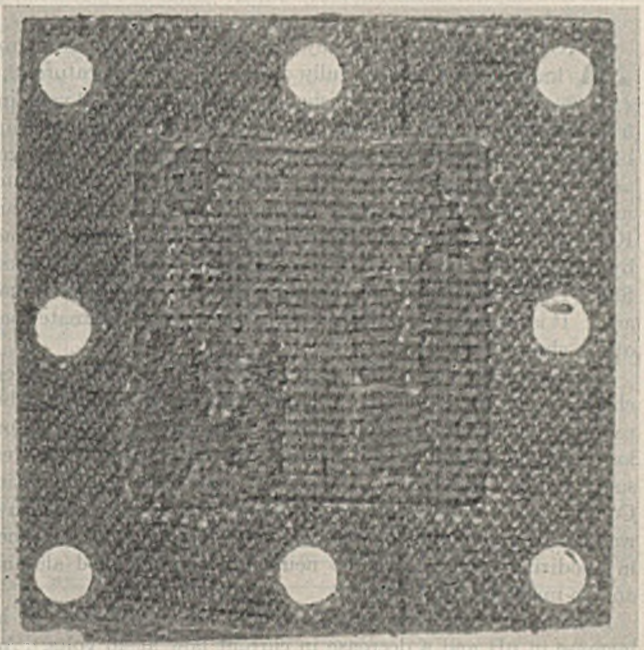


Figure 2. Sample of Plastic Laminate Worn by High Speed Water Abrasion

Further studies might determine whether the observed abrasion effect is associated with the heterogeneous structure of the laminate, which is composed of two brittle elements, glass and resin, having different elastic properties. Theoretical analysis might shed some light on the behavior of such materials under impact. Experimental studies should be made to determine the effect of speed, drop size, and other relevant factors.

This paper is based on work done for the Office of Scientific Research and Development under contract OEMsr-262 with the Radiation Laboratory of M.I.T.

Modified Chromic Acid Anodizing Process for Aluminum

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A wartime shortage of chromic acid made necessary a study of chromic acid anodizing by a process in which bath maintenance is achieved by sulfuric acid additions. The sulfate content of such baths introduces corrosion difficulties when steel tanks are used. However, with protected tanks and carbon cathodes and by controlling the operation on the basis of anode current density, the process appears from the laboratory test to offer promise of a considerable saving in chromic acid consumption. The relations between current density, voltage, sulfate content, and coating weight are described.

ANODIZING aluminum by the chromic acid process is well known and has been fully described in the literature (*2, 3, 4, 8, 9*). Briefly, it is accomplished by electrolysis at 40 volts in a 5 to 10% chromic acid solution at 95° F. (35° C.), the aluminum being the anode with the steel tank acting as cathode. Chromic acid is consumed in the process by reaction with part of the aluminum oxide that forms on the aluminum anode. Edwards and Keller (*7*) showed that only about half the aluminum oxide formed by electrolysis remains on the aluminum surface as the oxide film. The remainder dissolves in the bath and neutralizes chromic acid. It is generally agreed that this accounts for the greater part of the chromic acid loss.

Some chromic acid is also reduced electrolytically to trivalent chromium at the cathode (*5*), accounting for an additional but relatively small loss in free chromic acid. Spray and drag-out losses are considerable, and methods for minimizing them were suggested in Conservation Bulletin 16, issued by the Operating Committee on Aircraft Materials Conservation (*1*), in which it was also reported that over 90% of the chromic acid consumed in anodizing baths is used to neutralize the dissolved alumina and to maintain proper pH.

Decrease in anodizing activity of the bath is evidenced by an increase in pH and a decrease in current flow at 40 volts. According to one maintenance procedure, periodic additions of chromic acid are made to replace the losses. This results in building up the total chromium content of the bath, and the entire bath must be discarded when satisfactory oxide coatings are no longer produced. Another common maintenance procedure consists of periodically drawing off a portion of the used solution and replacing it with fresh chromic acid solution. This tends to keep the total chromium content constant and the pH in the desired range. In either case, considerable amounts of chromic acid are consumed.

A War Production Board survey indicated that supplies of chromic acid were limited and that, whenever possible, conservation measures should be taken to extend the supply for essential uses. The anodizing of aluminum alloy aircraft parts is an important application accounting for the consumption of large quantities of chromic acid.

A modification of the conventional procedure, involving the use of sulfuric acid instead of chromic acid for rejuvenation of the bath, has been used at the Naval Air Station at San Diego, Calif. The station reported to the Project Committee that the method was successful in markedly reducing chromic acid consumption with improved control of the coating quality. Relatively small additions of sulfuric acid were required to keep the anode current density within a specified range. Oxide coatings having substantially the same characteristics as those produced in a straight chromic acid bath were obtained.

When the process was used in trial runs at two aircraft plants, corrosion of the steel tanks and heating coils was encountered. It was felt that additional information was needed on the corrosion characteristics and other phases of the modified process. A laboratory investigation, therefore, was conducted for the Office of Production Research and Development, War Production Board, under the supervision of the War Metallurgy Committee of the National Research Council. Some of the more significant results that were obtained in that "restricted" investigation are reported here.

A stock solution was made up to contain approximately the same proportions of chromic acid and aluminum that might be present in a used commercial bath. Sufficient freshly prepared aluminum hydroxide was dissolved in a solution containing 100 grams per liter of chromic acid to increase the pH to about 1.0. Chemical analysis showed the composition of this solution (in grams per liter) to be: total Cr^{+6} 50.3, Cr^{+3} 0.3, Al_2O_3 14.8, SO_4^{--} 4.7. The presence of 4.7 grams per liter of sulfate is an indication that the gelatinous aluminum hydroxide was not washed completely free of sulfate. Test baths were prepared by adding different quantities of aluminum sulfate to portions of the stock solution; this procedure approximates the composition of baths that have been operated for various intervals and maintained by sulfuric acid additions.

Experiments designed to obtain information on the corrosion of steel cathodes, control of the solutions, and anodizing characteristics of aluminum alloys were conducted in 3.5-liter glass battery jars, immersed in a water bath controlled to maintain the temperature in the jars at 95° ± 1° F. (35° ± 0.6° C.). The pH measurements were made with a Leeds & Northrup glass-electrode meter, calibrated against solutions of known free chromic acid content. The weights of the anodic coatings were determined by difference in specimen weights, before and after stripping, in a bath containing 20 grams of chromic acid and 35 ml. of 85% phosphoric acid in 1 liter of water as described in the literature (*6, 9*).

CORROSION OF STEEL CATHODES

Exploratory tests verified that corrosion of steel cathodes was likely to occur in chromic acid anodizing baths containing sulfuric acid. The results were erratic and indicated that various types of behavior might be expected, depending on the cathode current density, bath sulfate content, agitation, and possibly other factors.

To show the effect of cathode current density, four baths having the following composition were prepared:

Bath No.	1	2	3	4
	Grams per Liter			
Cr^{+6}	50.3	50.0	48.7	48.5
Cr^{+3}	0.3	0.1	0.3	0.3
SO_4^{--}	4.7	19.2	33.1	47.1
Al_2O_3	14.8	19.8	24.2	29.0

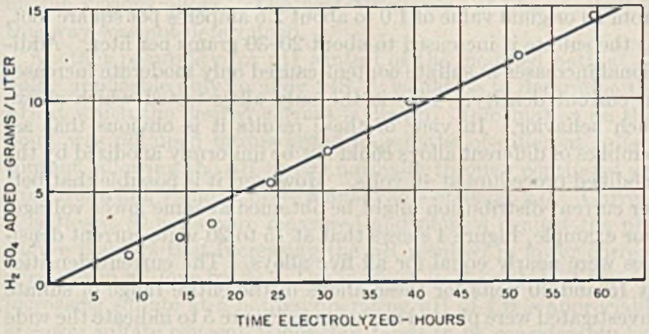

Figure 1. Rate of Adding Sulfuric Acid to Maintain Chromic-Sulfuric Acid Bath with Carbon Cathodes for Anodizing 24S-T Aluminum Alloy at 40 Volts and 95° F.

Several sizes of steel cathodes were electrolyzed in these baths; the anodes were 24S-T or 2S aluminum alloy to give a range of current densities at 40 volts, which is the voltage normally used in commercial work. The tests were carried out at cathode current densities ranging from 0.8 to 186 amperes per square foot in 10% total chromic acid baths containing from about 7.5 to 112.5 grams per liter of sulfate. The baths were adjusted to pH 1.0 with sulfuric acid at the start of each run. The pH increased so rapidly during these runs because of the large quantities of iron dissolved by the acid, that the sulfate content of the baths was doubled or trebled before the tests were completed. Therefore, direct comparisons at constant sulfate content were not always possible. However, it was possible through examination of the surface appearance of the steel specimens and weight loss determinations to divide the specimens into three groups, each representing a characteristic type of behavior. The results may be summarized as follows:

Group 1. Cathode current density below 1.0 ampere per square foot. No attack observed at sulfate contents up to about 60 grams per liter. Above that, mild etching occurred at the solution line.

Group 2. Cathode current densities between 1.5 and 7.0 amperes per square foot. Results erratic, but severe surface pitting and large weight losses, increasing with sulfate content.

Group 3. Cathode current densities between 13 and 186 amperes per square foot. Surface of the cathodes not corroded but more or less covered with a dull chromium electrodeposit; different degrees of solution line corrosion observed, accounting for considerable weight loss especially at the higher sulfate contents.

These results show that freedom from serious attack can be expected only at very low cathode current densities and in baths containing relatively small quantities of sulfuric acid. Such limitations would defeat the purpose of the modified procedure.

A particularly severe pitting attack sometimes occurred on steel specimens immersed in the baths without current. This type of corrosion could not be duplicated at will or be related to any known variable. It usually occurred on cathodes that had been electrolyzed and then left in the baths overnight. It is possible that several factors, such as deposition of impurities on the steel surface, activation of the steel during electrolysis, concentration of sulfate in the bath, etc., might combine to produce the corrosive conditions.

Air agitation of the baths was shown to be an important variable affecting the corrosion of steel immersed without current in chromic acid solutions containing more than about 40 grams per liter of sulfate. It was also observed in these tests that steel specimens, which were allowed to stand in chromic acid before being tested, did not corrode so readily as those with a freshly cleaned and pickled, active surface. This factor was investigated further by testing the effect of air agitation on both activated and passivated steel specimens in baths containing up to 90 grams per liter of sulfate. In these tests no attack occurred on the specimens, either with or without air agitation at a sulfate content of 34–37 grams per liter. At 70 grams per liter, however, air agitation caused solution line attack on the active surfaces, but not on the passive surfaces; at 90 grams per liter, air agitation caused corrosion of the entire immersed active surfaces and solution line attack of the passive surfaces. No corrosion was observed in any of these tests in the absence of air agitation.

The results indicate that corrosion difficulties may be expected when the modified process is carried out in unprotected steel tanks. Cathode current density, sulfate concentration, air agitation, and condition of the steel surface all influence the extent of corrosion.

CORROSION PREVENTION METHODS

Supplementary cathodes of several metals and alloys were hung in front of the steel and tested for efficiency in protecting the steel against the corrosive attack. The distribution of current between the steel and the supplementary cathodes was measured and the surfaces were examined for corrosion. Considerable variation in current distribution resulted, depending on the metal being tested, but no significant decrease in corrosive attack on the steel was detected. In some instances corrosion was actually accelerated. More promising results were obtained through the use of carbon cathodes. A few tests indicated that carbon cathodes connected to the steel cathodes drew practically all of the current and prevented corrosion of the steel during electrolysis. However, the steel was still subject to the solution line attack caused by air agitation as described earlier. These results indicate that steel tanks should be protected with an acid-resisting paint, and inert cathodes should be used to carry the current.

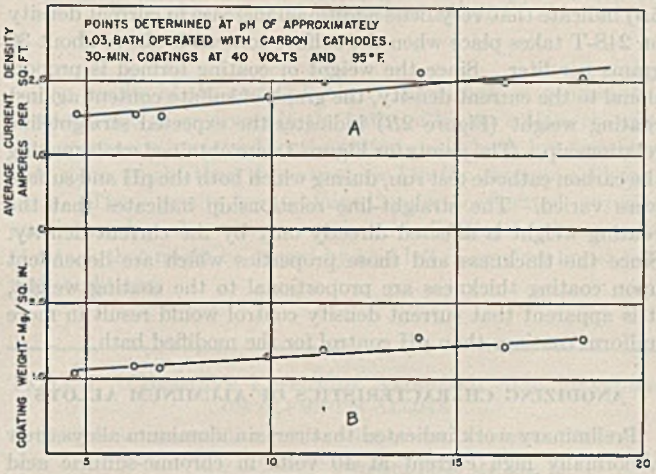

Figure 2. Effect of Sulfate Concentration on Current Density and Coating Weight of 24S-T

Pickling inhibitors added to the baths failed to prevent corrosion of the steel, and experiments along this line did not appear promising.

CARBON CATHODES

Information on the behavior of carbon cathodes, without the interfering effect of iron corrosion products, was obtained by operating a bath contained in a glass jar, using cathodes made from National Carbon Company's furnace electrode stock, grade AGR. Specimens of 24S-T alloy were anodized at 40 volts and 95° ± 1° F. to age the bath, and 30-minute coatings were prepared periodically for coating weight determination. Starting with the stock solution at pH 1.05, electrolysis was continued until the pH had increased to between 1.15 and 1.20, and then sulfuric acid was added to reduce the pH to 1.00–1.05. This procedure was repeated throughout the two-week test period. The carbon electrodes were left immersed in the bath during idle periods. No appreciable change in appearance or evidence of disintegration of the carbon cathodes was visible at the end of the test. The operating relationships and results of the test are shown by graphs. Figure 1 gives the rate at which sulfuric acid was added to maintain the bath when used exclusively for anodizing 24S-T. It is expected that the rate might be different for other aluminum alloys. The straight-line relationship indicates that a schedule for sulfuric acid additions based on the hours of electrolysis could be developed. Figure 2*A* shows the effect of increasing sulfate content on the current density at constant pH. Evidently, as the sulfate content increases, an increase in anode current density also results. The graph shows this to be a fairly consistent gradual increase, but it should be remembered that this relationship applies only in the low-sulfate range. Other experiments (Figure 5*B*) indicate that very little additional increase in current density on 24S-T takes place when the sulfate content is above about 30 grams per liter. Since the weight of coating formed is proportional to the current density, the graph of sulfate content against coating weight (Figure 2*B*) indicates the expected straight-line relationship. The points for Figure 3 were obtained while making the carbon cathode test run, during which both the pH and sulfate were varied. The straight-line relationship indicates that the coating weight is affected directly only by the current density. Since the thickness and those properties which are dependent upon coating thickness are proportional to the coating weight, it is apparent that current density control would result in more uniform coatings than pH control for the modified bath.

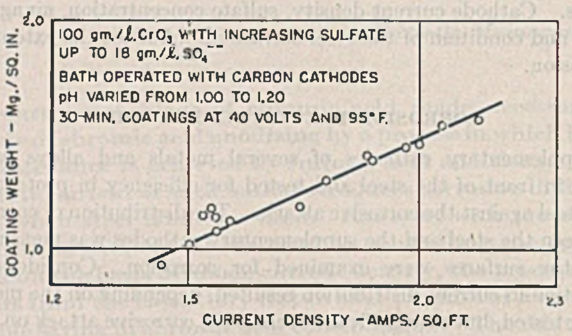

Figure 3. Effect of Anode Current Density on Weight of Anodic Coatings on 24S-T

ANODIZING CHARACTERISTICS OF ALUMINUM ALLOYS

Preliminary work indicated that certain aluminum alloys drew abnormally high current at 40 volts in chromic-sulfuric acid baths. This is an important point to consider when different alloys are being anodized simultaneously in the same tank. Therefore, further tests were made to establish the voltage-current relationships for several aluminum alloys in the various baths used in this investigation.

The voltage was applied to the alloy being tested and raised in 5-volt steps up to 50 volts. The current was recorded at each voltage after allowing a few minutes to reach equilibrium. In several cases at the higher sulfate content, the breakdown voltage of the film was exceeded; excessive current flow resulted, and the tests were stopped before 50 volts was reached.

Results of these tests verified the fact that the addition of sulfuric acid causes relatively large increases in current flow on most aluminum alloys. Figure 4 is a representative graph showing the widespread variation in current density with increasing voltage on five aluminum alloys in a 10% chromic acid solution containing 56.8 grams per liter of sulfate. The difference between the alloys is striking, but it is also interesting to note the relatively small increase in current on alloy 24S-T. Earlier experiments had indicated that the current density on 24S-T at 40 volts increases from an original value of 1.0 to about 2.5 amperes per square foot, as the sulfate is increased to about 20–30 grams per liter. Additional increases in sulfate content caused only moderate increases in current density. This is the only alloy tested which shows such behavior. In view of these results it is obvious that assemblies of different alloys could not be uniformly anodized by the modified procedure at 40 volts. However, it is possible that better current distribution might be obtained at some lower voltage. For example, Figure 4 shows that at 15 to 20 volts current densities were nearly equal for all five alloys. The current densities at 15 and 40 volts for these alloys in the entire range of sulfate investigated were plotted as shown in Figure 5 to indicate the wide differences existing between these two extremes. One straight line sufficed to cover all the points for the five alloys at 15 volts. This is a desirable condition, making it possible to anodize assemblies composed of several different aluminum alloys at a relatively constant current density in baths containing various quantities of sulfate. In contrast, the curves at 40 volts show not only that the current flow to the different alloys varies widely, but also that increasing the sulfate content of the bath results in large increases in current density on all but alloy 24S-T. Obviously, those properties of the coatings that are influenced by their thickness are also subject to the same wide variations because the weight of the oxide film has been shown to be almost directly proportional to the current density.

BATH CONTROL

The question of bath control was mentioned briefly in the discussion of the carbon-cathode test results, and it was indicated that the process should be controlled by regulating the anode current density rather than the pH of the bath. Control of anodizing activity by adjustment of pH, however, has been widely used in commercial anodizing installations. Since current density at 40 volts varies so markedly with sulfate content at constant pH in the chromic-sulfuric acid baths, it is obvious that for general all-round work pH control would result in variations in coating thickness with varying sulfate content and alloy composition. It is possible, however, that pH control may be useful under certain conditions. For example, the points for the curve of current density against sulfate at 15 volts in Figure 5*A* were determined at constant pH of 1.01–1.04. The current density on all five alloys remained practically constant over the entire sulfate range. Therefore, at 15 volts, pH control should be feasible and should permit the maintenance of relatively constant current densities

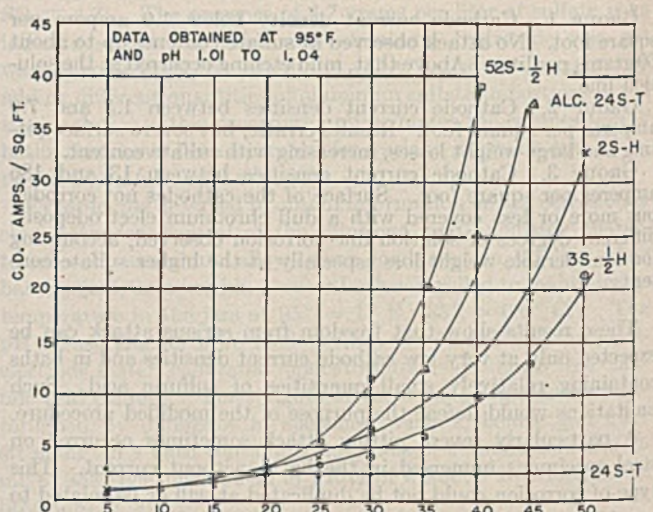

Figure 4. Current-Voltage Relationship for Aluminum Alloys in 10% Chromic Acid Plus 56.8 Grams per Liter of Sulfate

on the various alloys. The protective value of films formed in this way was not determined.

Another possibility for pH control of the modified bath at 40 volts, applicable only to alloy 24S-T, would be to determine the pH at which the desired current is drawn. Information on this point was obtained by operating four baths of different sulfate content, allowing the pH to rise normally through continued use from a starting value of 1.0 to a final value of about 2.0. Current densities at 40 volts were measured and plotted against the pH; Figure 6 shows that increasing the pH resulted in lower current densities in all four baths. The increase in current density with increasing sulfate at a normal operating pH of 1.0 is appreciable at lower sulfate concentrations, but tends to be considerably less in the upper range of 35 to 117 grams per liter of sulfate. Control of anodizing by pH maintenance in the upper range may be possible if the allowable tolerance in current density variation is within that shown by the upper three curves in Figure 6. The following tabulation taken from the curves indicates how much variation in current density may be expected on 24S-T at several pH values:

pH	Av. Anode Current Density, Amp./Sq. Ft.	pH	Av. Anode Current Density, Amp./Sq. Ft.
1.0	3.0 ± 0.2	1.3	1.9 ± 0.25
1.1	2.6 ± 0.2	1.4	1.6 ± 0.2
1.2	2.2 ± 0.2	1.5	1.4 ± 0.2

If the variation in properties of the coatings obtained with these tolerances is acceptable, it should be possible to select the desired pH and maintain it by sulfuric acid additions as required. The foregoing information was obtained with steel cathodes and may have been influenced by the irregular effects due to the iron corrosion products. However, it is undoubtedly accurate enough to indicate the trend.

With these exceptions it appears that more consistent results would be obtained by current-density control than by pH control.

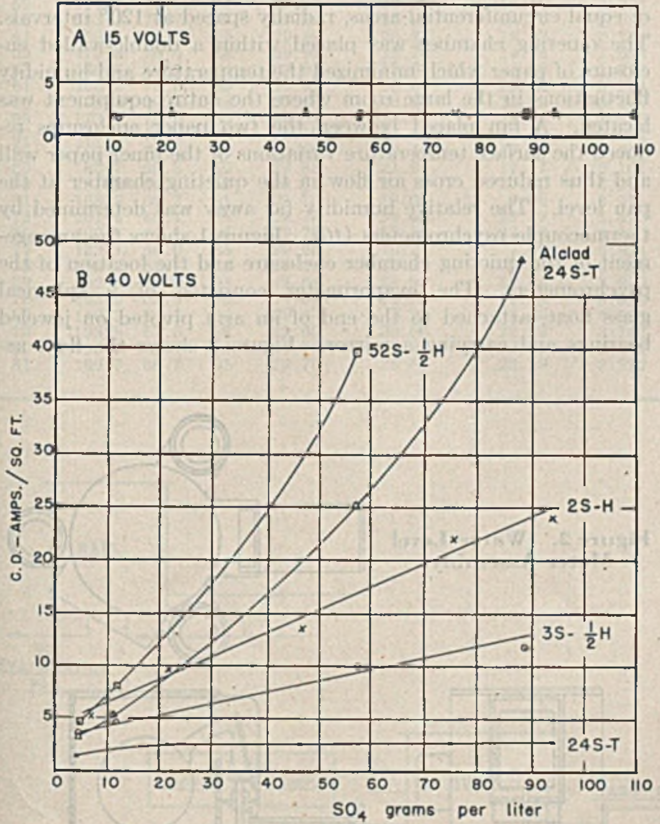

Figure 5. Variation in Current Density on Aluminum Alloys at 15 and 40 Volts in 10% Chromic Acid Containing Various Amounts of Sulfate at pH 1.01–1.04 and 95° F.

CORROSION OF ALUMINUM

The corrosion of aluminum in chromic-sulfuric acid mixtures was investigated briefly to determine the effect of acid retained in crevices and joints of assembled structures. Specimens of several alloys were immersed in portions of a used commercial chromic acid anodizing bath containing various quantities of aluminum sulfate. One set of specimens was immersed in a 15% sulfuric acid solution containing 54 grams per liter of additional sulfate for comparison. Weight loss determations were made to indicate the severity of the corrosion.

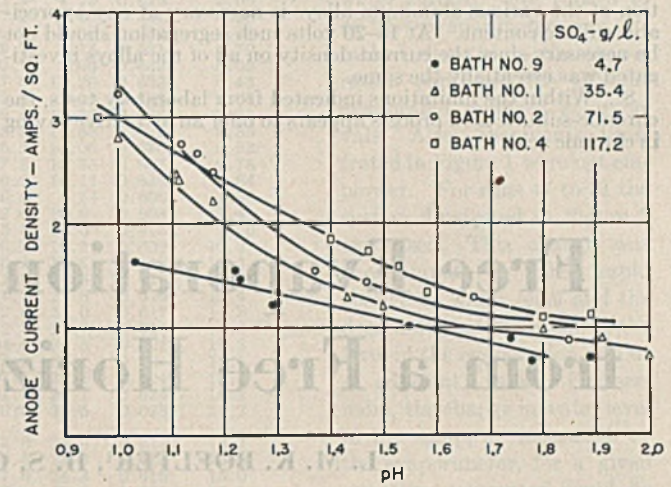

Figure 6. pH *vs.* Current Density at 40 Volts in 10% Chromic Acid Baths Containing Various Quantities of Sulfate and Anodes of 24S-T

The results of the tests (Table I) show that, in general, the corrosion was more severe in the baths of higher sulfate content. The specimens immersed in the sulfuric acid bath lost considerably more weight than those immersed in the chromic acid mixtures. These results were obtained under accelerated corrosive conditions, but they may serve as an indication of the amount of attack that might be caused by acid left in crevices under normal conditions.

Table I. Corrosive Effect of Anodizing Acid Mixtures on Aluminum Alloys

(Specimens immersed in corroding solutions for 72 hours at 120° F.)

Solution, Grams/Liter	Weight Loss, Mg./Sq. In. 24S-T	52S-½H	3S-½H	Alclad 24S-T
130[a] CrO_3 + 0.3 SO_4	4.2	1.2	0.9	2.8
130[a] CrO_3 + 20.0 SO_4	13.4	11.4	11.2	12.5
130[a] CrO_3 + 80.0 SO_4	15.8	13.2	12.5	11.9
165 H_2SO_4 + 54.0 SO_4	173.0	70.9	70.8	90.7

[a] A used, commercial anodizing solution was used as the base for these baths and the sulfate ion was added as aluminum sulfate.

CONCLUSIONS

1. Operation of the modified chromic acid anodizing bath using sulfuric acid for maintenance, introduces a severe corrosion hazard to the steel tanks that are commonly used for the straight chromic acid process. The corrosion of steel is affected by several factors—sulfate content, air agitation, and cathode current density. Protective coatings should be applied to all steel surfaces exposed to the action of the chromic-sulfuric acid electrolyte.
2. From the laboratory tests described, carbon appears to be a satisfactory cathode material for use in protected steel tanks.
3. The weight of coating produced is determined by the anode current density and time of treatment, and is independent of the sulfate content, at least in the lower sulfate range.

4. The sulfuric acid maintenance procedure causes radical changes in the current density–voltage relationships as the sulfate content increases at constant pH. Coating thickness, therefore, cannot usually be controlled by maintaining a constant pH, voltage, and treatment time.

5. The thickness of the oxide film is effectively controlled by maintaining operating conditions to give a constant anode current density. This can be accomplished by changing the pH of the solution as the sulfate content increases or by changing the voltage.

6. In the special case of the 24S-T alloy, anodized in chromic acid containing more than about 35 grams per liter of sulfate, operation at constant pH and voltage results in a current density that is essentially independent of sulfate content.

7. With the modified process, operated at 40 volts, segregation of the various aluminum alloys is necessary at any appreciable sulfate content. At 15–20 volts such segregation should not be necessary since the current density on all of the alloys investigated was essentially the same.

8. Within the limitations indicated from laboratory tests, the chromic-sulfuric acid process appears to offer an attractive saving in chromic acid.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Anonymous, *Metal Finishing*, 41, 617 (1944).
(2) Bengough, G. D., and Stuart, J. M., U. S. Patent 1,771,910 (1930).
(3) Bengough, G. D., and Sutton, H., *Engineering*, 122, 274–7 (1926).
(4) Buzzard, R. W., *J. Research Natl. Bur. Standards*, 18, 251–7 (1937).
(5) Buzzard, R. W., and Wilson, J. H., *Ibid.*, 18, 53–8 (1937).
(6) Edwards, J. D., *Proc. Am. Soc. Testing Materials*, 40, 959–66 (1940).
(7) Edwards, J. D., and Keller, Fred, *Trans. Electrochem. Soc.*, 79, 135–44 (1941).
(8) Mozley, P. P., *Metal Finishing*, 39, 301–5 (1941).
(9) Tarr, O. F., Darrin, Marc, and Tubbs, L. G., Ind. Eng. Chem., 33, 1575–80 (1941).

Free Evaporation into Air of Water from a Free Horizontal Quiet Surface

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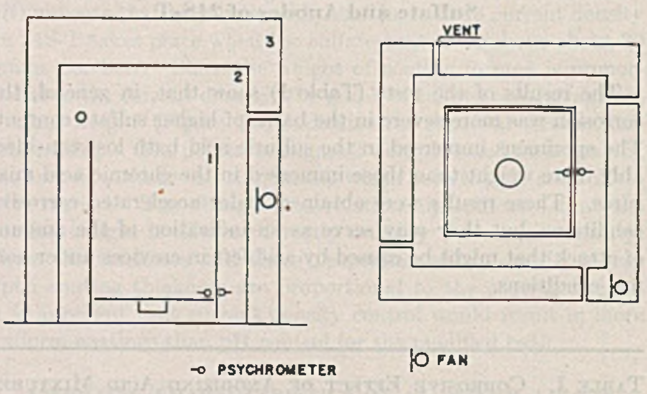

Figure 1. Elevation and Plan of Quieting Chamber

THE results of experimental studies made prior to June, 1938, at the University of California on the evaporation of water under conditions of free convection were published previously (*12*). Data were presented for the evaporation of distilled water, within the temperature limits of 63° and 93° F., from a one-foot-diameter surface placed flush with the surrounding floor into quiet air at 71° ± 1° F. and 50 to 54% relative humidity. Since that time data have been obtained and results computed which justify the extension of the range of application of the analogy between thermal free convection and diffusional free convection to wider limits. Hence, the data presented here supplement those in the earlier paper; the curves and equations cover the evaporation of distilled water from a one-foot-diameter surface, within the temperature limit 63° and 200° F., into quiet air at 65° to 80° F. and 54 to 98% relative humidity.

The apparatus was essentially the same as that previously described (*12*) with the exception of the quieting chamber and evaporimeter. Ten thermocouples were employed to measure the water surface temperature and were placed at the centroids of equal circumferential areas, radially spaced at 120° intervals. The quieting chamber was placed within a double-walled enclosure of paper which minimized the temperature and humidity fluctuations in the large room where the entire equipment was located. A fan placed between the two paper enclosures reduced the surface temperature variations of the inner paper wall and thus reduced cross air flow in the quieting chamber at the pan level. The relative humidity far away was determined by thermocouple psychrometers (*10*). Figure 1 shows the arrangement of the quieting chamber enclosure and the location of the psychrometers. The evaporimeter consisted of a spherical glass float, attached to the end of an arm pivoted on jeweled bearings and carrying a mirror. Figure 2 shows the float as-

Figure 2. Water Level Meter Assembly

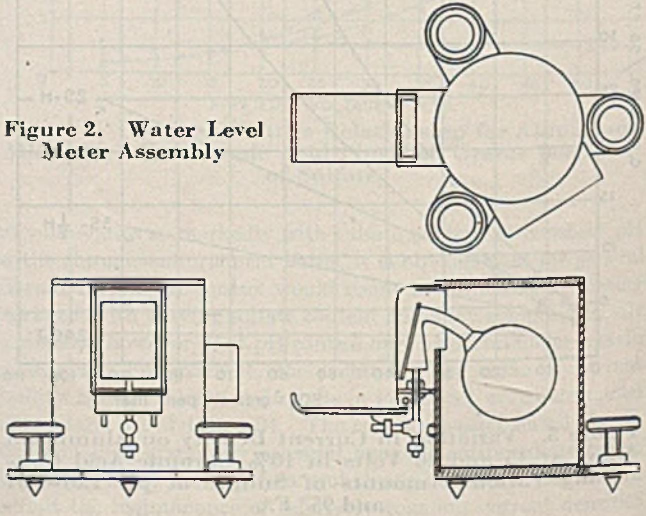

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Table I. Data and Results

Run No.	t_w, ° F.	t_∞, ° F.	rh_∞, %	Barometer, In. Hg.	$C_{vw} - C_{v\infty}$ × 10³	$P_{vw} - P_{v\infty}$	e	Nu'	Gr' × 10⁻⁷	Pr'	$Gr' \times Pr'$ × 10⁻⁷
3	75.2	71.9	64	29.84	0.58	....	0.0168	29.3	0.89	0.618	0.55
4	78.0	72.9	66	29.85	0.65	....	0.0261	40.5	1.10	0.618	0.68
5	84.1	71.0	69	29.90	0.96	....	0.0409	42.8	2.26	0.619	1.40
6	87.9	75.4	64	29.73	1.13	....	0.0467	40.7	2.26	0.619	1.40
7	88.2	75.3	65	29.73	1.10	....	0.0482	43.2	2.26	0.621	1.40
8	91.2	72.5	73	29.73	1.28	....	0.0637	49.0	3.03	0.622	1.88
9	91.3	73.2	72	29.73	1.28	....	0.0615	47.2	2.92	0.623	1.82
10	93.1	74.5	73	29.73	1.37	....	0.0675	48.2	3.07	0.621	1.91
11	103.3	75.2	73	29.76	2.11	....	0.1294	56.3	4.49	0.624	2.80
12	103.2	75.2	73	29.76	2.10	....	0.1168	53.6	4.49	0.624	2.80
13	103.6	75.1	74	29.76	2.12	....	0.1157	52.5	4.52	0.624	2.82
14	103.2	73.5	79	29.80	2.03	....	0.1077	51.2	4.73	0.625	2.96
16	125.2	77.6	84	29.80	4.33	....	0.2670	57.2	7.86	0.631	4.98
17	125.4	76.5	88	29.79	4.30	....	0.2748	59.3	8.00	0.630	5.04
18	129.0	73.2	90	29.77	5.04	....	0.3404	62.7	9.18	0.631	5.79
19	131.6	77.8	90	29.76	5.27	....	0.3400	59.1	9.00	0.632	5.69
20	136.2	77.1	86	29.76	6.15	....	0.3980	57.0	10.20	0.633	6.43
21	142.1	79.3	83	29.66	7.25	....	0.4845	60.0	11.15	0.633	7.06
23	144.9	80.2	83	29.67	7.80	....	0.5210	59.6	11.37	0.636	7.36
24	151.3	76.4	85	29.68	9.42	....	0.6925	65.5	13.88	0.637	8.85
25	151.2	76.6	87	29.61	9.35	....	0.6995	66.2	14.06	0.636	8.93
26	154.4	72.8	88	29.63	10.32	....	0.7870	67.8	15.35	0.637	9.78
27	153.9	72.9	88	29.63	10.16	....	0.8110	70.9	15.11	0.638	9.64
28	85.5	66.7	68	30.05	1.14	0.782	0.057	50.8	5.54	0.606	3.36
29	103.8	64.6	79	29.93	2.39	1.67	0.153	62.4	10.6	0.608	6.41
30	132.3	71.1	85	29.82	5.69	3.81	0.283	45.8	15.6	0.615	9.56
31	131.0	67.3	87	30.03	5.56	3.76	0.338	56.3	16.9	0.609	10.3
32	130.0	65.0	89	29.70	5.49	3.67	0.354	60.2	16.4	0.616	10.1
33	144.0	67.5	95	29.79	7.59	5.73	0.682	77.8	21.5	0.616	13.2
34	143.7	67.1	93	29.81	7.92	5.73	0.672	77.1	21.8	0.616	13.4
35	155.9	67.7	95	29.92	10.78	7.81	0.873	72.0	24.0	0.617	14.8
36	155.1	66.8	96	29.92	10.80	7.67	0.876	72.3	23.7	0.616	14.6
37	162.5	66.5	95	29.70	12.69	9.61	1.503	104.5	29.5	0.622	18.3
42	169.7	70.2	98	29.78	14.89	11.36	1.311	76.3	29.1	0.624	18.1
43	169.7	70.2	98	29.79	14.89	11.36	1.336	77.8	29.1	0.624	18.1
44	169.7	70.2	98	29.80	14.89	11.36	1.401	81.6	29.1	0.624	18.1
46	181.1	69.2	97	29.95	19.27	15.00	1.812	80.3	38.5	0.628	24.2
47	148.7	65.6	91	30.05	9.01	6.74	0.715	71.6	22.3	0.615	13.7
48	149.7	65.6	92	30.06	9.33	6.92	0.730	70.5	24.3	0.616	15.0
49	149.8	65.6	92	30.06	9.33	6.91	0.740	71.5	24.3	0.616	15.0
50	163.7	73.3	88	30.13	12.92	9.78	1.083	73.1	27.6	0.621	17.1
51	164.0	73.2	90	30.21	13.01	9.88	1.067	71.6	27.7	0.621	17.2
52	164.3	71.8	91	30.22	13.14	9.98	1.126	74.7	28.2	0.622	17.6
53	182.5	75.8	59	30.11	20.11	15.65	1.784	74.7	37.6	0.623	23.5
54	182.5	76.0	59	30.12	20.12	15.65	1.716	71.9	37.6	0.623	23.5
55	182.9	76.5	59	30.13	20.46	15.76	1.765	72.7	37.9	0.623	23.6
56	173.1	77.7	68	30.00	16.25	12.26	1.339	70.2	31.1	0.622	19.3
57	176.5	79.3	59	29.88	17.55	13.60	1.699	82.0	32.7	0.623	20.3
58	174.7	73.3	68	29.81	16.72	12.86	1.776	91.0	33.6	0.622	20.9
59	190.1	71.3	91	29.93	23.37	18.40	2.375	85.2	43.7	0.632	27.6
60	193.1	70.7	77	29.89	25.03	19.72	2.650	88.4	47.3	0.630	29.8
61	193.4	70.4	75	29.89	25.22	19.87	2.755	91.3	49.4	0.630	31.1
62	179.8	70.4	84	29.91	18.78	14.54	1.684	76.3	39.1	0.625	23.4
63	180.3	72.1	84	29.91	18.94	14.73	1.712	76.5	36.5	0.626	22.8
64	198.9	73.0	95	29.99	28.03	22.20	3.228	95.5	50.2	0.627	31.4
65	199.0	69.4	96	29.99	28.10	22.25	3.320	98.0	54.1	0.625	33.8
66	173.7	72.6	86	29.91	16.40	12.42	1.456	76.2	32.7	0.625	20.4
67	173.8	73.3	86	29.89	16.41	12.41	1.334	69.6	32.5	0.625	20.3
68	187.3	69.8	86	29.90	22.13	17.37	2.352	89.8	42.9	0.629	26.5
69	186.7	69.3	80	29.88	21.94	17.17	2.101	81.0	42.9	0.626	26.5
70	187.2	69.6	82	29.87	22.14	17.35	2.329	89.0	43.2	0.625	27.0
71	163.3	69.7	81	29.76	13.01	9.86	0.911	61.5	28.5	0.620	17.7
72	201.6	66.1	95	29.77	29.68	23.59	4.320	120.9	57.1	0.636	36.3
73	200.9	65.7	95	29.76	29.28	23.19	4.060	115.4	56.6	0.635	35.9
74	153.1	66.0	85	29.65	10.21	7.60	0.824	69.8	26.0	0.616	16.0
75	153.2	65.7	86	29.65	10.24	7.61	0.834	70.4	26.0	0.616	16.0
76	192.9	63.7	98	29.64	24.93	19.66	3.060	113.8	50.1	0.631	31.6
77	192.5	62.9	98	29.64	24.73	19.68	3.020	113.4	50.6	0.631	31.9
78	140.3	64.4	95	29.69	7.25	5.35	0.501	63.3	21.0	0.613	12.8
79	198.9	67.5	98	29.69	28.06	22.23	3.142	93.3	55.4	0.625	34.6
80	199.7	67.2	98	29.70	28.64	22.59	3.272	94.8	56.3	0.625	35.1
81	199.7	66.7	95	29.70	28.64	22.59	3.279	95.0	55.8	0.625	34.9

sembly and the meter body. The reflection of a scale was read with a telescope provided with cross hairs. The apparent change in the position of the cross hairs upon the scale and the distance from the pivot point to the scale and to the effective center of the float were interpreted in terms of the change of level of the water surface. For runs 3 to 46 the evaporimeter was attached directly to the evaporation pan, and the amount evaporated replaced at intervals. Also, the vents illustrated in Figure 1 were not employed. For runs 47 to 81 the system illustrated in Figure 3 was used. This change was necessitated by the rapid change of water level and the desirability of maintaining the level in the evaporation pan at a constant value. Furthermore, the change in water level in the sump, as measured by the evaporimeter, for a given quantity evaporated could be governed by changing the surface area of the sump.

The experimental technique (*3, 4*) differed from that previously described (*12*) only when required by the instrumentation. The results of the measurements are given in Table I and plotted in Figures 4, 5, and 6.

UNIT EVAPORATION RATES

Figure 4 shows the unit evaporation rate as a function of concentration difference. Between the limits of concentration difference,

$$0.001 \leq (C_{vw} - C_{v\infty}) \leq 0.025 \text{ lb./cu. ft.}$$

the empirical relation

$$e = 251\,(C_{vw} - C_{v\infty})^{1.25} \text{ lb./(hr.) (sq. ft.)} \qquad (1)$$

best expresses the experimental data. This equation represents the range of water surface temperature from approximately 80° to 190° F. For lower values of surface temperature—that is, concentration difference—the equations given by Sharpley and Boelter (*12*) express the experimental results more exactly:

$$e = 18.75(C_{vw} - C_{v\infty}) \text{ lb./(hr.) (sq. ft.)} \qquad (2)$$

$$\text{for } 0 \leq (C_{vw} - C_{v\infty}) \leq 5 \times 10^{-4} \text{ lb./cu. ft.}$$

$$e = -0.024 + 65\,(C_{vw} - C_{v\infty}) \text{ lb./(hr.) (sq. ft.)} \qquad (3)$$

$$\text{for } 5 \times 10^{-4} \leq (C_{vw} - C_{v\infty}) \leq 0.001 \text{ lb./cu. ft.}$$

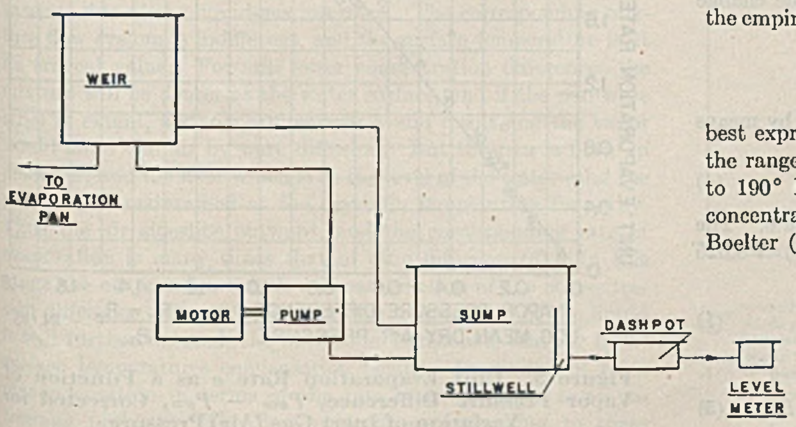

Figure 3. Water Supply Piping for Runs 47 to 81

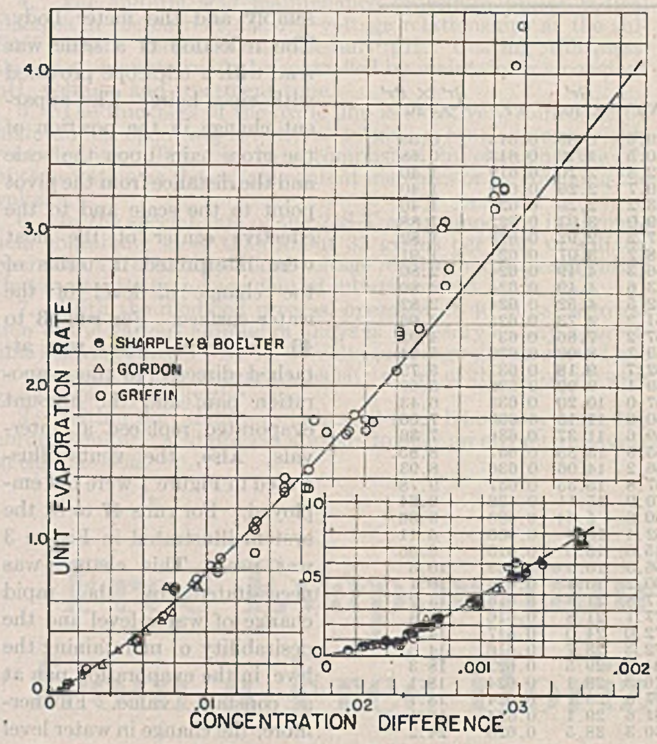

Figure 4. Unit Evaporation Rate e as a Function of Concentration Difference, $C_{vw} - C_{v\infty}$

Departure of the data from the curve representing the empirical relation (Figure 4) at magnitudes of concentration difference greater than 0.025 lb./cu. ft. may be attributed to phenomena associated with boiling. Observation indicated that the water in the pan, at temperatures above 190° F., was in a state of ebullition due to the formation of small bubbles at several points on the bottom of the pan.

The curve in Figure 4 represents the unit evaporation rate for $t_\infty = 70°$ F. and $rh_\infty = 50\%$. At high evaporation rates the relative humidity far away does not contribute an appreciable "back" potential so that the curve may also be used for higher humidities. Other conditions far away will cause evaporation rates which differ from those represented by this curve and, for want of more extensive experimental data, may be predicted from the generalized equation (7).

The experimental results of this paper were also replotted (as suggested by A. P. Colburn) on Figure 5 in which unit evaporation rate e is plotted against the vapor pressure difference (at the interface and far away) divided by the log mean dry air vapor pressure. The scattering of points above the extrapolated line evidenced at high concentration differences in Figure 4 is reduced when the partial pressure difference is corrected for the change in inert gas pressure.

UNIT CONDUCTANCE

The unit conductance for mass transfer, f', defined by means of the equation

$$e = f'(C_{vw} - C_{v\infty}) \quad (4)$$

is plotted against the concentration difference in Figure 6. The unit evaporation rate in the range $0.001 \leq (C_{vw} - C_{v\infty}) \leq 0.025$ lb./cu. ft. is given by

$$e = 251(C_{vw} - C_{v\infty})^{1.25} \quad (1)$$

Calculating f' from Equations 1 and 4,

$$f' = 251\ (C_{vw} - C_{v\infty})^{0.25} \text{ lb./(hr.) (sq. ft.) (lb./cu. ft.)} \quad (5)$$

for the same range of concentration differences.

ANALOGY BETWEEN HEAT TRANSFER AND DIFFUSION

Figure 7 is a plot of the Nusselt modulus (Nu) and modulus prime (Nu') as functions of the Grashof prime times the Prandtl ($Gr'Pr$) and Grashof prime times Prandtl prime ($Gr'Pr'$), respectively. The value for the thermal free-convection boundary modulus, Nu, was obtained by multiplying the experimental results given by ten Bosch (*2*) for a vertical plate by 1.2; corrections due to the difference in the methods of evaluating the fluid properties as used here and that employed by ten Bosch, were applied (*2*). For a range of

$$10^7 \leq (Gr'Pr) \leq 10^9$$

the data may be satisfactorily expressed by the relation

$$Nu = 0.75\ (Gr'Pr)^{0.25} \quad (6)$$

for a horizontal plate in free convection losing heat upward.

The evaporation data presented by Sharpley and Boelter (*12*), together with that contributed subsequently (*3, 4*), are also plotted in Figure 7. Within the limits of

$$10^7 \leq (Gr'Pr') \leq 2 \times 10^8$$

the expression

$$Nu' = 0.643\ (Gr'Pr')^{0.25} \quad (7)$$

is found to represent the combined data best. From the foregoing equations the following ratio is computed:

$$Nu = 1.17\ Nu' \quad (8)$$

This result indicates that the "equivalent film thickness" for nonisothermal mass transfer is 1.17 times the thickness of the "equivalent film thickness" for heat transfer for the system under consideration, in the range of experimental variables, and within the accuracy of measurement.

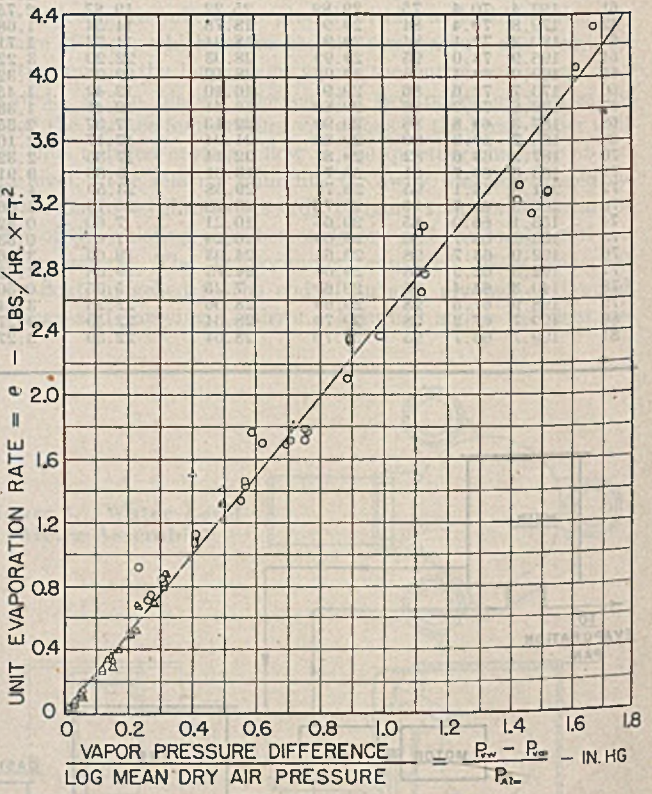

Figure 5. Unit Evaporation Rate e as a Function of Vapor Pressure Difference, $P_{vw} - P_{v\infty}$, Corrected for Variation of Inert Gas (Air) Pressure

△ Gordon, ○ Griffin

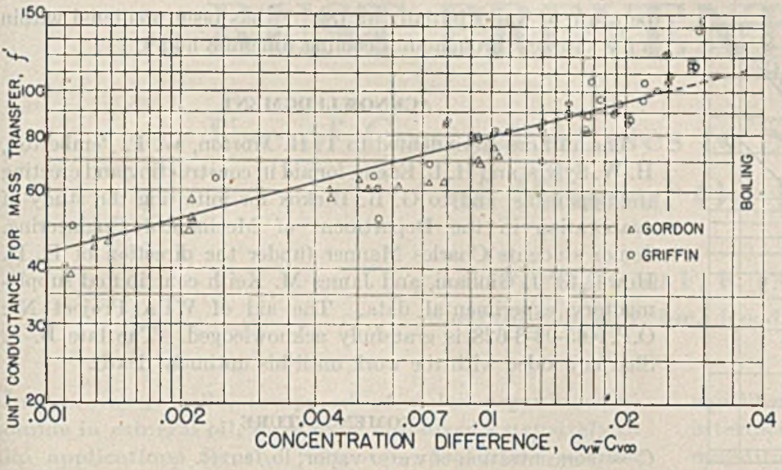

Figure 6. Unit Conductance for Mass Transfer, f', as a Function of Concentration Difference, $C_{vw} - C_{v\infty}$

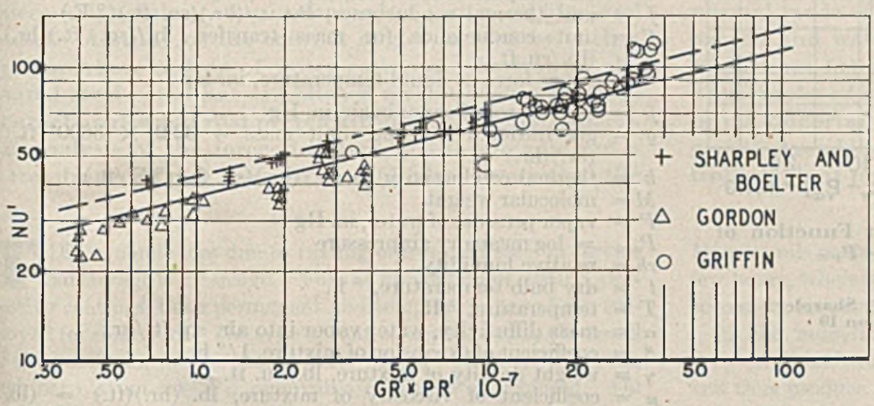

Figure 7. Nusselt Modulus Prime Plotted as a Function of Grashof Modulus Prime × Prandtl Modulus Prime

For comparison the heat transfer modulus (Nu) is also plotted as a function of Grashof modulus prime × Prandtl modulus

- - - - $Nu = 0.75 (Gr'Pr)^{0.25}$ ——— $Nu' = 0.643 (G'Pr')^{0.25}$

DESCRIPTION OF PHENOMENON

The vapor stream issuing from the liquid serves as a jet for concentration differences above the critical. Air is induced into the jet by virtue of its momentum. In the laminar region the unit conductance for mass transfer should vary as the one quarter power of the concentration difference (*1*), but as $Gr'Pr'$ is increased and the flow becomes turbulent, the exponent approaches one third. As the evaporation rate decreases due to a reduced concentration difference, a point is reached where the density of the mixture far away equals the density of the mixture on the gaseous side of the liquid-gas interface. The corresponding mixture flow system is indifferent, and the surface temperature is at its critical value. For still lower concentration differences the mixture will be denser at the water surface, and if the pan were large in extent, a stable atmosphere would result and the vapor would enter the air by pure diffusion. But the pan is finite in diameter, and the floor which is at the level of the water (and the pan rim) is maintained at the dry-bulb temperature far away. Thus the air sideslips outward, and the corresponding rate of evaporation is many times that of pure diffusion (*6*). In this range the evaporation rate is a linear function of the concentration difference. Finally, if the surface temperature of the liquid is still further reduced, the dew point is reached, and for lower surface temperatures condensation begins. Prediction of rates of condensation in terms of the rate of evaporation is an intriguing problem. The flow patterns corresponding to these cases are shown in Figure 8.

Certain errors have been found in the results published by Sharpley and Boelter (*9*). These errors were corrected prior to the inclusion of their results in the curves and equations presented here. An error had been made in the value for the viscosity of air which had been taken from tables at the incorrect temperature; i.e., the temperature in degrees Fahrenheit was employed in a table in which the viscosity was listed in terms of degrees centigrade. Also, the values of Pr' given in Table I of the previous paper (*12*) are in reality those for Stanton's modulus prime, which is the reciprocal of Prandtl's modulus prime. The values given for $Gr'Pr'$ were, however, correctly computed with the exception of the incorrect choice of the viscosity. Finally the equations given for unit evaporation rate e and Nusselt modulus prime Nu' are not numerically compatible.

LITERATURE SURVEY

Evaporation data are sometimes cited with no specification of the wet-bulb temperature far away. This procedure is obviously not greatly in error for low humidities and when the vapor pressure on the gaseous side of the liquid-gas interface is high compared to the vapor pressure far away. For instance, water at 150° F. evaporating into air at 70° F. and 50% *rh* will exert a vapor pressure of 3.72 pounds per square inch while the vapor pressure of the moisture in the air is 0.18 pound per square inch. Neglect of the latter will cause an error of about 5% in the prediction of the evaporation rate.

Box (*13*) suggested that "the rate of evaporation of water, alcohol, benzoline, and ether" when exposed to "perfectly calm air at natural temperatures could be calculated by means of the equation:

$$R = 378 (F - \bar{f}) \tag{9}$$

where R = rate of evaporation, grains/(sq. ft.)(hr.)

$F - \bar{f}$ = difference between "force of vapor of given liquid at temperature of ambient air" and "force of vapor actually present in the air"

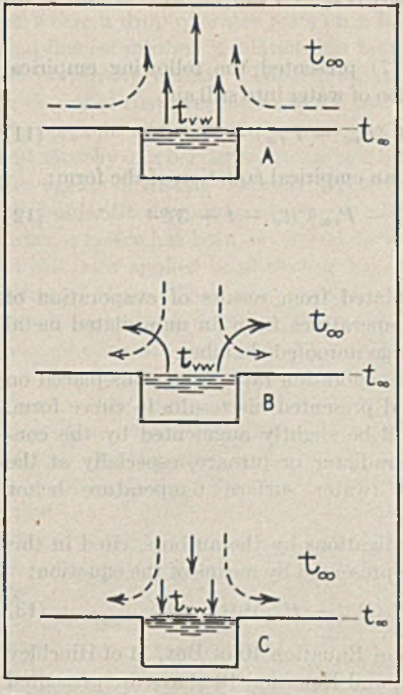

Figure 8. Mixture Flow Diagrams above the Pan

t_{vw} = surface temperature of the liquid
t_∞ = dry bulb temperature far away, and also that of the floor
- - - - air flow; ——— vapor flow
A = parallel flow evaporation, $\gamma_w < \gamma_\infty$ $C_{vw} > C_{v\infty}$
B = contraflow evaporation, $\gamma_w > \gamma_\infty$, $C_{vw} > C_{v\infty}$
C = condensation, $C_{vw} < C_{v\infty}$

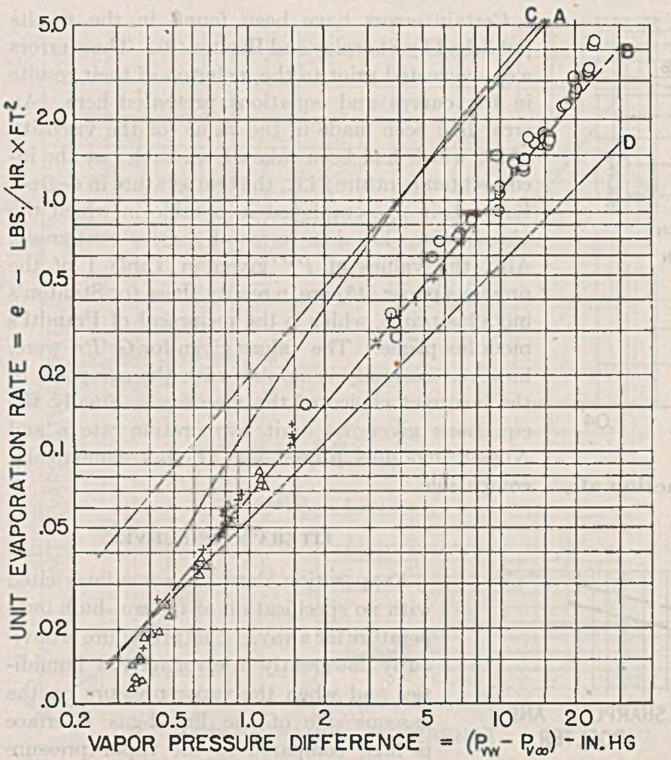

Figure 9. Unit Evaporation Rate *e* as a Function of Vapor Pressure Difference, $P_{vw} - P_{v\infty}$

A. Hinchley and Himus, Equation 11
B. Equation 13: ○ Griffin; + Gordon; △ Sharpley
C. Rohwer, Equation 12 *D.* Box, Equation 10

This equation becomes

$$e = 0.054\ (P_{vw} - P_{v\infty}) \tag{10}$$

in the units of this paper.

Hinchley and Himus (*7*) presented the following empirical equation for the evaporation of water into still air:

$$e = 0.20\ (P_{vw} - P_{v\infty})^{1.20} \tag{11}$$

Rohwer (*11*) developed an empirical equation of the form:

$$e = 0.0173\ (P_{vw} - P_{v\infty})\ (t_w - t + 3)^{0.6} \tag{12}$$

where $(t_w - t) > -3$

This equation was formulated from results of evaporation of water at normal room temperatures from an uninsulated metal square pan located in a large unroofed chamber.

Kratz (*5*, *8*) measured evaporation rates from pans placed on radiators and furnaces and presented his results in curve form. The evaporation rates will be slightly augmented by the convection stream from the radiator or furnace, especially at the lower evaporation rates (water surface temperature below 180° F.).

The results of the investigations by the authors, cited in this paper, can be fairly well represented by means of the equation:

$$e = 0.067\ (P_{vw} - P_{v\infty})^{1.22} \tag{13}$$

The numerical evaluation of Equation 10 of Box, 11 of Hinchley and Himus, 12 of Rohwer, and Equation 13 above are presented in Figure 9 for comparison. The results of Rohwer and Hinchley and Himus are high, probably as a result of extraneous air currents; those of Box should not be extrapolated to high vapor pressure differences.

The generalized equations presented here have been employed successfully to predict rates of evaporation and cooling times of vessels of water and of alcohol into air at room temperatures under conditions of transient cooling. For instance, the temperature of water initially at 180° F. has been predicted within a few degrees throughout a cooling time of 3 hours.

ACKNOWLEDGMENT

The authors are indebted to T. H. Morton, W. F. Pemberton, H. W. Sylvis, and H. L. Eagles for aid in constructing and erecting the apparatus, and to G. H. Hickox for initiating the study of evaporation in the Department of Mechanical Engineering. Senior students Charles Manner (under the direction of E. D. Howe), F. J. Giuliani, and James M. Keith contributed supplementary experimental data. The aid of WPA Project No. O.P. 465-03-3-628 is gratefully acknowledged. The late B. F. Sharpley aided with the work until his untimely death.

NOMENCLATURE

C = concentration of water vapor, lb./cu. ft.
C_p = unit heat capacity of mixture at constant pressure, B.t.u./(lb.) (° F.)
D = pan diameter, ft.
e = unit evaporation rate, lb./(sq. ft.) (hr.)
f = unit thermal conductance, B.t.u./(hr.)(sq. ft.)(° F.)
f' = unit conductance for mass transfer, lb./(sq. ft.)(hr.) (lb./cu. ft.)
F = vapor force at liquid temperature, in. Hg
$\bar{f}$ = vapor force of vapor in air, in. Hg
g = gravitational force per unit mass = 32.2 × 3600² ft./(hr.)(hr.)
k = thermal conductivity, B.t.u./(hr.)(sq. ft.)(° F./ft.)
M = molecular weight
P = vapor pressure of water, in. Hg
P_{atm} = log mean dry air pressure
rh = relative humidity
t = dry bulb temperature, ° F.
T = temperature, ° R.
α' = mass diffusivity, water vapor into air, sq. ft./hr.
β = coefficient of expansion of mixture, 1/° F.
γ = weight density of mixture, lb./cu. ft.
μ = coefficient of viscosity of mixture, lb./(hr.)(ft.) = (lb. sec./sq. ft.)(32.2)(3600)

Subscripts
v = water vapor
w = gaseous side of liquid-gas interface
∞ = far away

Dimensionless moduli
$Nu' = f'D/\alpha'$, Nusselt modulus prime
$Nu = fD/k$, Nusselt modulus
$Gr' = \dfrac{gD^3\gamma^2}{\mu^2}\left(\dfrac{M_\infty T_w}{M_w T_\infty} - 1\right)$, Grashof modulus prime
$Gr = \dfrac{gD^3\gamma^2}{\mu^2}\beta(t_w - t_\infty)$, Grashof modulus
$Pr' = \mu/\alpha'\gamma$, Prandtl modulus prime
$Pr = \mu C_p/k$, Prandtl modulus

LITERATURE CITED

(1) Boelter, L. M. K., Cherry, V. H., and Johnson, H. A., "Heat Transfer Notes", 3rd ed., Chap. XII, pp. 29–37, Berkeley, Univ. of Calif. Press, 1942.
(2) Bosch, M. ten, "Die Wärmeübertragung", 3rd ed., p. 174, Berlin, Julius Springer, 1936.
(3) Gordon, H. S., M.S. thesis, Univ. of Calif., 1938.
(4) Griffin, J. R., *Ibid.*, 1939.
(5) Harding, L. A., and Willard, H. C., "Heating, Ventilating and Air Conditioning", p. 590, New York, John Wiley & Sons, 1937.
(6) Hickox, G. H., Ph.D. dissertation, Univ. of Calif., 1940.
(7) Hinchley, J. W., and Himus, G. W., *Trans. Inst. Chem. Engrs.* (London), 2, 57 (1924).
(8) Kratz, A. P., Univ. Illinois Eng. Expt. Sta., *Bull.* 230 (1931).
(9) LeFevre, E. J., private communication, Dec. 6, 1938.
(10) Lorenzen, C., "Construction and Use of a Thermoelectric Psychrometer", Temperature Symposium, p. 660, New York, Reinhold Pub. Corp., 1941.
(11) Rohwer, Carl, U. S. Dept. Agr., *Tech. Bull.* 271 (1931).
(12) Sharpley, B. F., and Boelter, L. M. K., Ind. Eng. Chem., 30, 1125 (1938).
(13) Siebel, J. E., "Compend of Mechanical Refrigeration", 7th ed., p. 102, Chicago, Nickerson and Collins Co., 1906.

RUST PREVENTIVE OILS

Use of Contact Angles to Study the Action of Mineral Oil Films

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Rust preventive oils, composed of polar organic compounds in mineral oil, have been employed extensively in film applications for the temporary protection against rusting of iron and steel parts during manufacturing operations, storage, shipment, and use. The condensation of moisture in droplets on such oil-coated steel parts produces a dynamic system composed of water, oil film, and metal. A study of the contact angles formed by such a system where a drop of water rests on a horizontal oil-coated steel panel has established a relationship between contact angles and rust preventive ability. A mathematical analysis of the forces involved in the spreading of a water drop on a rust preventive oil film has shown that the equilibrium surface tensions of the water and oil and their interfacial tension are the major factors determining the magnitude of the contact angle. These findings are in agreement with the theory of rust prevention which postulates orientation of the polar organic additive at the oil-metal interface and establishment thereby of a barrier to normal mode of entry of the causative agents of rusting—oxygen and water. Contact angles were measured by a microscope fitted with a goniometer eyepiece; they have been employed in determining that solubility in water is of prime importance among the physical properties of rust preventive additives and have found application in controlling plant production of rust preventive oils.

THE economic loss due to rusting of iron and steel in service and storage is extensive. For the prevention of rusting, protective coatings, both permanent and temporary, have been employed for some time; the type of coating depends upon the needs of the particular application. Early practice made use of grease and petrolatum when a removable coating was required. Oil type coatings, more desirable from the standpoint of ease of removal, were not widely accepted as satisfactory protective coatings until it was demonstrated that the rust preventive capacity of an oil could be increased more than tenfold by the incorporation of certain types of polar organic compounds. These polar organic additives, such as petroleum sulfonates, are now being employed in a wide variety of oils used not only as protective coatings but also as lubricants.

The necessity for rust preventive lubricating oils and for easily removable coatings was emphasized early in World War II by the problem of inordinate rusting in the extreme humidity of such localities as the South Pacific. Acceleration was therefore given to the development of rust preventive gun, instrument, turbine, hydraulic, gear, engine preservative, package, and other oils for protection of iron and steel parts during manufacturing operations, storage, shipment, and use.

This development produced two fairly distinct types of rust preventive oils, one for use in bulk applications such as in the lubrication of turbines (*5*) and hydraulic systems, the other for film type applications as a protective coating. The first requires only a small concentration of polar organic compound because any local depletion of additive is replenished by the remaining bulk of the oil. The oil film type of rust preventive has no means for replenishment of depleted additive and requires, in general, a much higher concentration of additive. This paper deals with the latter type—namely, oil film rust preventives.

As temporary protective coatings on exposed steel surfaces, oil film rust preventives are effective for a period of several months to a few years, depending on the severity of exposure conditions. For a rapid evaluation of protective ability, humidity cabinets are commonly used. Their function is to accelerate rusting of oil-coated steel specimens by means of elevated temperature and humidity. Comparisons of rust preventive effectiveness are made by noting the time which elapses before rusting occurs. Mineral oils containing no additive (undoped) allow rusting in a few hours, whereas effective rust preventive oils protect the steel specimens for several hundred hours in a humidity cabinet.

In the humidity cabinet the oil-coated steel panels collect droplets of moisture by condensation from the humid atmosphere and thus produce a dynamic system composed of water, oil film, and metal. A study of the contact angles formed by such a system where a drop of water rests on a horizontal oil-coated steel panel has established a relationship between contact angles and rust preventive ability. These findings are in agreement with the theory of rust prevention which postulates orientation of the polar organic additive at the oil-metal interface and establishment thereby of a barrier to the normal mode of entry of the causative agents of rusting—namely, oxygen and water.

A standardized procedure using a microscope fitted with a goniometer eyepiece has been developed for measuring contact angles and has been applied in predicting the effectiveness of rust preventive oil films. These predictions are based on data correlating contact angles with degree of protection in a humidity cabinet. Undoped mineral oils yield contact angles of 70° to 85° and offer protection to a steel panel for only a few hours in the humidity cabinet. When a rust preventive additive is dissolved in increasing amounts in a mineral oil, a decrease in contact angle results such that an angle of about 55° corresponds to a humidity cabinet life of 100 hours, an angle of 30–35° to 200 hours, etc. The prediction of rust preventive capacity from contact angles is valid for most of the different types of rust preventive oils examined. These represented a great variety of oil and additive types. The validity of the method is not influenced by the presence of nonpolar additives such as the common pour-point depressants, antioxidants, and viscosity-index improvers.

Since contact angles are influenced by such variables as oil and additive composition and oil viscosity, the most reliable predictions of rust preventive ability are made where these variables are minimized—for example, in the use of a given oil and a given additive where concentration of additive is the only variable. The contact angle method is therefore well suited as a control test in plant production of rust preventive oils.

A mathematical analysis of the forces involved in the spreading of a water drop on a rust preventive oil film has shown that the equilibrium surface tensions of the water and oil and their interfacial tension are the major factors determining the magnitude of the contact angle.

Among the physical properties of the polar organic compounds used as rust preventive additives, solubility in water is of prime importance since it determines to a large extent the rate at which these compounds are leached from the oil film under humid conditions producing condensation of moisture. The contact angle method has been employed for determining the rate at which polar additives are leached from rust preventive oils.

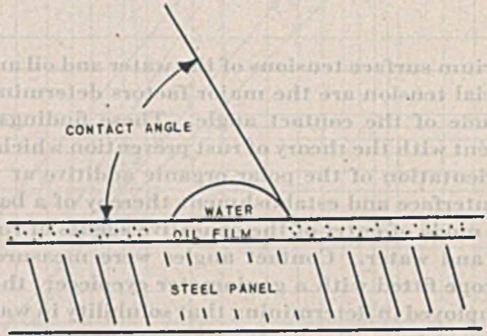

Figure 1. Illustration of Contact Angle

The contact angle method does not apply when additive concentrations are high (above 10%) and also fails to indicate protection against rusting which is attained by mechanical means, such as is achieved by nonpolar suspended material in an oil blend. In such cases the actual protection is greater than that predicted by the contact angle.

EVALUATION OF RUST PREVENTIVE COATINGS

The evaluation of temporary protective coatings is accomplished by means of artificial weathering devices in which standardized conditions are maintained. Their function is to create severe weathering conditions which will accelerate rusting and the breakdown of protective films, and thus allow in a short time a prediction of the protection which can be expected in outdoor service. The three most common devices employed for accelerated weathering are the ultraviolet weathering unit, the salt fog cabinet, and the humidity cabinet. These consist essentially of systems in which clean steel panels covered with the protective coating are exposed at an elevated temperature, respectively, to ultraviolet light, to a fog of salt water, or to an atmosphere of high humidity. The steel panels are examined periodically and the rust preventive capacity of a coating is determined by noting the time which elapses before rusting occurs. The heavier types of temporary protective coatings, such as resins, greases, and petrolatum, are evaluated more readily in the ultraviolet and salt fog cabinets; but for the evaluation of oil film types which, in general, have a shorter life of protection, the humidity cabinet has been the chief tool.

Many different types of humidity cabinets are now in use, most of which operate at a relative humidity of 100% and a temperature of 100° or 120° F. Because of varied design and operation, these cabinets do not agree in evaluating a given protective oil coating. Several laboratories, however, are now cooperating in the development of a standardized cabinet which will aid in minimizing these differences. The study described here is sufficiently fundamental in nature to yield information which is largely independent of the variables affecting results from humidity cabinet tests. Without entering the argument over optimum operating conditions of a humidity cabinet, we believe that the reasonably precise results obtained in the cabinet used for the present study can form a basis for valid conclusions. The operation of this cabinet is as follows: A continuous stream of air is humidified by bubbling through a column of warm water and is then passed through the cabinet at such a rate that a complete change of air within the cabinet is provided approximately 1.5 times per hour. Immersion heaters control the temperature of the water in the humidifier so that the stream of air which enters the cabinet is saturated with water vapor and is at a temperature slightly above 100° F. By means of a thermoregulator and immersion heaters, a water bath in the bottom of the cabinet serves to maintain the cabinet temperature at 100° F. Adequate insulation of the cabinet is instrumental in rendering constant the rate of condensation of water vapor on the steel test panels and interior of the cabinet. Humidity cabinets of constant and uniform exposure conditions have recently been described by Todd (*9*) and by an Army-Navy specification (*2*).

In the normal operation of the humidity cabinet in these laboratories, the oil-coated steel panels collect droplets of moisture by condensation from the humid atmosphere and thus produce a dynamic system composed of water, oil film, and metal. A study of this system by physical-chemical means, using interfacial tension and contact angles, has led to the establishment of a relationship between contact angles and rust preventive capacity; it has given support to the theory that rust prevention is obtained by the orientation of polar organic molecules on the metal surface to form a multimolecular layer, partially or completely impermeable to water.

A THEORY OF RUST PREVENTION

When a homogeneous oil solution of a polar compound, such as oleic acid dissolved in a mineral oil, is brought in contact with iron or steel, orientation of the polar compound on the metal surface occurs (*7*, *10*). This orientation consists in a concentration of the polar compound at the oil-metal interface and the deposition of orderly aligned layers of molecules; the polar group of each molecule of the first layer (e.g., the carboxyl group) is aligned at the metal surface by adsorptive forces, and the nonpolar residue (e.g., the alkenyl group of oleic acid) extends outward from the metal surface. The existence of such an adsorbed layer was postulated by Bulkley and Snyder (*3*) from experiments using oleic acid. According to Karplus (*7*) and Trillat (*10*), the forces of orientation of the random polar molecules out of solution extend over a distance of 9000 Å. and lead to the deposition of multimolecular oriented layers similar to those described by Langmuir (*8*) and by Clark, Sterrett, and Leppla (*4*). Hardy and co-workers (*6*) also showed that attractive forces which possess an unexpectedly large sphere of activity (2–6μ) emanate from boundary surfaces—ranges which closely approximate the average film thickness of an oil layer. These forces of attraction which emanate from a boundary surface are thus not limited in their influence to a monomolecular layer but extend far into the layer of oil. The discovery by Trillat (*10*) that such polar compounds, toward which metals exert an especially strong attractive influence, form lamellar structures of 400–500 molecular layers without the assistance of any external forces is in excellent agreement with results obtained by Hardy. There are, however, reasons to question the multimolecular layer theory; for example,

TABLE I. EFFECT OF SEVERAL VARIABLES ON CONTACT ANGLES

(Distilled water drop deposited on sandblasted steel panel coated with a rust preventive oil)

Drainage Conditions for Oil-Coated Panel			
Time, hr.	Temp., ° F.	Size of Water Drop, Ml.	Contact Angle after 3 Minutes
2	Room	0.05	12°
0.5	130	0.05	2°
1	130	0.05	5°
2	130	0.05	17°
2	130	0.10	17°
2	130	0.20	18°
16	130	0.05	18°

it is difficult to conceive that the oleophilic surface of the first oriented layer should attract the polar additive in preference to oil. On the other hand, it is possible that the free energy of formation for a multimolecular layer, corresponding to a crystal of the polar additive, is more favorable than for a mixed layer and that the existence of the multilayer of additive would consequently be favored.

It is conceivable that between these oriented layers and the polar molecules in solution, there is established an adsorption-desorption equilibrium. These oriented layers serve to prevent rusting of the metal by interrupting the normal mode of entry of water and oxygen. Such an equilibrium would offer an explanation as to why the amount of additive actually required in service for adequate rust prevention is greatly in excess of that required to form an oriented layer on the metal surface. Although such a layer may be sufficient to prevent rusting, it is theorized that further increments of antirust agent are instrumental in shifting this equilibrium strongly in favor of further adsorption and maintaining it until the additive has been depleted to the extent that the adsorption-desorption equilibrium is reversed. When desorption becomes extensive, the oil film no longer remains impervious to water and oxygen, and rusting results. The effectiveness of polar organic compounds as rust preventive agents in mineral oil would then depend on the polarity of the organic compounds toward iron and steel; other factors which change the adsorption-desorption equilibrium, such as temperature, molar concentration of additive, and chemical structure of hydrocarbon radical, would be held constant.

When a drop of water forms on an oil-coated horizontal steel surface by condensation of moisture, the extent of spreading of the water drop is influenced, among other factors, by the attraction of oil-soluble polar substances to the water-oil interface. With certain exceptions these oil-soluble polar substances are effective as rust preventive additives and orient also at the oil-metal interface. It is probably fortuitous that the types of polar compounds now used as rust preventives possess structures and solubilities which relate their orientations at water-oil and oil-steel interfaces[1]. The extent to which a drop of water spreads on oil-coated steel surfaces is, therefore, an indirect measure of the strength and extent of orientation at the oil-metal interface and is likewise an indirect measure of the rust preventive capacity of the oil film. Spreading of a drop of water in such a system is easily followed by measuring the angle of contact at the air-water-oil interface. Contact angles of such a system, therefore, offer a convenient and valuable tool for studying rust preventive oils.

CONTACT ANGLES

In the humidity cabinet used for testing rust preventive oils, the oil-coated test panels collect drops of moisture by condensation from the humid atmosphere so that the system composed of water, oil film, and metal prevails wherever a water drop has formed on the panel. This system is illustrated in Figure 1. Contact angles have therefore been measured for such a system by using the sessile drop method. Various other methods such as the rotating cylinder, tilting plate, etc., could be used.

The observation was made that a drop of distilled water on a steel panel coated with a thin film of oil formed a definite and reproducible contact angle at the water-air-oil film interface. Rough measurements revealed that contact angles varied to some extent with different base stocks. Cursory experiments in which rust preventive oils were used indicated that smaller angles were formed with these oils as a group than with the base stocks. However, when it was noted that the contact angle varied with the experimental conditions, it was deemed advisable to establish a standard procedure for measuring contact angles. Some time was devoted, therefore, to the control of variables which might affect the reproducibility of these measurements. Among these variables are drainage time, drainage temperature, the size of the water drop, and the length of time between deposition and observation of the drop. The temperature at which the oil was drained from the plate as well as the drainage time were found to have great influence on the extent to which a water drop would spread on the resultant oil film and, consequently, on the size of the contact angle. The introduction of a specific drainage period and temperature was therefore a necessary prerequisite for distinguishing between a good and a mediocre rust preventive oil.

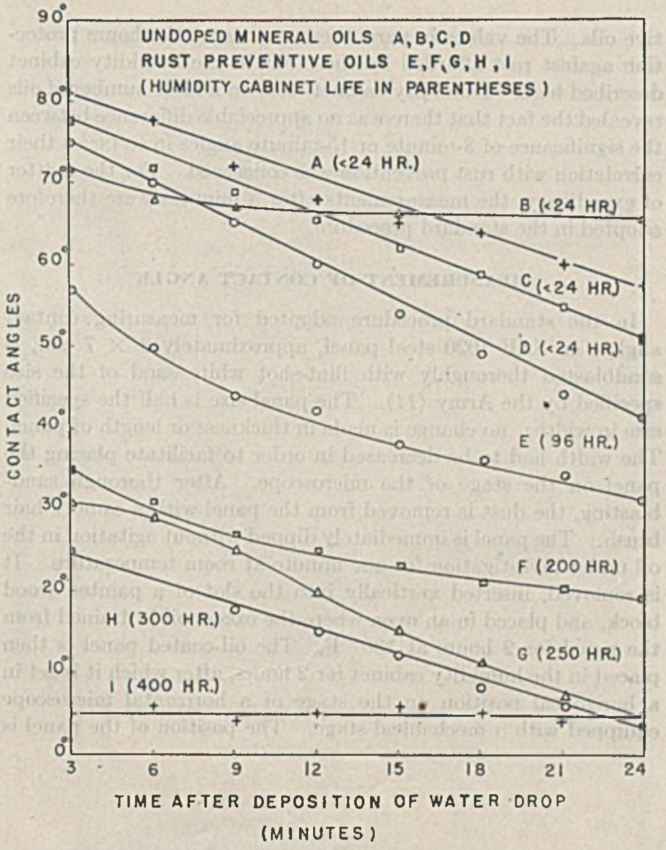

Figure 2. Effect of Time on Contact Angle for Several Base Stocks and Rust Preventive Oils

Throughout the entire work the dipping time of the panel in the blend was maintained at one minute, as recommended in a number of government specifications for rust preventive oils. Theoretically, the volume of the water drop deposited on a panel should have no effect on the contact angle. Table I illustrates that such is the case in the range of drop size used, for a fourfold variation in the volume of the drop deposited did not affect the magnitude of the contact angle. An increase in drainage temperature, from room temperature (about 75° F.) to 130° F. brought about a significant increase in the size of the angle. This increase can, in part, be attributed to the lens effect created by the water drop on the less dense mineral oil when a thick oil film is used.

On the basis of these and similar experiments with oils of other viscosity, a drainage time of 2 hours at 130° F. was adopted. Since a decrease of contact angle with time was observed in every case, angles were determined for a number of blends at 3-minute intervals for a 24-minute period after deposition of a water drop on the panels. The observed decrease in contact angle is believed to represent the tendency for the system to re-establish equilibrium after creation of the water-oil interface. Figure 2 illustrates these results for four base stocks and five rust preven-

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[1] Structural types of rust preventive additives are conceivable for which the present relation between orientations at the water-oil and oil-steel interfaces would be considerably altered—namely, compounds whose polarity toward steel was considerably stronger and whose hydrophilic tendency was considerably weaker than those of existing compounds.

tive oils. The values in parentheses represent the hours protection against rust afforded by these oils in the humidity cabinet described here. Humidity cabinet tests on a large number of oils revealed the fact that there was no appreciable difference between the significance of 3-minute or 15-minute angles in so far as their correlation with rust prevention was concerned. For the matter of expediency, the measurements after 3 minutes were therefore adopted in the standard procedure.

MEASUREMENT OF CONTACT ANGLE

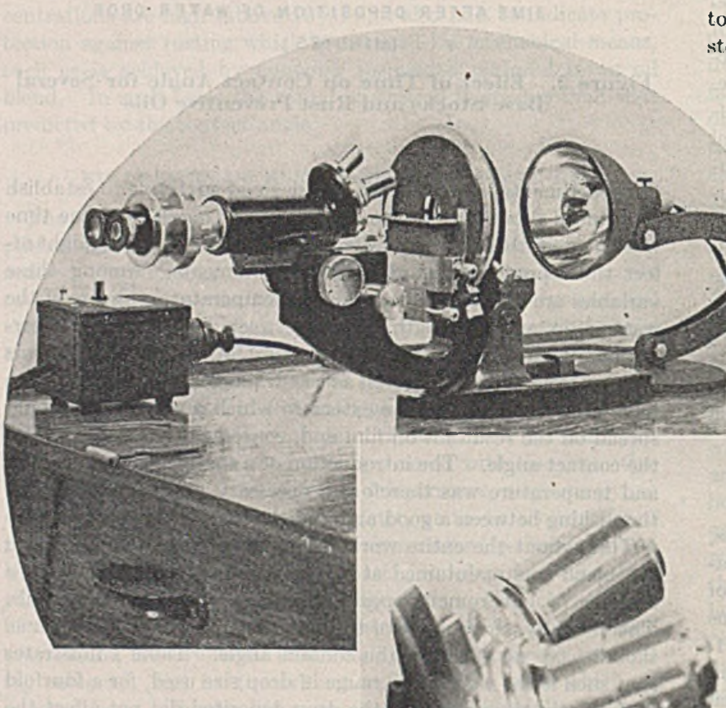
In the standard procedure adopted for measuring contact angles, an SAE 1020 steel panel, approximately 3 × 7 cm., is sandblasted thoroughly with flint-shot white sand of the size specified by the Army (*11*). The panel size is half the specified size in width; no change is made in thickness or length of panel. The width had to be decreased in order to facilitate placing the panel on the stage of the microscope. After thorough sandblasting, the dust is removed from the panel with a camel's hair brush. The panel is immediately dipped without agitation in the oil under investigation for one minute at room temperature. It is removed, inserted vertically into the slot of a painted wood block, and placed in an oven where the excess oil is drained from the panel for 2 hours at 130° F. The oil-coated panel is then placed in the humidity cabinet for 2 hours, after which it is set in a horizontal position on the stage of a horizontal microscope equipped with a mechanical stage. The position of the panel is adjusted so that its upper surface is in the field of view (Figures 3 and 4). A drop of distilled water from an eye dropper is placed on the steel panel near the front edge, and the contact angle at the air-water-oil film interface is measured after 3 minutes by means of a goniometer eyepiece as illustrated in Figure 5. The reproducibility of measurements is about ±1°.

APPLICATIONS OF THE METHOD

When the 3-minute contact angles were measured on a series of base stocks, the values ranged from 70° to 85°. Severe rusting occurred within 24 hours in the humidity cabinet when any one of these base stocks was tested. However, as the amount of rust prevention given by an oil increases as a result of the incorporation of specific polar additives, a decrease in contact angle takes place which can be attributed to the concentration or polarity of the additives or to both.

The correlation between contact angle and rust prevention is illustrated in Figure 6 by plotting the humidity cabinet life against the contact angles of an oil containing increasing amounts of an effective rust preventive additive. In Figure 7 a wide variety of additive and nonadditive oils is correlated according to contact angle and humidity cabinet life. The additive oils range from nonrust preventive to strongly rust preventive blends. A numerical designation has been used for convenience.

The difference noted in the angles of the various undoped oils may be due primarily to their degree of refinement or the extent to which polar impurities were removed in the refining process. These polar impurities are not of the correct molecular structure to act in preventing rust. An 85° angle was obtained when a steel panel was coated with Nujol, a highly refined oil from which polar compounds had been almost completely removed. This represents the largest angle found for a mineral oil. However, a drop of water on paraffin wax yielded an angle of 105°, which is in good agreement with results of other observers. In addition to the values for the base stocks, data are tabulated for a number of oils containing organic additives which serve purposes other than for rust prevention, namely, antifoam agents, antiwear agents,



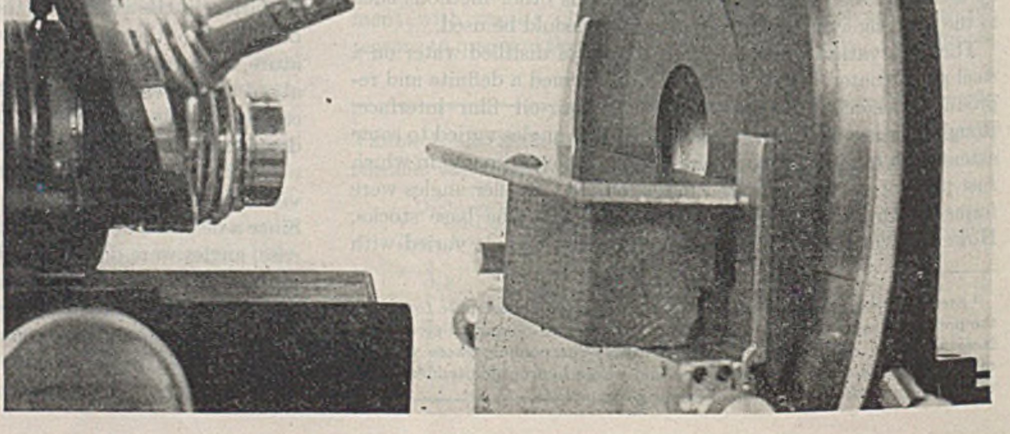


Figure 3 (*Above*). Apparatus for Measuring Contact Angles (Light Source, Microscope, and Goniometer Eyepiece)

Figure 4 (*Right*). Close-up View of Sessile Drop of Water on Oil-Coated Steel Panel

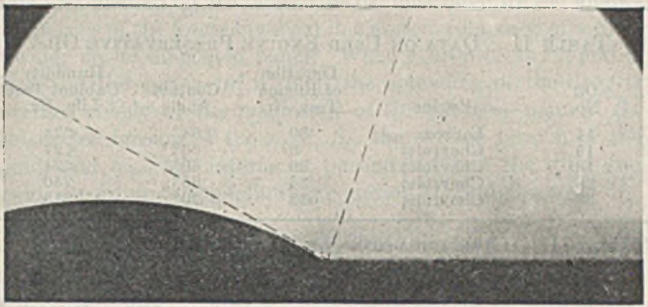


Figure 5. Image of Water Drop as Viewed through Goniometer Eyepiece, Showing Alignment of Eyepiece Cross Hair with Edge of Drop When Measuring Contact Angle

antiring-sticking agents, antioxidants, detergents, pour-point depressants, and viscosity-index improvers. None of these compounds is polar enough to exhibit a significant depression of contact angles. Some detergents, which are weakly polar, exhibit a slight effect on the contact angle. Rust preventive oils as a class, however, exert an effect on contact angle which increases with the degree of rust prevention. The increase in rust prevention shown in Figure 2 was achieved primarily by increasing the concentration of the common types of antirust agents, such as sodium petroleum sulfonates. Oils which yield a 3-minute angle of about 50–55° afford protection for 100 hours in the humidity cabinet; likewise, an angle of 15 to 35° corresponds to a humidity cabinet life of 200 to 300 hours, and an angle of about 5 to 10° corresponds to a life of 400 hours. Since the values of Figure 7 represent a large variety of oils of different viscosities and degrees of refinement and containing different types of polar compounds as additives, it is not expected that all points will fall on the curve. When the variables of oil and additive type and oil viscosity are minimized (e.g., with a given oil and a given additive where concentration of additive is the only variable) excellent correlation is obtained, as shown by Figure 6. The contact angle method is, therefore, well suited as a control test in plant production of rust preventive oils. Figure 8 gives examples of such an application.

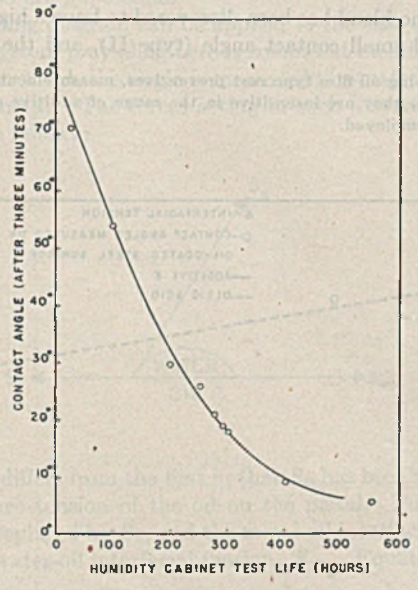


Figure 6. Effect of Humidity Cabinet Life on Contact Angle for an Oil Containing Increasing Amounts of Additive

Some used engine preservative oils are represented in Figure 7; oils 14, 15, and 18 produced large angles and gave no protection against rusting. It is obvious, therefore, that the polar rust preventive compounds originally present in the oil have been destroyed. Oils 28 and 38 had small angles and gave good rust prevention. Pertinent data for these oils are given in Table II.

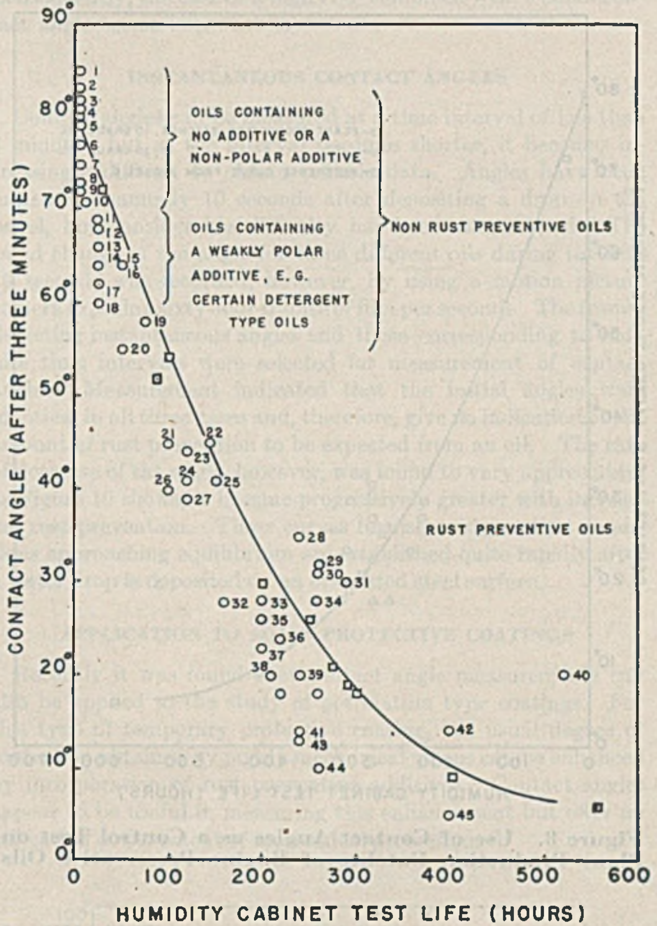


Figure 7. Effect of Humidity Cabinet Life on Contact Angle for a Variety of Additive and Nonadditive Oils

The contact angle data for these used oils were obtained prior to the adoption in the procedure of the 2-hour leaching period in the humidity cabinet. This may account for the reversal in the contact angle–humidity cabinet correlation of samples 28 and 38, since it is possible that water-soluble oxidation products may have been formed in the deterioration of oil 38 which would influence the size of the contact angles but not the rust preventive capacity of the oil. This effect might, consequently, have been avoided if the leaching procedure adopted later had been employed. A more comprehensive discussion of the mechanism and application of this procedure is given in a later section of this paper.

A series of oils of varying viscosity in which the identity and concentration of additive were maintained constant is included in the data of Figure 7. This is illustrated by 39, 41, 43, 44, and 45 which correspond, respectively, to oils having 65, 100, 200, 500, 750, and 2000 seconds Saybolt Universal viscosity at 100° F. The conclusion could be drawn on the basis of these results that increasing viscosity causes a corresponding increase in rust prevention and decrease in contact angle, but it is believed that solubility and other factors are equally if not more important.

CLASSIFICATION OF OIL TYPES

Since the contact angle as measured in this study is undoubtedly influenced by orientation at the water-oil interface, it seemed logical to compare contact angles and interfacial tensions (*IFT*) for different types of oils. On the basis of these two measure-

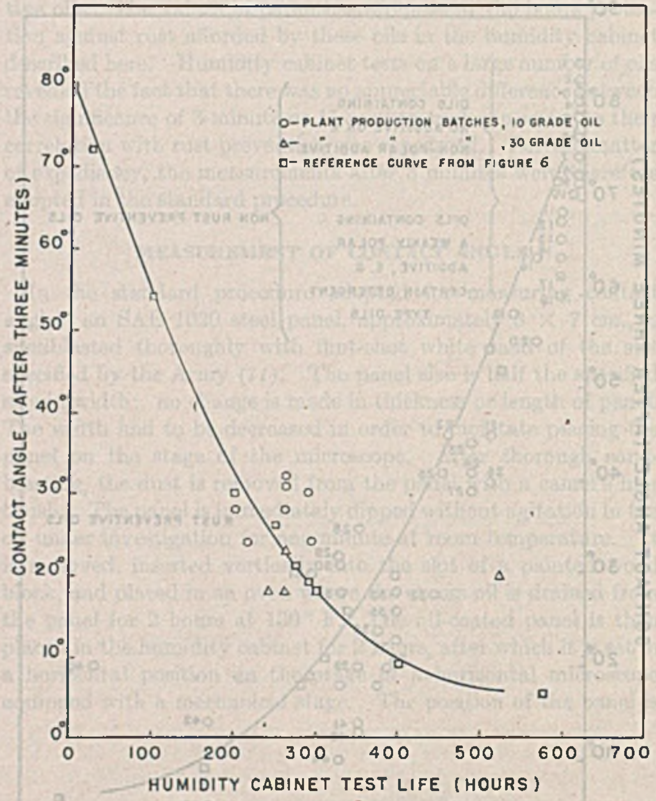


Figure 8. Use of Contact Angles as a Control Test on Plant Production Batches of Engine Preservative Oils

Table II. Data on Used Engine Preservative Oils

Oil No.	Engine	Duration of Engine Test, Hr.	Contact Angle	Humidity Cabinet Test Life, Hr.
14	Lauson	80	64°	<24
15	Chevrolet	6	60°	<24
18	Chevrolet	36	60°	<24
28	Chevrolet	36	35°	240
38	Chevrolet	36	20°	215

Table III. Classification of Oil Types According to Contact Angle and Interfacial Tension

Oil Type	Interfacial Tension	Contact Angle	Representative Example	Contact Angle after 3 Min.	1-Min. IFT, Dynes/Cm.	Humidity Cabinet Life, Hours
I	High	Large	Base stocks	60–85°	20–50	<24
II	High	Small	None known	....	...	.....
III	Low	Large	Soluble oils	60–85°	1–10	<24
IV	Low	Small	Rust preventive oils	0–50°	1–10	100 and over

ments oils can be classified in major groups (Table III). It is evident that in the case where both the contact angle and interfacial tension are high (type I), little resistance to rusting is offered. The rust prevention afforded is likewise negligible for blends showing a low interfacial tension and a large contact angle (type III). This is in good agreement with previous observations that a low interfacial tension does not establish an oil as being a good rust preventive. Rust preventive oils (type IV) are characterized by a low *IFT* and small contact angle.

When a rust preventive compound is added in increasing amounts to a mineral oil, the changes which take place in contact angle and interfacial tension illustrate that oils of type III can be intermediate between types I and IV. For example, in Figure 9 oils of zero additive content (type I) are represented by the ordinate and show high *IFT* and large contact angles on steel panels. When a polar rust preventive is added in small quantity to a mineral oil, a rapid decrease in *IFT* occurs, but the contact angle is only slightly decreased. These are the characteristics of oils of type III. Whereas only small amounts of polar additive are sufficient to decrease *IFT* by orientation at the water-oil interface, comparatively larger amounts of additive are necessary before sufficient orientation at the oil-water interface occurs to affect the contact angle significantly. Oils of type III would thus be expected to be inferior or ineffective rust preventives.

The further addition of rust preventive additive to a mineral oil causes a further slight decrease of *IFT* beyond the already very small value[2], whereas a significant decrease in contact angle occurs and continues until a definite concentration, characteristic of each additive (about 5–25%), is reached where no further appreciable decrease of contact angle is noted. Rust preventive oils (type IV) show these characteristics of low *IFT* and small contact angles. For oils of type IV apparently enough additive has been incorporated to shift the adsorption-desorption equilibrium strongly in favor of oriented layers of polar molecules on the metal surface.

To date no blend has been discovered to have a high interfacial tension and small contact angle (type II), and the possibilities

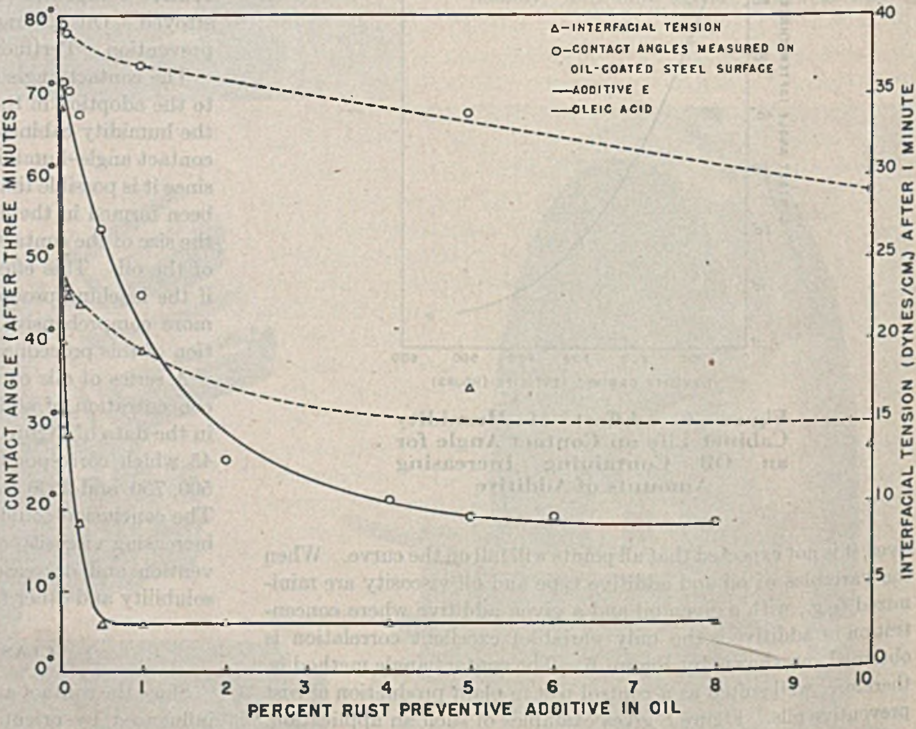


Figure 9. Change of Contact Angle and Interfacial Tension with Increase in Concentration of Rust Preventive Additive

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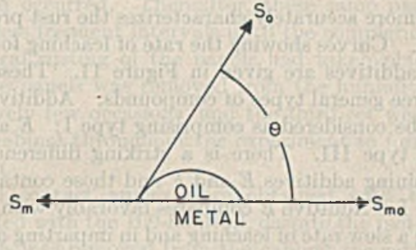
[2] For studying oil film type rust preventives, measurements of *IFT* have little use since they are insensitive in the range of additive concentrations customarily employed.

of finding such an oil are remote, as demonstrated by the following analysis of the forces involved in a system composed of a drop of water on an oil-coated panel: When a drop of any liquid is placed on the surface of a solid, the spreading of the drop is governed chiefly by the magnitude of three forces—namely, S_m the surface tension of the solid, S_o, the surface tension of the liquid, and S_{mo}, the interfacial tension between the solid and liquid, according to the following equation (*1*) and diagram:

$$S_m - S_{mo} = S_o \cos \Theta_{mo} \qquad (1)$$



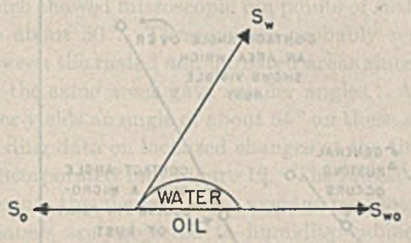
where Θ = contact angle

Subscripts *m*, *o*, *w* = solid (metal), organic liquid (oil), and water phases, respectively

In all cases the values are those of phases in equilibrium and not of pure substances; for example, pure water has an S_w value of 72, but water in equilibrium with oil containing a trace of sodium oleate would have a much lower S_w value.

The type of system shown by Equation 1 would be representative of the case where a liquid such as oil is placed on a steel surface. However, since most mineral oils and additive oils spread to a thin layer on a steel surface, the contact angle is zero, so that measurements are impossible.

The preceding diagram can be applied to the case at hand although the system prevailing here is somewhat modified, for the water drop on which the angle is measured is situated on the oil film on the metal. The forces acting in such a system may be illustrated as follows:



This system differs from the first in that S_m has been replaced by S_o, the surface tension of the oil on the metal. Furthermore, S_o has been replaced by S_w, and the metal-oil interfacial tension, S_{mo}, by the water-oil interfacial tension, S_{wo}. Equation 1 thus becomes

$$\begin{aligned} S_o - S_{wo} &= S_w \cos \Theta \\ \text{or } \cos \Theta &= (S_o - S_{wo})/S_w \end{aligned} \qquad (2)$$

Recent experimental work, not yet completed, indicates that under equilibrium conditions Equation 2 may be applicable as a close approximation to the first system.

Since each of the three forces is independent of the other, numerous possible relations may exist. Thus, when interfacial tension S_{wo} is low, cos Θ will depend primarily on the values of S_o and S_w, and will vary between 1 and 0, corresponding to a variation in contact angle of 0 to 90°. However, when interfacial tension S_{wo} is high, the surface tension of the water drop will be high; cos Θ will tend to be small and the contact angle will be large. Consequently, the case of a high *IFT* combined with a small contact angle seems improbable.

INSTANTANEOUS CONTACT ANGLES

Contact angles can be measured at a time interval of less than 3 minutes, but as the interval becomes shorter, it becomes increasingly difficult to obtain reliable data. Angles have been measured manually 10 seconds after depositing a drop on the panel, but considerable difficulty has been encountered. The rapid change of the angle for three different oils during the first 10 seconds was recorded, however, by using a motion picture camera exposing sixty-four frames of film per second. The frames depicting instantaneous angles and those corresponding to definite time intervals were selected for measurement of contact angles. Measurement indicated that the initial angles were identical in all three cases and, therefore, give no indication of the amount of rust prevention to be expected from an oil. The rate of decrease of the angle, however, was found to vary appreciably; as Figure 10 shows, it became progressively greater with increasing rust prevention. These curves furnish evidence that conditions approaching equilibrium are established quite rapidly after a water drop is deposited on an oil-coated steel surface.

APPLICATION TO SOLID PROTECTIVE COATINGS

Recently it was found that contact angle measurements can also be applied to the study of petrolatum type coatings. For this type of temporary protective coating, the usual degree of protection obtained by purely mechanical means can be enhanced by incorporation of rust preventive additives. Contact angles appear to be useful in measuring this enhancement but offer no indication of the extent of mechanical protection.

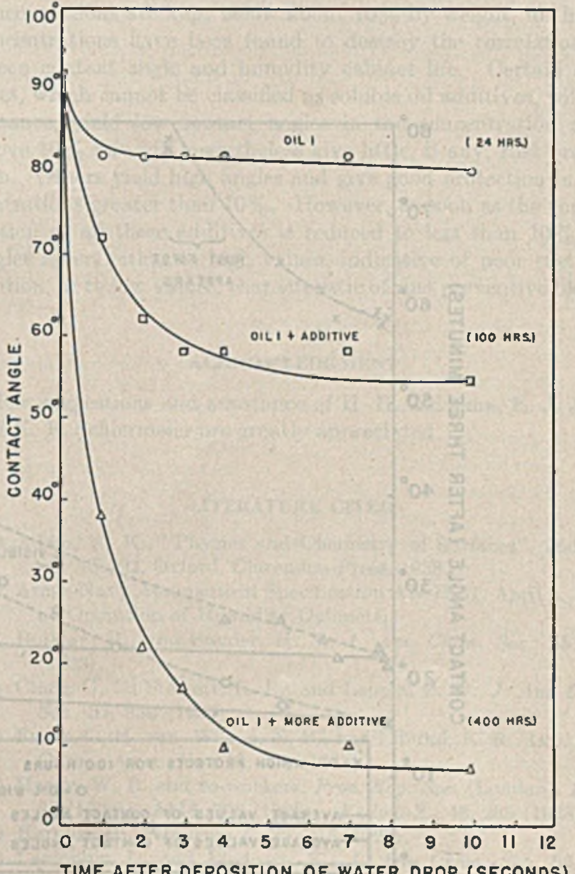


Figure 10. Rate of Change of Contact Angle during First 10 Seconds (Humidity Cabinet Life in Parentheses)

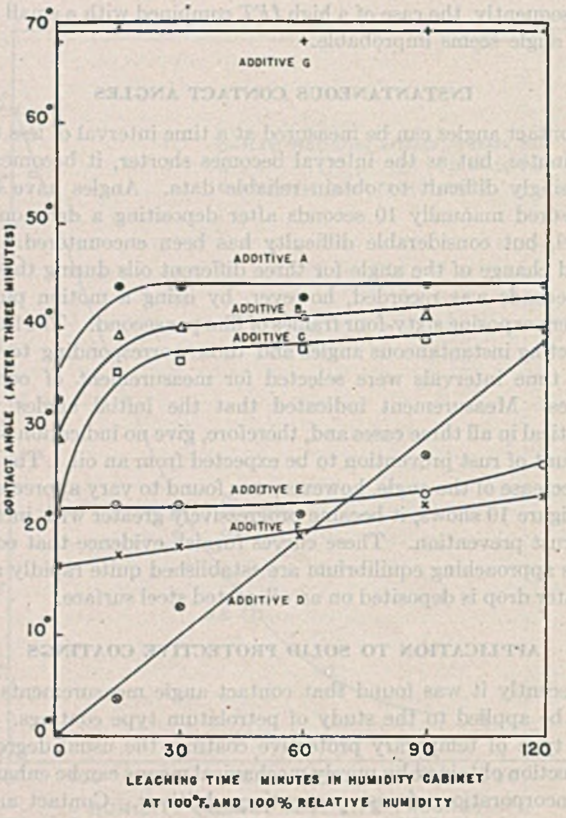


Figure 11. Leaching Rates of Rust Preventive Additives (3% Additive in an Oil of 100 Saybolt Universal Seconds Viscosity at 100° F.)

SOLUBILITY OF RUST PREVENTIVE ADDITIVES IN WATER

Because of the water-soluble nature of certain polar additives employed in rust preventive oils, very small contact angles may be obtained which are misleading since they predict a greater degree of protection than is actually obtained. However, when a 2-hour leaching period in the humidity cabinet is employed prior to contact angle measurement, a more accurate evaluation of the rust preventive capacity of such oils can be made. During this period in the humidity cabinet, water-soluble additives and easily emulsified additives (which form oil-in-water emulsions) are leached from the oil. The contact angle then reverts to a larger value which more accurately characterizes the rust prevention of such a blend. Curves showing the rate of leaching for a number of common additives are given in Figure 11. These additives represent three general types of compounds: Additives *A*, *B*, *C*, and *D* may be considered as comprising type I; *E* and *F*, type II; and *G*, type III. There is a striking difference between blends containing additives *E* and *F* and those containing additives of type I. Additive *E* compares favorably with additive *F* in possessing a slow rate of leaching and in imparting a small contact angle to an oil blend. Additive *D*, on the other hand, is leached at a medium rate from the oil coating and constitutes an example of an additive possessing appreciable water solubility. Because of the polarity of this compound, the contact angle after 2-hour leaching is still indicative of an oil affording considerable rust prevention. However, after 4-hour leaching, this angle reverts to a value of 60° which is more truly representative of the mediocre rust prevention given by this blend. *A*, *B*, and *C* are characterized by an initial rapid rate of leaching followed by a much slower rate. The initial rapid leaching probably represents the removal of constituents which are appreciably more soluble in water than the bulk of the additive. The change of contact angle during this initial period is roughly twice as large for additive *C* as for *A* and *B*.

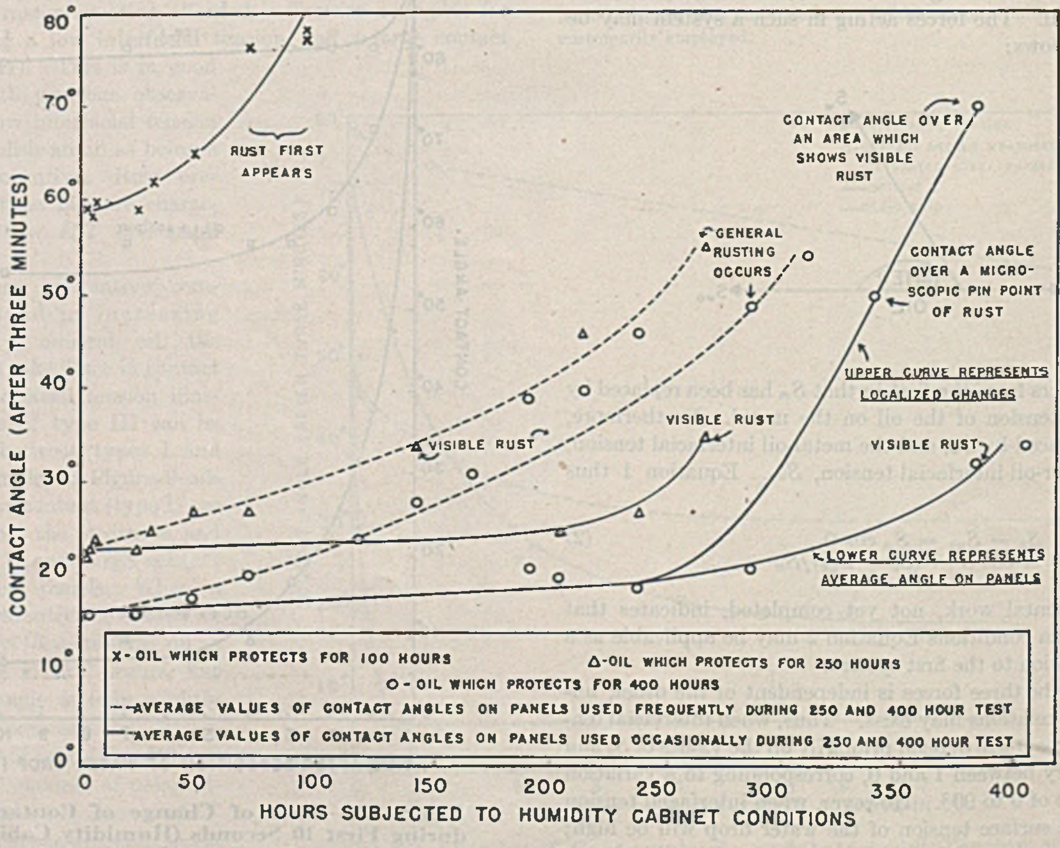


Figure 12. Effect of Humidity Cabinet Conditions on Contact Angles of Certain Blends

This study of leaching has been extended in order that the effect of humidity cabinet conditions on the contact angle during the entire humidity cabinet test might be observed. Three blends offering various degrees of rust prevention were chosen for this work and are listed in the legend of Figure 12. Triplicate panels were used for each of the three blends and were drained 2 hours at 130° F. before being placed in the humidity cabinet. During the first 50 hours of humidity cabinet testing, one of each of the triplicate panels was removed at frequent intervals in order to measure the contact angle and to observe whether any rusting had occurred. Thereafter, these same panels were removed at less frequent intervals until the completion of the test when general rusting of the panels had taken place. Another set of three panels was removed from the humidity cabinet on comparatively few occasions, and the third set was kept in the humidity cabinet throughout the experiment to form a basis for comparison.

Identical contact angles were obtained with the triplicate panels coated with the 100-hour oil, despite the fact that none of these panels was removed from the cabinet the same number of times. A gradual increase in the angle was noted until 76–78° was reached; at this point the first traces of rust were detected. The effect of frequent removal of the panels from the cabinet was more pronounced in the case of the 250- and 400-hour oils, for rust was noticed on the first set of panels coated with these oils after 150–200 hours, respectively, which falls far short of the actual humidity cabinet life as determined with the third set of panels.

The general trend of increasing values for the contact angle with increasing time in the humidity cabinet is an indication of a gradual depletion of additive in the oil film which eventually leads to local rusting. With the exception of the 100-hour oil, rust on the panels first became visible to the naked eye when an angle of 30–35° was reached. These values were obtained, however, when the angle was measured on an unrusted portion of the panel. When water drops were placed on rusted areas of a panel, they formed angles of about 70° (values which would be characteristic of a nonadditive oil or of an oil which had been depleted of additive). Similarly, when small drops of water were placed on areas which showed microscopic pin points of rust, the contact angles were about 50°. These values probably represented an average between the rusted and unrusted areas since larger drops of water on the same areas gave smaller angles. A microscopic drop of water yields an angle of about 65° on these areas.

The preceding data on localized changes at the time of rusting have been incorporated into Figure 12. The lowest curve on the graph represents the change in the average contact angle as the oil-coated panels are subjected to humidity cabinet conditions for 400 hours. When rusting occurs at a localized point and develops to visible rust, this average contact angle is not affected as greatly as would be expected; the angle increased by only 10°. However, the rate and magnitude of change of contact angle is much greater over the areas showing localized rusting. The upper extension of the curve represents these localized changes; it is believed that a similar curve would result from a study of the areas of incipient rusting on any oil-coated panel in the humidity cabinet.

Two possible mechanisms by which rusting could occur in the system under study are as follows:

1. The oil-film is ruptured. This bares the steel surface, allows contact to be made between water and steel, and permits rusting by removal of all protective media from a localized area.

2. The rust preventive additive in the oil film is depleted. In this case the oil film is not ruptured but merely loses its rust preventive additive by the continual leaching action of the humidity cabinet. The intact oil film now has the characteristics of an undoped mineral oil (contact angle 70° or higher), and no longer prevents water from permeating to the steel surface to cause rusting.

Our data indicate that the latter is the correct mechanism since a drop of water on an uncoated, sandblasted panel yields an angle below 50° (usually around 35–45°). Values in this range are obtained on either freshly prepared or rusted panels. If the former mechanism were correct, then the 100-hour oil (Figure 12) would show a rapid decrease of angle to a value below 50°, once the oil film became discontinuous. The fact that this did not occur substantiates the view that case 2 more accurately describes the true mechanism.

These experiments serve to demonstrate more clearly that the solubility of rust preventive additives in water is an important factor in the development, evaluation, and use of rust preventive oils.

LIMITATIONS OF CONTACT ANGLE METHOD

The contact angle offers no indication of protection against rusting which is achieved by mechanical means—for example, by petrolatum or asphalt as a component in an oil blend. In these cases the humidity cabinet life predicted from the contact angle is less than that actually realized. The contact angle in such cases indicates a minimum life and the humidity cabinet itself or one of the other test procedures such as the salt fog test designed for such coatings must be used for evaluation.

The results of contact angle measurements can strictly be applied in predicting protection only to the area actually contacted by the water drop.

The method is most reliable in the range of contact angles between 10 and 80°, and consequently becomes inaccurate for predicting a humidity cabinet life in excess of 350 hours.

The contact angle method is applicable only when additive concentrations are kept below about 10% by weight, for higher concentrations have been found to destroy the correlation between contact angle and humidity cabinet life. Certain additives, which cannot be classified as soluble oil additives, will, for instance, yield low contact angles in the concentration range above 10% but will nevertheless give little, if any, rust prevention. Others yield high angles and give good protection in concentrations greater than 10%. However, as soon as the concentration of all these additives is reduced to less than 10%, the angles revert either to high values, indicative of poor rust prevention, or to low values, characteristic of rust preventive blends.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Adam, N. K., "Physics and Chemistry of Surfaces", 2nd ed., pp. 178–92, Oxford, Clarendon Press, 1938.

(2) Army-Navy Aeronautical Specification AN-H-31, April 2, 1945, on Operation of Humidity Cabinets.

(3) Bulkley, R., and Snyder, H. S., *J. Am. Chem. Soc.*, 55, 194 (1933).

(4) Clark, G. L., Sterrett, R. R., and Leppla, P. W., *J. Am. Chem. Soc.*, 57, 330 (1935).

(5) Fuchs, G. H. von, Wilson, N. B., and Edlund, K. R., IND. ENG. CHEM., ANAL. ED., 13, 306 (1941).

(6) Hardy, W. B. and co-workers, *Proc. Roy. Soc.* (London), **A112**, 62 (1922); **A118**, 209 (1928); *Kolloid-Z.*, 46, 268 (1928).

(7) Karplus, H., *Petroleum Z.*, 25, 375 (1929).

(8) Langmuir, I., and Blodgett, K., *J. Am. Chem. Soc.*, 56, 495 (1934); 57, 2007 (1935).

(9) Todd, F., IND. ENG. CHEM., ANAL. ED., 16, 394 (1944).

(10) Trillat, J. J., *Compt. rend.*, 182, 843 (1926); 187, 168 (1928).

(11) U. S. Army Specification 2-120 for a Special Lubricating Oil, March 25, 1944.

Molecular Volumes of Mononuclear Aromatic Hydrocarbons

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The molecular volumes of 1-phenylalkanes and 2-phenylalkanes at any given fraction of the critical temperature are linear functions of the number of carbon atoms. Molecular volumes of fourteen homologous series of mononuclear aromatic hydrocarbons at 20° C. are also linear functions of the number of carbon atoms. Both of these relationships may be expressed by equations of the form:

$$M/d = V = a + bn$$

Constants a and b are simple functions of the reduced temperature. These functions may be expressed by equations of the form:

$$a \text{ or } b = k + pT_R + qT_R^2$$

THE study reported here correlates existing density data with structure for fourteen homologous series of mononuclear aromatic hydrocarbons, and thus provides a method for estimating the molecular volumes (molecular weight divided by density) and densities of unknown or unmeasured members of the series.

Comparisons of molecular volumes must be made at specified temperatures because of the variation of density with temperature. Comparisons may be made at a constant temperature, such as 20° C. (*1, 2, 7, 9, 10, 12, 13, 15, 18*), or at characteristic temperatures such as the boiling point (*6, 14*), the melting point (*8, 16*), or a given fraction of the critical temperature. The latter is preferred (*5*) when the necessary data are available.

The studies already published are concerned principally with aliphatic and alicyclic compounds. The present correlation was carried out for fourteen homologous series of aromatic hydrocarbons at 20° C. and for two series at corresponding reduced temperatures (fractions of the critical temperatures). By both of these methods the molecular volume was found to be an additive function of the number of carbon atoms within a homologous series. This relationship may be expressed by the equation

$$M/d = V = a + bn \qquad (1)$$

where M = molecular weight
d = liquid density
V = molecular volume
n = number of carbon atoms

Constants a and b vary from one series to another and are characteristic of the series.

The density data used to calculate the molecular volumes are values found in the literature (*4*). When the molecular volume at a temperature other than 20° C. was required, it was calculated from the "best" value of the density at 20° C. and the temperature coefficient of density. In some cases no equation for the variation of density with temperature has been calculated. However, the temperature coefficient of density for hydrocarbons has been shown to bear a definite relationship to molecular weight (*17*). Thus, the constants of a density-temperature equation for any hydrocarbon may be accurately estimated from the molecular weight. These estimated values, in conjunction with the density at some given temperature, were used to determine the molecular volume of compounds for which the experimental data were inadequate.

In order to compare molecular volumes at corresponding reduced temperatures, the critical temperatures must be known. The critical temperature of a compound may be calculated from the boiling point and the parachor (*11*) if the experimental values are not available. The boiling points used in calculating the critical temperatures were the calculated values from a previous study on mononuclear aromatic hydrocarbons (*3*). These boiling points in most cases agree well with the experimental values. Calculated values for critical temperatures were used throughout this study. The calculated and experimental values are shown in Table I. The experimental values in the table are averages of all the available data in the literature and were taken from Egloff (*4*).

The requirement that both density and boiling point data be available for comparisons of molecular volumes at reduced tem-

TABLE I. CRITICAL TEMPERATURES

No. of C Atoms	1-Phenylalkane Series: Compound	T_c, ° K.: Calcd.	T_c, ° K.: Exptl.	2-Phenylalkane Series: Compound	T_c, ° K.: Calcd.	T_c, ° K.: Exptl.
(6)	(Benzene)	(556.64)	(561.6)	......	...	...
7	Toluene	587.75	593.5	......	...	...
8	Ethylbenzene	614.95	625.0	......	...	...
9	*n*-Propylbenzene	639.79	638.7	Isopropylbenzene	627.71	628.1
10	*n*-Butylbenzene	661.62	...	2-Phenylbutane	648.48	...
11	*n*-Pentylbenzene	682.29	...	......	...	...
12	*n*-Hexylbenzene	700.79	...	2-Phenylhexane	684.80	...
13	*n*-Heptylbenzene	717.39	...	2-Phenylheptane	701.01	...
14	*n*-Octylbenzene	732.88	...	2-Phenyloctane	715.25	...
15	*n*-Nonylbenzene	747.83	...	2-Phenylnonane	729.31	...

TABLE II. MOLECULAR VOLUME AT T_R = 0.50

No. of C Atoms	1-Phenylalkane Series: t, ° C.	V, ml. per mole: Exptl.	V, ml. per mole: Calcd.	ΔV	2-Phenylalkane Series: t, ° C.	V, ml. per mole: Exptl.	V, ml. per mole: Calcd.	ΔV
(6)	(3.8)	(87.33)	(87.32)	(+0.01)	...	...	...	...
7	21.0	106.43	105.92	+0.51	...	...	...	...
8	34.2	124.31	124.52	−0.21	...	...	...	...
9	45.9	143.14	143.12	+0.02	40.7	142.27	142.32	−0.05
10	58.2	161.76	161.72	+0.04	51.1	160.68	160.66	+0.02
11	67.2	179.66	180.31	−0.65	...	...	...	...
12	79.6	198.85	199.02	−0.17	69.2	196.96	197.34	−0.38
13	83.2	217.53	217.51	+0.02	77.4	216.44	215.68	+0.76
14	96.9	235.94	236.11	−0.17	84.5	233.92	234.02	−0.10
15	104.7	255.22	254.71	+0.51	91.5	252.13	252.36	−0.23

Table III. Effect of Reduced Temperature on *a* and *b*

	1-Phenylalkane Series				2-Phenylalkane Series			
T_R	*a* exptl.	*a* calcd.	*b* exptl.	*b* calcd.	*a* exptl.	*a* calcd.	*b* exptl.	*b* calcd.
0.400	...	...	...	...	−19.62	−19.61	17.081	17.080
0.425	−22.79	−22.79	17.699	17.699	−20.53	−20.55	17.393	17.394
0.450	−23.28	−23.29	17.991	17.991	−21.37	−21.38	17.708	17.708
0.475	−23.79	−23.78	18.291	18.290	−22.13	−22.11	18.025	18.023
0.500	−24.26	−24.26	18.598	18.598	−22.73	−22.73	18.339	18.340
0.525	−24.72	−24.72	18.913	18.914	−23.23	−23.25	18.656	18.656
0.559	−25.17	−25.17	19.238	19.238	...	...	...	...

peratures limited the scope of this study to two homologous series: the 1-phenylalkane and the 2-phenylalkane series. Data were available for only the first two or three members of all other series.

For comparison of molecular volumes at 20° C., only density data at or near this temperature are required. Sufficient data were available to determine relationships for fourteen homologous series.

MOLECULAR VOLUMES AT CORRESPONDING TEMPERATURES

The molecular volumes of normal alkanes is a linear function of the number of carbon atoms at any reduced temperature (*5*). Molecular volumes of the two aromatic series studied are also linear with respect to the number of carbon atoms, and may be expressed by Equation 1. The constants of this equation were evaluated by the method of least squares at several reduced temperatures, T_R. Molecular volumes with $T_R = 0.50$ are shown in Table II. The calculated molecular volumes in most cases show good agreement with those computed from experimental data, using calculated values of critical temperatures. Benzene, although not a 1-phenylalkane, fits well into the series.

The constants *a* and *b* were found to be simple functions of the reduced temperature for the normal alkane series (*5*). This was found to be true also for the two aromatic series studied. However, *a* is not a linear function of T_R in the aromatic series as it is in the alkane series, and a T_R^2 term must be added. The effect of the reduced temperature on *a* and *b* is given by the following equation:

For the 1-phenylalkane series,

$$a = -12.01 - 30.215\, T_R + 11.426\, T_R^2$$

$$b = 13.972 + 6.039\, T_R + 6.428\, T_R^2$$

For the 2-phenylalkane series,

$$a = 10.07 - 108.608\, T_R + 86.019\, T_R^2$$

$$b = 12.164 + 12.051\, T_R + 0.599\, T_R^2$$

Values based on experimental density data and calculated values for *a* and *b* at several reduced temperatures are shown in Table III. The equations were calculated by the method of least squares, and reproduce the experimental values with a deviation of no more than 2 in the last decimal place.

MOLECULAR VOLUMES AT 20° C.

The molecular volume of saturated aliphatic hydrocarbons is substantially a linear function of the number of carbon atoms at 20° C. (*15*). Short-chain compounds, however, deviate appreciably from the linear relationship. An additional term, 29.0/*n*, was found to correct this deviation (*12*).

For the aromatic series studied, a linear function of the form of Equation 1 was found to be accurate within the limits of error. The constants of this equation were evaluated by the method of least squares for fourteen homologous series. The values for constants *a* and *b* are shown in Table IV.

The values for constant *b* are nearly the same in all of the series. Values of *b* for aliphatic and alicyclic series are also in this range. This indicates that the increment in molecular volume resulting from the addition of a CH_2 group to a chain is nearly constant, irrespective of structure. However, the differences in *b* are in many cases greater than the standard errors of *b*, which shows that the structure of the molecule as a whole does affect the increment resulting from addition of a CH_2 group. The lowest value of *b* is found in the phenylcyclane series, an indication that molecular volume is less affected by enlarging a ring—for example, from cyclopropane to cycloheptane—than by lengthening a chain.

A comparison of the three dialkylbenzene series shows that the molecular volumes are in the order ortho < meta < para, as would be expected. The metadialkylbenzenes have nearly the same molecular volumes as 1- and 2-phenylalkanes of the same molecular weight.

Table IV. Constants of Molecular Volume Equations at 20° C.

Series	No. of Compounds	*a*	*b*	Standard Deviation of *b*
1-Phenylalkane	13	− 9.50	16.507	0.011
2-Phenylalkane	11	− 8.57	16.400	0.059
o-Dialkylbenzene	8	−13.87	16.690	0.020
m-Dialkylbenzene	10	− 8.01	16.356	0.107
p-Dialkylbenzene	10	− 8.51	16.441	0.114
Phenylcyclane	5	− 5.13	14.560	0.133
1-Phenyl-1-alkene	5	−10.19	15.638	0.229
1-Phenyl-(*n* − 1)-alkene	5	−15.23	16.374	0.063
2-Phenyl-*x*-alkene[a]	6	−19.77	16.608	0.106
1-Cyclopentyl-*n*-phenylalkane	5	−16.40	15.730	0.112
1-Phenyl-1-alkyne	5	−23.70	16.540	0.270
1,1-Diphenylalkane	6	−50.14	16.600	0.074
1,*n*-Diphenylalkane	7	−59.25	17.142	0.166
1,1-Diphenyl-1-alkene	9	−63.51	16.845	0.198

[a] Position of double bond not known for some compounds in this series.

Compounds containing a double bond have smaller molecular volumes at 20° C. than do the corresponding saturated compounds. Change from a double to a triple bond further decreases the molecular volume. Cyclization also decreases the molecular volume, as shown by the difference between phenylcyclanes and phenylalkanes having the same number of carbon atoms.

Addition of a second phenyl group to alkanes or alkenes increases the molecular volume, as reflected in the larger values of constant *a* for the diphenyl series. The increase in molecular volume is, however, smaller than the molecular volume of benzene itself.

LITERATURE CITED

(1) Calingaert, G., Beatty, H. A., Kuder, R. C., and Thomson G. W., Ind. Eng. Chem., 33, 103 (1941).

(2) Calingaert, G., and Hladky, J. W., *J. Am. Chem. Soc.*, 58, 153 (1936).

(3) Corbin, N., Alexander, M., and Egloff, G., Ind. Eng. Chem., 38, 156 (1946).

(4) Egloff, G., "Physical Constants of Hydrocarbons", Vol. III, New York, Reinhold Pub. Corp., 1946.

(5) Egloff, G., and Kuder, R. C., Ind. Eng. Chem., 34, 372 (1942).

(6) Egloff, G., and Kuder, R. C., *J. Phys. Chem.*, 45, 836 (1941).

(7) *Ibid.*, 46, 281 (1942).

(8) *Ibid.*, 46, 296 (1942).

(9) Francis, A. W., Ind. Eng. Chem., 33, 554 (1941).

(10) *Ibid.*, 35, 442 (1943).

(11) Herzog, R., *Ibid.*, 36, 997 (1944).

(12) Huggins, M. L., *J. Am. Chem. Soc.*, 63, 116 (1941).

(13) *Ibid.*, 63, 916 (1941).

(14) Kopp, H., *Ann.*, 41, 79 (1842); 96, 155 (1855).

(15) Kurtz, S. S., Jr., and Lipkin, M. R., Ind. Eng. Chem., 33, 779 (1941).

(16) Le Bas, G., *J. Chem. Soc.*, 91, 112 (1907); *Phil. Mag.*, [6] 16, 60 (1908).

(17) Lipkin, M. R., and Kurtz, S. S., Jr., Ind. Eng. Chem., Anal. Ed., 13, 291 (1941).

(18) Taylor, W. J., Pignocco, J. M., and Rossini, F. D., *J. Research Natl. Bur. Standards*, 34, 413 (1945).

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ACTION OF ANTIFOULING PAINTS

Solubility and Rate of Solution of Cuprous Oxide in Sea Water

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The solubility of cuprous oxide, the most commonly used antifouling toxic, has been measured in oxygen-free sea water. It is proportional to the hydrogen ion concentration and agrees with calculations from thermodynamic data, assuming that the dissolved copper exists as the complex ions $CuCl_2^-$ and $CuCl_3^{--}$. The rate of solution of cuprous oxide in sodium chloride–nitrate–borate buffers is proportional to the hydrogen ion concentration and is a linear function of the square of the chloride ion concentration at constant ionic strength. It is concluded that the dissolution occurs principally by a process whose rate determining step is the formation of $CuCl_2^-$, together with a small contribution from a process which does not involve chloride ions.

THE effective suppression of marine growths by an antifouling paint is associated with the dissolution of a toxic substance from the paint into sea water. For paints containing copper compounds as toxics, the leaching rate must exceed about 10 micrograms of copper per sq. cm. of paint surface per day to prevent the attachment and growth of fouling organisms (*5*). On this basis the ideal copper antifouling paint is one whose surface can steadily release toxic over a very long period at a rate which is somewhat greater than the critical value (to provide a reasonable factor of safety) but not excessively greater (to prevent wastage of toxic).

The design of a paint to approach this ideal depends upon the properties of the toxic ingredients as well as those of the binder or matrix. The present series of papers describes the relevant properties of certain commonly used and effective toxics and toxic-matrix systems.

The primary characteristic of the toxic is its solubility. The classical dilemma in the theory of toxic action, as stated by Young (*12*), is that an insoluble toxic will be ineffective and a soluble toxic will be washed away to leave an exhausted surface. The selection of a toxic with an adequate, but not excessive, solubility may facilitate the resolution of this dilemma. This paper and the one to follow (*3*) are concerned with the solubilities and rates of solution of toxics in sea water.

By far the most widely used toxic substance in ship-bottom paints is cuprous oxide. The solubility of this material in sea water can be measured only in the absence of oxygen, since cuprous copper is rapidly oxidized in solution. This paper reports a study of the solubility of cuprous oxide in air-free sea water, and the dependence of its rate of solution in sea water and other chloride solutions upon temperature, hydrogen and chloride ion concentrations, and ionic strength.

The solubility measurements were carried out with Baker's C.P. cuprous oxide. The rate measurements were made with an electrolytically prepared cuprous oxide, compounded with a small proportion of insoluble binder.

MEASUREMENT OF SOLUBILITY

Cuprous oxide was placed in the equilibration vessel, which was then evacuated and flushed with nitrogen. Air-free sea water was forced into the vessel under nitrogen pressure. In some cases agitation was produced by bubbling nitrogen; in others, the vessel was closed, disconnected, and rotated in a water bath. All equilibrations were made at 25° C. After equilibration, the solution was forced out through a sealed-in sintered glass filter by applying nitrogen pressure, and samples were collected for analysis. The pH was quickly measured with a Beckman glass electrode. After exposure to the air, the cuprous copper in solution became oxidized to the cupric form, and was partially reprecipitated as a mixture of basic cupric carbonate and oxychloride (*3*). Any such precipitate was redissolved by adding citric acid, and the copper content was determined colorimetrically with sodium diethyl dithiocarbamate (*2, 5*).

Further details in procedure for several different series of solubility measurements follow:

SERIES 1. The sea water was deaerated by evacuation and flushing with nitrogen, and the pH was allowed to rise as carbon dioxide was removed along with oxygen.

SERIES 2. The sea water was treated to remove carbonates by addition of hydrochloric acid following the procedure of McClendon *et al.* (*8*), and the pH was adjusted by addition of sodium hydroxide. Subsequent deaeration did not change the pH.

SERIES 3. The sea water was deaerated as before, and a small amount of gaseous carbon dioxide was introduced to bring the pH back to approximately that of normal sea water.

SERIES 4. The procedure was the same as in series 3, except that the nitrogen was freed of the last traces of oxygen by passing it over hot copper turnings, and extreme precautions were taken in evacuating and flushing the equilibration vessel and its connections.

SERIES 5. The procedure was the same as in series 4, except that the saturating body, instead of being finely divided cuprous oxide, was a surface coated with a mixture of cuprous oxide, celite, rosin, and Vinylite resin.

TABLE I. SOLUBILITY OF CUPROUS OXIDE IN OXYGEN-FREE SEA WATER

pH	Solubility, Moles Cu/Liter × 10^4	Series No.	pH	Solubility, Moles Cu/Liter × 10^4	Series No.
7.11	8.35	5	8.51	0.26	4
7.40	3.26	2	8.56	0.29	4
7.70	2.34	2	8.60	0.22	1
7.80	1.73	3	8.73	0.14	1
8.12	0.74	3	8.88	0.11	1
8.12	1.57	1	8.92	0.19	1
8.46	0.49	4	8.96	0.14	1

The solubilities of cuprous oxide measured at 25° C. are given in Table I and their logarithms are plotted against pH in Figure 1. Concentrations are given in moles (gram atoms) of copper—i.e., half moles of cuprous oxide—per liter.

The data are well represented by the equation,

$$\log S = 4.03 - \text{pH}$$

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which shows that the solubility is directly proportional to the hydrogen ion concentration. The solubility of cuprous oxide in normal sea water, of pH 8.1, is 8.6 × 10^{-5} moles of copper per liter.

Bodländer and Storbeck (*1*) showed that cuprous ion in chloride solutions forms the complexes $CuCl_2^-$ and $CuCl_3^{--}$. It may be assumed that the following equilibria are established between cuprous oxide and sea water:

$$\begin{aligned} {}^1/{}_2Cu_2O + {}^1/{}_2H_2O &= Cu^+ + OH^- \\ Cu^+ + 2Cl^- &= CuCl_2^- \\ Cu^+ + 3Cl^- &= CuCl_3^{--} \end{aligned}$$

These equilibria are described by the equations

$$\begin{aligned} (Cu^+) &= k_s(H^+)/k_w \\ (CuCl_2^-) &= k_2(Cu^+)(Cl^-)^2 \\ (CuCl_3^{--}) &= k_3(Cu^+)(Cl^-)^3 \end{aligned}$$

where k_s = solubility product $(Cu^+)(OH^-)$
k_w = ion product $(H^+)(OH^-)$
k_2, k_3 = association constants for respective complexes

On this basis the expected solubility of cuprous oxide can be calculated from data in the literature. We take the values $k_s = 1.2 \times 10^{-15}$ and $k_w = 1.0 \times 10^{-14}$ from Latimer (*6*), and $k_3 = 6.9 \times 10^6$ from Náray-Szabó and Szabó (*9*). The constant k_2 is derived from the value of $(CuCl_2^-)/(Cl^-)$ in equilibrium with cuprous chloride, given by Noyes and Chow (*10*) as 0.066, and the solubility product of cuprous chloride (*6*), 1.85 × 10^{-7}; thus $k_2 = 3.5 \times 10^5$. In sea water chloride ion concentration[2] is 0.48 *M*. The total dissolved cuprous copper is the sum of the concentrations of $CuCl_2^-$ and $CuCl_3^{--}$, free cuprous ion being negligible by comparison. The solubility of cuprous oxide in sea water, expressed as moles of copper per liter, is calculated from these data to be

$$(9.7\gamma^2_{Cl^-}/\gamma_{CuCl_2^-} + 9.2\gamma^3_{Cl^-}/\gamma_{CuCl_3^{--}}) \times 10^3(H^+)$$

where γ = activity coefficient of ion indicated

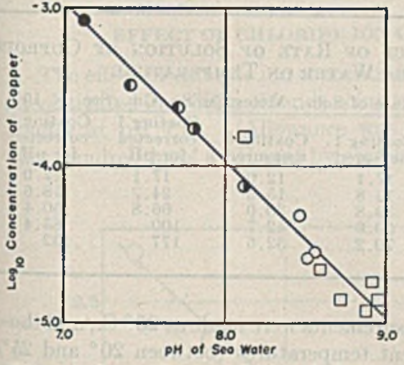

Figure 1. Logarithm of Solubility of Cuprous Oxide (in Moles of Copper per Liter) in Sea Water *vs.* pH

☐ series 1, ◐ series 2, ◑ series 3, ○ series 4, ● series 5

This expression reduces to the experimentally determined function if all the activity coefficients are taken as 0.67, a reasonable value in sea water, the ionic strength of which (*7*) is 0.63. The agreement between calculated and measured solubilities indicates that the ionic equilibria of cuprous ion in sea water are the same as those which have been described for simpler systems containing chloride ions.

EFFECT OF OXYGEN ON RATE OF SOLUTION

Studies of the rate of solution of cuprous oxide were made on glass surfaces coated with cuprous oxide suspended in a binder. The exposed area of solute is not known under these circumstances, but the data provide relative measurements of the dependence of rate of solution upon different experimental conditions. The order of magnitude of the specific rate constant for solution can also be estimated from these studies.

In air the copper dissolved from cuprous oxide in sea water is oxidized and is eventually partially reprecipitated as a mixture of basic cupric carbonate and chloride. However, the rate of solution from a surface covered with cuprous oxide does not appear to be affected by the presence of oxygen.

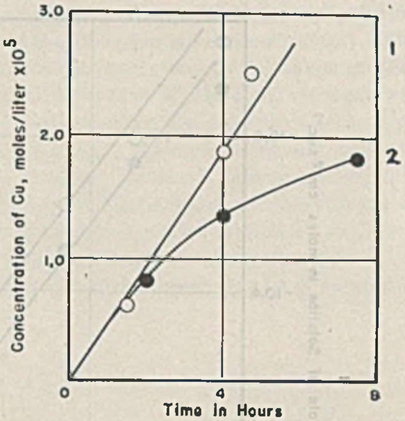

Figure 2. Course of Dissolution of Cuprous Oxide, (1) in the Absence of Air and (2) in the Presence of Air

Microscope slides (total area 39 sq. cm.) were coated with a standard Navy paint of the "cold plastic" type containing 40% of cuprous oxide, and were rigidly supported inside centrifuge bottles containing 190 cc. of sea water. The bottles were rotated at 30 r.p.m., and samples were withdrawn at different times for analysis. The analytical method was the same as in the solubility measurements. This experiment was performed both in the presence of air and with careful exclusion of air (as in series 4 of the solubility measurements). The results are given in Figure 2. Although the rate of solution in air falls off after a copper concentration of 1 × 10^{-5} *M* has been attained, the initial rates with and without atmospheric oxygen appear to be the same. The remaining experiments were carried out in the presence of air, using the following procedure.

Three different cuprous oxide coatings were applied with a volatile solvent to ground glass panels 3 × 4 inches in size. Their dry compositions were as follows: 1, 90% cuprous oxide, 10% Vinylite resin; 2, 80% cuprous oxide, 20% Vinylite; 3, 80% cuprous oxide, 15% Vinylite, and 5% rosin.

Each panel was agitated in 1500 cc. of sea water by an apparatus, originally designed for Warburg respirometers, which produced an oscillatory motion of the panel perpendicular to its own plane. Both the frequency of oscillation and the distance of travel could be varied. Samples of solution were removed at intervals for analysis. The rate of solution was calculated as moles of copper (half moles of cuprous oxide) per sq. cm. of panel surface per second. According to the time intervals chosen, agreement between successive values of the rate of solution showed that the course of dissolution followed the linear portion of the curve in Figure 2.

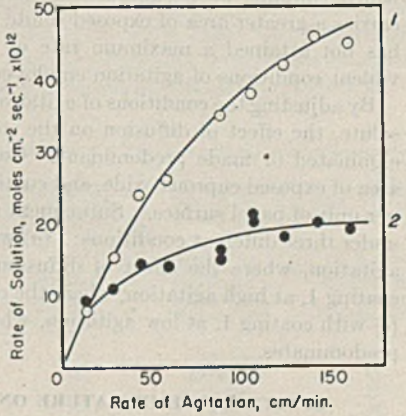

Figure 3. Rate of Solution of Cuprous Oxide in Sea Water Plotted against Rate of Agitation

Curve 1 = coating 1; curve 2 = coating 2

The agreement between values of the rate of solution determined over successive time intervals also showed that the area of exposed cuprous oxide was not varying during the experiment. Occasionally, however, the initial value was

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[2] There is, of course, some variation in chloride content (*7*); the value of 0.48 *M* (17 parts per thousand) was selected as a standard for laboratory investigations of antifouling paints (*5*).

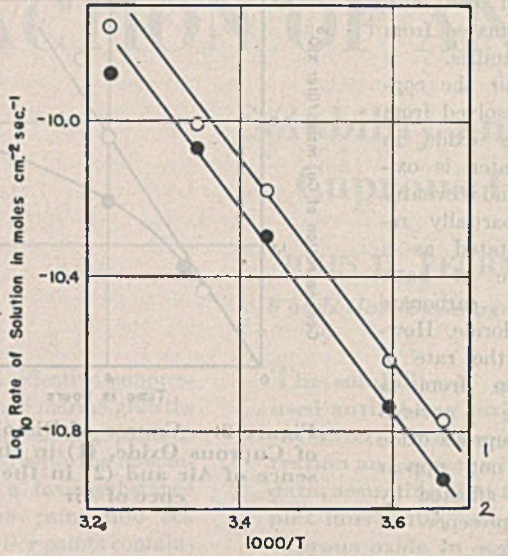

Figure 4. Rate of Solution of Cuprous Oxide in Sea Water, Plotted Logarithmically against Reciprocal Absolute Temperature after Correction for Shift in pH

Curve 1 = coating 1; curve 2 = coating 3

low and was discarded. It was concluded that, if the binder formed any superficial layer of resin on the cuprous oxide particles exposed at the surface of the coating, it must have been very tenuous and, ordinarily, quickly removed after immersion.

The rates of solution from three panels which had been coated at the same time were usually measured simultaneously under identical conditions; the agreement in the individual values was ordinarily within 15%. The average of the three values is reported in each case.

EFFECT OF AGITATION ON SOLUTION RATE

The rates of solution from three panels covered with coatings 1 and 2 were measured in normal sea water at 20° C. under different conditions of agitation. The frequency of oscillation was varied from 75 to 135 cycles per minute and the distance of travel from 0.2 to 1.2 cm. The product of frequency and distance was taken as a measure of the agitation, and the results are plotted against this quantity in Figure 3. In the case of coating 2, containing 80% of cuprous oxide, the rate of solution appears to have attained a maximum value at the highest agitation employed, and it may be concluded that processes of diffusion at the surface are not limiting the solution rate under these conditions. Coating 1, which contains 90% cuprous oxide, and therefore presumably carries a greater area of exposed solute per unit of panel surface, has not attained a maximum rate of solution under the most violent conditions of agitation employed.

By adjusting the conditions of agitation and the area of exposed solute, the effect of diffusion on the solution rate can be either eliminated or made predominant. Coating 1 provided a large area of exposed cuprous oxide, and coatings 2 and 3 smaller areas, per unit of panel surface. Subsequent measurements were made under three different conditions: (*a*) with coating 2 or 3, at high agitation, where the effect of diffusion is eliminated; (*b*) with coating 1, at high agitation, where the effect of diffusion is slight; (*c*) with coating 1, at low agitation, where the effect of diffusion predominates.

EFFECT OF TEMPERATURE ON SOLUTION RATE

The rates of solution of three panels covered with each of coatings 1 and 3 were measured in normal sea water at several different temperatures from 0° to 36.5° C. Several conditions of agitation were also employed; the rates of solution obtained at rates of agitation of 108, 126, 144, and 162 cm. per minute were averaged at each temperature. The results, given in Table II, show a range of about fourfold over the temperature range employed. In the neighborhood of 20° C. the change of the measured rate of solution with temperature is about 3% per ° C.

The measured rates of solution do not reflect the effect of temperature alone, since the pH of sea water in equilibrium with atmospheric carbon dioxide increases with increasing temperature. Table II also gives the pH shifts from a temperature of 0° C., taken from the data of McClendon (*8*); our own measurements of pH confirmed the magnitude of these shifts, showing that equilibrium with the atmosphere was established under our experimental conditions.

In order to calculate the effect of temperature alone on rate of solution, the measured values were corrected to the pH at 0° C. on the assumption that the rate is directly proportional to the hydrogen ion concentration, as shown in the next section. These values are also given in Table II, and their logarithms are plotted against the reciprocal absolute temperature in Figure 4. For coating 3, containing 80% of cuprous oxide, the Arrhenius relation appears to be quite closely followed; the slope of the straight line corresponds to an activation energy of 12,000 calories. The magnitude of this value is further indication that diffusion is not limiting the rate of solution under the conditions employed. For coating 1, containing 90% of cuprous oxide, the points fall on a line with the same slope at the lower temperatures. At the higher temperatures the points fall off somewhat, a further indication that diffusion influences the rate of solution to a slight extent when a larger area of cuprous oxide is exposed.

TABLE II. DEPENDENCE OF RATE OF SOLUTION OF CUPROUS OXIDE IN SEA WATER ON TEMPERATURE

Temp., ° C.	pH Shift from 0° C.	Rate of Soln., Moles Cu/Sq. Cm./Sec. × 10^{12} Coating 1 measured	Coating 3 measured	Coating 1 corrected for pH	Coating 3 corrected for pH
0	0	17.1	12.0	17.1	12.0
5	0.085	19.8	15.3	24.2	18.6
18	0.225	39.8	30.0	66.8	50.4
26	0.300	50.0	42.7	100	85.4
36.5	0.400	70.2	52.6	177	132

Most subsequent measurements were made at 20° C., and those made at slightly different temperatures (between 20° and 25°) were reduced to 20° by applying a correction of 3% per ° C. (Table II).

EFFECT OF pH ON SOLUTION RATE

For study of the effect of hydrogen ion concentration, artificial solvents were employed, containing 0.48 *M* sodium chloride and 0.1 *M* borate buffer, with the pH ranging from 7.08 to 8.48.

In the course of measurements in artificial solvents, in this series and those described later, many different sets of triplicate panels were employed. Their rates of solution in normal sea water at an agitation of 144 cm. per minute were measured before and after the determinations in the artificial solvents. The rates at the beginning and at the end of the experiment agreed usually within 15% and often within 5%, an indication that no sensible change in the surface of the cuprous oxide had occurred during the measurements. Usually each set of panels was used successively in several different artificial solvents. The averages of the rates at beginning and end showed considerable variation, ranging from 37 to 65 × 10^{-12} mole cm.$^{-2}$ sec.$^{-1}$ with most of the values falling between 46 and 56. This variation was attributed to differences in the area of exposed cuprous oxide, due to uncontrolled conditions in the coating of panels and evaporation of solvent from the binder. Accordingly, all results were reduced to a standard sea water solution rate of 50 × 10^{-12} by multiplying by the factor $50/R_s$, where R_s is the average sea water solution rate for the particular set of panels employed.

Table III. Effect of pH on Rate of Solution of Cuprous Oxide in Sodium Chloride-Borate Buffers at 20° C. (Coating 1)

pH	Rate of Soln.[a], Moles Cm.$^{-2}$ Sec.$^{-1}$, × 10^{12} Agitation, 15 cm./min.	Agitation, 162 cm./min.
7.08	95	430
7.29	67	250
7.48	49	178
7.65	34	133
7.83	18	60
7.89	..	67
7.89	..	63
8.18	11.6	42
8.48	6.4	32

[a] Reduced to a standard sea water solution rate of 50 × 10^{-12}.

The results of varying the pH are given in Table III and the rates of solution are plotted logarithmically against pH in Figure 5. The points for high agitation, at which the influence of diffusion may be expected to be slight, lie along a straight line with a slope of −0.94. This is probably not significantly different from −1, and it may be concluded that the rate of solution of cuprous oxide in sodium chloride solutions is proportional to the hydrogen ion concentration. The points for low agitation lie along a line with a slope of −0.85. Even when the dissolution is controlled largely by diffusion, therefore, its rate is not very far from proportional to the hydrogen ion concentration.

The rates of solution in sea water, also plotted in Figure 5, are somewhat lower than in a buffer solution with the same pH and chloride concentration.

EFFECT OF CHLORIDE ION CONCENTRATION

The effect of chloride ion concentration on rate of solution was investigated in sodium chloride solutions containing 0.1 M borate buffer at pH 7.88. (Allowance was made for deviations of a few hundredths of a pH unit by correcting the results to 7.88, the prevailing pH of the laboratory sea water, with the rate of solution considered proportional to the hydrogen ion concentration.) The contribution of the borate to the ionic strength was taken as 0.03. At chloride concentrations below 0.48 M, the ionic strength was kept constant at 0.51 by replacing sodium chloride with sodium nitrate. Above 0.48 M, the ionic strength increased with the chloride concentration; however, as shown below, the effect of ionic strength on the rate of solution of cuprous oxide is small in this range, so that this series demonstrates essentially the effect of chloride concentration at constant ionic strength. The conditions of agitation were chosen both to minimize and to emphasize the effect of diffusion.

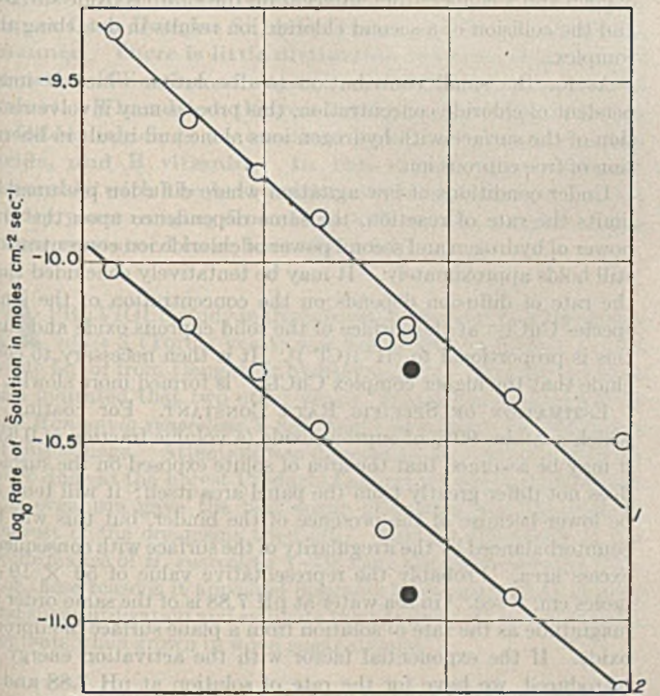

Figure 5. Rate of Solution of Cuprous Oxide from Coating 1 in Artificial Solvents ○, and in Sea Water ●, Plotted Logarithmically against pH

Curve 1, agitation = 162 cm./min.; curve 2, agitation = 15 cm./min.

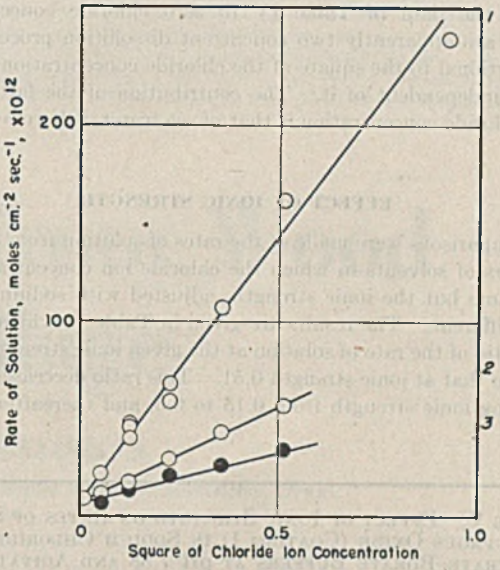

Figure 6. Rate of Solution of Cuprous Oxide in Artificial Solvents, Plotted against the Square of the Chloride Concentration

1, coating 1, agitation 144 cm./min.; 2, coating 1, agitation 15 cm./min.; 3, coating 2, agitation 144 cm./min.

The values for rate of solution for coating 1 were reduced to a standard sea water solution rate of 50 × 10^{-12} as described in the preceding section, and those for coating 2 were similarly reduced to a standard rate of 20 × 10^{-12}. The data are given in Table IV and plotted in Figure 6 against the square of the chloride ion concentration. It is apparent that the rate of solution is a linear function of the square of the chloride ion concentration, at both high and low agitation.

The intercept at zero chloride concentration, which for coating 1 at high agitation is about 7 × 10^{-12}, may be interpreted as a rate of solution in the absence of chloride ions. This interpretation is supported by measurements in chloride-free solvents.

Table IV. Rates of Solution of Cuprous Oxide in Sodium Chloride–Sodium Nitrate–Borate Buffers at 20° C. and pH 7.88

Molar Chloride Concn.	Molar Ionic Strength	Rate of Soln., Moles Cm.$^{-2}$ Sec.$^{-1}$, × 10^{12} Coating 1[a], agitation, 15 cm./min.	Coating 1[a], agitation, 144 cm./min.	Coating 2[b], agitation, 144 cm./min.
0.12	0.51	..	9	..
0.24	0.51	12	22, 22	8
0.36	0.51	18	40, 46, 48	15
0.48	0.51	30	59, 68	21
0.60	0.63	44	107	26
0.72	0.75	57	161	34
0.96	0.99	..	244	..

[a] Reduced to a standard sea water solution rate of 50 × 10^{-12}.
[b] Reduced to a standard sea water solution rate of 20 × 10^{-12}.

RATE OF SOLUTION IN CHLORIDE-FREE SOLVENTS

Measurements were made, in solutions of sodium nitrate containing 0.1 *M* borate buffer at pH 7.88 and agitation of 144 cm. per minute, on panels covered with coatings 1 and 2:

Ionic Strength	Rate of Soln., Moles Cm.$^{-2}$ Sec^{-1}, $\times 10^{12}$	
	Coating 1	Coating 2
0.03[a]	10	..
0.27	7	5
0.51	6	..
0.99	7	..

[a] Borate only.

The rate of solution, which does not vary much with ionic strength, is approximately equal to the value obtained by extrapolating the data of Table IV to zero chloride concentration. There are apparently two concurrent dissolution processes, one proportional to the square of the chloride concentration, and the other independent of it. The contribution of the latter, when the chloride concentration is that of sea water, is between 10 and 15%.

EFFECT OF IONIC STRENGTH

Comparisons were made of the rates of solution from coating 1 in pairs of solvents in which the chloride ion concentration was the same but the ionic strength, adjusted with sodium nitrate, was different. The results are given in Table V, which includes the ratio of the rate of solution at the given ionic strength in each case to that at ionic strength 0.51. This ratio decreases with increasing ionic strength from 0.15 to 0.5, and thereafter changes little.

TABLE V. EFFECT OF IONIC STRENGTH ON RATES OF SOLUTION OF CUPROUS OXIDE (COATING 1) IN SODIUM CHLORIDE–SODIUM NITRATE–BORATE BUFFERS AT pH 7.88 AND AGITATION OF 144 CM./MIN.

Molar Chloride Concn.	Molar Ionic Strength	Rate of Soln.[a], Moles Cm.$^{-2}$ Sec.$^{-1}$, $\times 10^{12}$		Ratio
		At given ionic strength	At ionic strength of 0.51	
0.12	0.15	17	9	1.89
0.24	0.27	29	22	1.32
0.36	0.39	52	45	1.16
0.48	0.51	68	68	1.00
0.48	0.63	66	68	0.97
0.48	0.75	79	68	1.16
0.48	0.99	65	68	0.96

[a] Reduced to a standard sea water solution rate of 50×10^{-12}.

Although the data do not permit extrapolation to zero ionic strength, it can be seen qualitatively that the dependence of the rate of solution on ionic strength is similar to that of the activity coefficient of a uni-univalent salt (*4*).

COMPARISON OF DILUTED SEA WATER WITH ARTIFICIAL SOLVENTS

Measurements were made of the rates of solution from coating 1 in sea water diluted with distilled water to various extents. Corrections for slight deviations from a pH of 7.88 were made as described above. The values are given in Table VI, together with the rates of solution in solvents of the same chloride concentration and ionic strength, estimated by multiplying the data of Table IV by ionic strength factors interpolated from Table V.

The rate of solution in the artificial solvent is in each case somewhat greater; it can be expressed approximately by the interpolation equation,

$$L_A = 6 + 1.2\ L_S$$

where L_S = rate of solution in diluted sea water

This difference may be due to a retarding effect of some constituent of sea water. It is small enough so that conclusions concerning the mechanism of the reaction which are drawn from the data in artificial solvents are probably applicable to sea water also.

TABLE VI. RATES OF SOLUTION OF CUPROUS OXIDE (COATING 1) IN DILUTED SEA WATER AND IN ARTIFICIAL SOLVENTS OF THE SAME CHLORIDE CONCENTRATIONS AND IONIC STRENGTHS

Molar Chloride Concn.	Molar Ionic Strength	Rate of Soln.[a], Moles Cm.$^{-2}$ Sec.$^{-1}$, $\times 10^{12}$		
		Diluted sea water	Artificial solvent	
			Measured[b]	Calcd.[c]
0.12	0.16	13	16	21
0.24	0.32	17	27	26
0.36	0.48	33	46	46
0.48[d]	0.63	50	66	66

[a] Reduced to a standard sea water solution rate of 50×10^{-12}.
[b] From Tables IV and V.
[c] Calculated as $6 + 1.2\ Ls$
[d] Undiluted sea water.

DISCUSSION

Under conditions of high agitation, the rate of solution of cuprous oxide is proportional to the hydrogen ion concentration and a linear function of the square of the chloride ion concentration. This is the relationship which would be expected if the process

$$^1/_2Cu_2O + H^+ + 2Cl^- = CuCl_2^- + {}^1/_2H_2O$$

is the rate determining step in dissolution. The dependence of rate of solution on ionic strength is also qualitatively in agreement with this mechanism. Following the Scatchard treatment (*11*), if one positively and two negatively charged univalent ions approach to form a complex with a single negative charge, the effect of ionic strength on the rate of reaction is the same as for the approach of two oppositely charged univalent ions—i.e., the same function as for the activity coefficient of a uni-univalent electrolyte. Although this relation was derived for reactions in solution, it should hold also at a solid-liquid interface. It may be concluded that the formation of $CuCl_2^-$ is the rate determining step of the process which predominates in dissolution. It is possible that one hydrogen and one chloride ion approach, respectively, an oxygen and a copper atom adjacent on the cuprous oxide surface, and the collision of a second chloride ion results in detaching the complex.

As for the small contribution to dissolution which is independent of chloride concentration, this process may involve reaction of the surface with hydrogen ions alone and result in liberation of free cuprous ion.

Under conditions of low agitation where diffusion presumably limits the rate of reaction, the same dependence upon the first power of hydrogen and second power of chloride ion concentration still holds approximately. It may be tentatively concluded that the rate of diffusion depends on the concentration of the ionic species $CuCl_2^-$ at the surface of the solid cuprous oxide and that this is proportional to $(H^+)(Cl^-)^2$. It is then necessary to conclude that the higher complex $CuCl_3^{--}$ is formed more slowly.

ESTIMATION OF SPECIFIC RATE CONSTANT. For coating 1, which contains 90% of cuprous oxide (a volume fraction of 0.65), it may be assumed that the area of solute exposed on the surface does not differ greatly from the panel area itself; it will tend to be lower because of the presence of the binder, but this will be counterbalanced by the irregularity of the surface with consequent excess area. Probably the representative value of 50×10^{-12} moles cm.$^{-2}$ sec.$^{-1}$ in sea water at pH 7.88 is of the same order of magnitude as the rate of solution from a plane surface of cuprous oxide. If the exponential factor with the activation energy is introduced, we have for the rate of solution at pH 7.88 and a chloride concentration of 0.48 *M* the value $0.040\ e^{-12,000/RT}$ moles cm.$^{-2}$ sec.$^{-1}$.

RELATION OF SOLUBILITY TO ANTIFOULING EFFECTIVENESS. The proved efficacy of cuprous oxide in antifouling paints indicates that its moderately low solubility and rate of solution permit the control of its leaching rate from a paint without undue difficulty. The selection of a toxic with these characteristics is the first step toward the resolution of the dilemma of Young (*12*). The solubility of cuprous oxide will be compared with those of other antifouling toxics in the second paper of this series (*3*).

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bodländer and Storbeck, *Z. anorg. allgem. Chem.*, 31, 1, 458 (1902).
(2) Coulson, *J. Assoc. Official Agr. Chem.*, 19, 219 (1936); 20, 178 (1937).
(3) Ferry, J. D., and Riley, G. A., Ind. Eng. Chem., to be published.
(4) Harned and Owen, "Physical Chemistry of Electrolytic Solutions", pp. 384, 395, New York, Reinhold Pub. Corp., 1943.
(5) Ketchum, B. H., Ferry, J. D., Redfield, A. C., and Burns, A. E., Jr., Ind. Eng. Chem., 37, 456–60 (1945).
(6) Latimer, W. M., "Oxidation States of the Elements", New York, Prentice-Hall, 1938.
(7) Lyman, J., and Fleming, R. H., *J. Marine Research*, 3, 134 (1940).
(8) McClendon, J. F., Gault, C. C., and Mulholland, S., *Carnegie Inst. Wash. Pub.*, 251, II, 23 (1917).
(9) Náray-Szabó, István, and Szabó, Zoltán, *Z. physik. Chem.*, A166, 228 (1933).
(10) Noyes, A. A., and Chow, Ming, *J. Am. Chem. Soc.*, 40, 739 (1918).
(11) Scatchard, G., *Chem. Rev.*, 10, 229 (1932).
(12) Young, C. T., "Fouling and Corrosion of Iron Ships", London, The London Drawing Assoc., 1867.

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Feeding Yeasts from Wood Sugar Stillage

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To explore the suitability of some lesser known yeasts for the utilization of wood sugar wastes, a comparative study was made with Torula, Mycotorula, and Hansenula strains. The three yeasts perform well on still waste liquor from Douglas fir hydrolyzates and in a comparable manner. There is little distinction between their rate of growth, utilization of sugar, yeast yield, and nutritional values. When dried, the yeasts may be expected to furnish a fodder which is an excellent source of protein, amino acids, and B vitamins. In this respect they compare favorably with the best strains of brewer's yeast. Yields of dry yeast ranging from 53 to 63% on the weight of the sugar consumed have been observed.

A PREVIOUS study in this laboratory showed that *Torulopsis utilis* 3 (Torula yeast) was well suited for growth in still waste liquor from Douglas fir hydrolyzate (*5*). Preliminary tests also indicated that two other yeasts, *Mycotorula lipolytica* P-13 and *Hansenula suaveolens* Y-838, might be suitable for utilization of this stillage. Attention was directed to *M. lipolytica* P-13 by work done at the Forest Products Laboratory which showed that this organism gave the best sugar utilization and the highest harvest of the organisms tried (*10*). Certain differences in the performance of *H. suaveolens* Y-838 have also been reported (*18*). For these reasons it appeared desirable to compare their growth and sugar utilization and estimate their amino acid and B vitamin contents when grown in wood sugar stillage.

PROCEDURES AND ANALYSES

Yeast Growth. Stock cultures of the three yeasts were maintained on glucose-agar slants. For comparative growth and sugar utilization studies, transfers were made into 8-inch Pyrex test tubes containing 20 ml. of medium. The solutions were all similarly aerated through 1-mm. capillary tubes. After incubation at 30 ± 1° C. for 24 to 48 hours, the cells were harvested by centrifuging, and the desired amounts were used for inocula for new growth tests. Repeated transfers were made in this manner, although aseptic conditions were not maintained after the initial transfer from the slants.

Still Waste Liquor. The still waste liquor used in this work was obtained from The Vulcan Copper & Supply Company (*5*). It contained 3.2% total solids, 0.81% reducing sugar calculated as xylose, and 1.42% total carbon. The pH was 5.0. Nutrients added were 0.05% diammonium phosphate and 0.05% urea.

Yeast Determination. Yeast cell counts were made under a microscope with the aid of a Bausch & Lomb haemacytometer cell. Dry weight was determined after washing the yeast precipitate with dilute hydrochloric acid and sodium carbonate as described previously (*5*).

Reducing Sugar Determination. The micromethod of Schaffer and Somogyi (*14*) was employed routinely. All values are given as c.p. xylose.

Protein Determination. Protein values are given as N × 6.25, as determined by the Kjeldahl method.

Amino Acid Assays. Determinations were carried out microbiologically using *Streptococcus faecalis* R as the test organism for all assays except phenylalanine, as recommended by Stokes and co-workers (*16*). *Lactobacillus delbruckii* LD3 was used to measure the phenylalanine content by the Stokes method (*16*). Good agreement was obtained among results calculated from different assay levels. Inasmuch as *S. faecalis* did not appear to require methionine for growth, this amino acid was not included in the determinations.

Vitamin Assays. Microbiological procedures were used for the determination of seven B vitamins. The following test organisms were employed: for thiamine, *L. fermenti* (*11*); for riboflavin, *L. casei* (*15, 17*); for nicotinic acid, pantothenic acid, and biotin, *L. arabinosus* 17-5 (*4, 12, 20*); for folic acid, *S. faecalis* (*8, 9*); and for *p*-aminobenzoic acid, *Acetobacter suboxydans* (*2, 6*).

ADAPTATION TO MEDIA

Initial growth of the yeasts was found to be relatively slow when they were transferred directly from agar slants to the still waste liquor. Under these conditions maximum yeast growth and removal of reducing sugar was obtained in 48 to 72 hours. Repeated transfers in stillage resulted in more rapid growth. Mycotorula and Torula gave throughout about equal performance, whereas Hansenula adapted itself more slowly. However, after about the tenth transfer the performance of the three yeasts was approximately equal, as observed from rate of growth, consumption of reducing sugar, yeast yield, and final pH of liquor.

The performance of the three yeasts was followed through twenty-five transfers. Table I lists the observations made at this transfer; they are representative of normal performance after the adaptation period. Optimum yields of yeast were obtained in 18 to 24 hours. It is probable that with more efficient means of aeration the growth period may be reduced below this minimum, for aeration has an important effect on the time (*5*). Growth periods longer than the time required for the assimilation of sugar usually resulted in appreciable autolysis and reduction of the yeast crop. The three yeasts were consistently similar in their ability to remove reducing sugars from an initial level of 0.81% in the liquor to approximately 0.19% in 24 hours. Incubation for 48 hours resulted in a further slight removal of reducing sugar to approximately 0.16%.

This residual reducing sugar in the spent yeast liquors probably contains incompletely hydrolyzed polysaccharides or sugar anhydrides formed under the drastic conditions of the hydrolysis of the wood substance. Thus, acid hydrolysis of the stillage before and after Torula growth increases the reducing sugar content (*5*). Earlier than 1890 sugar technologists recognized the formation of "reversion products" when sugar solutions are heated in the presence of acids (*19*). At low sugar concentrations the reversion products are hydrolyzed by acid, which indicates an equilibrium between reversion and hydrolysis. A recent study of such unfermentable reducing products in the distillery slops from molasses is reported by Sattler and Zerban (*13*).

The yield of new yeast crop may be obtained from Table I by deducting the dry weight of the inocula from the total dry weight of yeast obtained after the 24-hour growth period. This is for Mycotorula, Hansenula, and Torula, 0.33, 0.35, and 0.39%, respectively. Calculated on the basis of the dry weight of sugar consumed, the yield correspondingly ranges from 53 to 63%. A part of this yeast growth may probably be attributed to the partial consumption of the acids present in the liquor (*5*). The slightly greater yield of Torula yeast for this run is only indicative of some variations and was not consistently observed.

The ability of *Torulopsis utilis* 3 to utilize arabinose was investigated earlier (*5*). In the present study experiments were made to ascertain the ability of Mycotorula and Hansenula to utilize this pentose. For this purpose the multiplication of yeast cells and the reduction of the sugar content of media, to which *d*-arabinose (levorotatory) had been added, was followed. These findings are given in Table II.

The data show that under the conditions of the experiments Mycotorula and Hansenula have the capacity to multiply and remove arabinose from solution. This growth and consumption of arabinose is not so rapid as with the sugar in the still waste liquor and is faster when such sugar is present with the arabinose. The observation that Hansenula is able to utilize arabinose is contrary to the findings of Wise and Appling (*18*) who used this organism to assay xylose in the presence of arabinose. Experiments in this laboratory indicate that this organism multiplies much more rapidly in a xylose than in an arabinose medium, especially when freshly transferred from agar slants. However, it would appear from the present work that the adaptation of this organism to growth with arabinose might easily impose limitations upon its use for assay purposes of sugar mixtures derived from natural materials.

AMINO ACID CONTENTS

Table III gives comparative analysis of the three yeasts for nine essential amino acids. The values were obtained for acid- and alkali-washed samples (*5*) which were oven-dried 24 hours at 70° C. and then hydrolyzed with 10% hydrochloric acid or 20% sodium hydroxide (*16*). The near-identical values obtained are striking and indicate great similarity among the yeasts.

The approximate amino acid contents of a fat-free brewer's yeast of protein content similar to the three yeasts are included for comparison. The brewer's yeast values were reported by

Table I. Performance of Yeasts in Stillage

Yeast	Growth Period, Hr.	Yeast Yield: Wet cells in 100 ml. of medium, %	Yeast Yield: Dry yeast, %	Reducing Sugar, %	pH
Mycotorula	0	1.0	0.12	0.81	5.1
	24	3.7	0.45	0.19	7.3
	48	3.3	..	0.16	..
Hansenula	0	1.0	0.11	0.81	5.1
	24	4.1	0.46	0.19	7.0
	48	3.5	..	0.16	..
Torula	0	1.0	0.12	0.81	5.1
	24	4.2	0.51	0.18	7.5
	48	3.6	..	0.16	..

Table II. Utilization of Arabinose by Mycotorula and Hansenula

Medium	Growth Period, Hr.	Yeast Count, Million Cells/Ml.	Reducing Sugar, %
Mycotorula			
Stillage	0.0	70	0.81
	24.0	270	0.23
Stillage + equal vol. of 0.8% arabinose soln.	0.0	70	0.81
	24.0	170	0.33
Spent stillage[a] + equal vol. of 1.2% arabinose soln.	0.0	70	0.70
	24.0	90	0.55
Hansenula			
Stillage	0.0	100	0.56
	24.0	325	0.12
Stillage + equal vol. of 0.8% arabinose soln.	0.0	100	0.68
	24.0	230	0.24
Spent stillage[a] + equal vol. of 1.2% arabinose soln.	0.0	100	0.66
	24.0	125	0.43
Control			
Uninoculated stillage	0.0	..	0.81
	24.0	..	0.83

[a] Stillage after harvesting yeast growth.

Table III. Amino Acids and Protein Content of Yeasts (Percentage of Oven-Dry Weights)

Yeast	Mycotorula	Hansenula	Torula	Brewer's (*1*)
Total protein	51.0	53.4	52.9	51.8
Amino acid[a]				
Arginine	3.2	2.9	3.1	2.7
Histidine	1.4	1.4	1.5	1.3
Lysine	4.4	4.3	4.4	3.5
Phenylalanine	2.4	2.4	2.3	2.4
Tryptophan	0.3	0.3	0.3	0.8
Threonine	2.5	2.4	2.5	2.8
Leucine	3.7	3.6	3.8	3.7
Isoleucine	3.5	3.7	3.7	3.1
Valine	3.1	3.3	3.3	2.4

[a] Values are expressed in terms of the naturally occurring isomer.

Table IV. B Vitamin Content of Yeasts

	Vitamin Content, γ/Gram Dry Wt.		
	Mycotorula	Hansenula	Torula
Thiamine	5.3	8.5	6.2
Riboflavin	59	54	49
Nicotinic acid	600	500	500
Pantothenic acid	....	180	130
Biotin	1.8	1.7	1.8
Folic acid	3.1	1.7	2.8
p-Aminobenzoic acid	31	16	17

Block and Bolling for strain K 105 (*1*). This strain possessed the highest protein content of any studied by these authors. As far as amino acid content is concerned, the fodder yeasts are nutritionally equal or superior to this strain of brewer's yeast except for tryptophan and threonine. Where comparable, the findings correspond with those of Fink and Just (*3*).

VITAMIN CONTENTS

The comparative values for seven B vitamins in the dried fodder yeasts are listed in Table IV. The variations among the yeasts are somewhat larger here than were observed for amino acids, although for most vitamins the values are similar. These yeasts are excellent sources of B vitamins, particularly riboflavin, nicotinic acid, pantothenic acid, and *p*-aminobenzoic acid.

The content of several B vitamins in Torula yeast was reported by Lewis, Stubbs, and Noble (*7*). Their values parallel ours closely except for thiamine, which appears to be lower for all yeasts grown on stillage. This may not be surprising when it is considered that, of all the vitamins, thiamine tends to be removed from the growth medium rather than to be synthesized in large amounts (*7*). The stillage used was relatively low in thiamine content (2.7γ per gram of sugar compared to 3 to 12γ per gram of sugar for several fruit juices) and thus could furnish less thiamine than was available from the media used by Lewis *et al.*

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LITERATURE CITED

(1) Block, R. J., and Bolling, D., *Arch. Biochem.*, 7, 313 (1945).
(2) Cheldelin, V. H., and Bennett, M. J., *J. Biol. Chem.*, 161, 751 (1945).
(3) Fink, H., and Just, F., *Biochem. Z.*, 300, 84 (1938).
(4) Hoag, E. H., Sarett, H. P., and Cheldelin, V. H., Ind. Eng. Chem., Anal. Ed., 17, 60 (1945).
(5) Kurth, E. F., Ind. Eng. Chem., 38, 204 (1946).
(6) Landy, M., and Streightoff, F., *Proc. Soc. Exptl. Biol. Med.*, 52, 127 (1943).
(7) Lewis, J. C., Stubbs, J. J., and Noble, W. M., *Arch. Biochem.*, 4, 389 (1944).
(8) Luckey, T. D., Briggs, G. M., Jr., and Elvehjem, C. A., *J. Biol. Chem.*, 152, 157 (1944).
(9) Mitchell, H. K., and Snell, E. E., *Univ. Texas Pub.* 4137, 36 (1941).
(10) Peterson, W. H., Snell, J. F., and Frazier, W. C., Ind. Eng. Chem., 37, 30 (1945).
(11) Sarett, H. P., and Cheldelin, V. H., *J. Biol. Chem.*, 155, 153 (1944).
(12) Sarett, H. P., Pederson, R. L., and Cheldelin, V. H., *Arch. Biochem.*, 7, 77 (1945).
(13) Sattler, L., and Zerban, F., Ind. Eng. Chem., 37, 1133 (1945).
(14) Schaffer, P. A., and Somogyi, M. J., *J. Biol. Chem.*, 100, 695 (1933).
(15) Snell, E. E., and Strong, F. M., Ind. Eng. Chem., Anal. Ed., 11, 346 (1939).
(16) Stokes, J. L., Gunners, M., Dwyer, I. M., and Caswell, M. C., *J. Biol. Chem.*, 160, 35 (1945).
(17) Stokes, J. L., and Martin, B. B., *Ibid.*, 147, 483 (1943).
(18) Wise, L. E., and Appling, J. W., Ind. Eng. Chem., Anal. Ed., 17, 182 (1945).
(19) Wohl, A., *Ber.*, 23, 2084 (1890).
(20) Wright, L. D., and Skeggs, H. R., *Proc. Soc. Exptl. Biol. Med.*, 56, 95 (1944).

Fungistatic Vapors for Control of Mold in Packages and Equipment

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Tests are reported on forty-seven chemicals for the effectiveness of their vapor phases in controlling molding of materials in closed containers. The testing was done during the war, in response to a request for fungus-inhibiting measures needed for certain military supplies and equipment for which treatment with preservative solutions would be impracticable. Some of the most promising compounds, as indicated by trials on wood, leather, malt-agar, and pressure tape, were benzaldehyde, 2-chloropyridine, ethyl mercuric chloride, and *o*-chlorophenol.

MOLDING of military supplies and equipment was a major source of trouble in the humid war theaters of the Pacific. Numerous items can be and have been adequately protected against mold damage by direct treatment with solutions of permanent or semipermanent fungus-inhibiting materials. On the other hand, many of them cannot be taken care of in this way because technical difficulties would prevent thorough treatment or because such treatments would be incompatible with the operation or use of these items. For such cases consideration has been given by a number of agencies to the possibility of mold control by means of fungistatic vapors gradually liberated from appropriate chemicals, either free or contained in some absorptive solid. The use of mold-inhibiting vapors has been suggested for such items as enclosed electrical equipment, optical apparatus, and the contents of sealed packages. This method would be applicable only to enclosed materials, although tight sealing would not be needed where occasional replenishment of the volatile chemical is feasible.

This paper describes the mold control obtained with vapors of forty-seven different chemicals known, for the most part, to have moderate to high fungistatic action. The tests, made at various times over a period of approximately 9 months, were not concerned with any particular product; the plan was to make preliminary trials of a number of promising chemicals, to aid in the choice of chemicals for more intensive trials by those directly concerned with the protection of specific kinds of supplies and equipment. In addition to the effectiveness of the vapor against molds, factors such as volatility, solvent or corrosive action, condensation tendency, toxicity to people, injury to food flavors, and ease of application would need to be considered in the light of the nature and requirements of the individual item to be protected.

Table I. Test Conditions

Test	Container: Size and type	Container: Cover	Nominal Evaporating Surface of Chemical[a], Sq. In.	Condition of Liquid Chemicals	Period of Test, Weeks
A	6-oz. wide-mouth bottles	Firm but not airtight	0.5	Free	2
B	6-oz. wide-mouth bottles	Firm but not airtight	0.5 (1.25 for liquids)	Absorbed in 0.5-in. wood cubes	2.5
C	6-oz. wide-mouth bottles	Loose	0.5 (1.25 for liquids)	Absorbed in 0.5-in. wood cubes	2.5
D	64-oz. jars	Loose; raised about $^1/_{32}$ in. above jar rim at one side	1.75 (2.0 for ethyl mercuric chloride)	Free	2 to 4, mostly 3

[a] Considered as the inside cross-sectional area of the containing receptacle, the area of the blotting paper in the case of ethyl mercuric chloride, or the area of the five exposed block faces in the case of the liquids in tests B and C.

Some attention was given to the degree of volatility and corrosiveness of most of the more effective compounds, but because of the urgency for preliminary results at the time the work was planned, there was no extensive study of these factors.

TEST METHODS

The tests were carried out in glass containers with a high relative humidity maintained by a reservoir of water below the test materials. To ensure adequate moisture for molding, the dry materials were initially moistened with distilled water or were kept continuously wet at one end. The containers were of two capacities, 6-ounce and 64-ounce (2-quart canning jars). The covers were attached loosely on the larger ones, and both firmly and loosely on the smaller ones. This variation in capacity and cover attachment was largely an empirical measure to vary the partial vapor pressure of the respective chemicals. Most of the testing was done, however, with the larger containers (test D) after it was determined that this was the most severe and, probably, most practical test.

The solid chemicals were ground to roughly uniform particle size, the coarsest being about the size of fine sand. The exception was ethyl mercuric chloride which was precipitated from a 10% solution in acetone within squares of blotting paper. The liquid chemicals were introduced free in tests A and D, and in tests B and C they were first absorbed in $^1/_2$-inch cubes of ponderosa pine wood.

The test materials were new sole leather, sweet gum sapwood, autoclaved malt-agar (2.5–1.5%, respectively) medium, and cloth-backed pressure-adhesive tape of unspecified composition. The specimens of leather were approximately 1 × 2 × $^1/_4$ inch in size, the sweet gum specimens about 1 × 2 × $^1/_8$ inch, and the pressure tape about 1 × 3 inches. All these materials were known to be highly susceptible to molding; moreover, their diversity of chemical composition favored the occurrence of a wide variety of molds.

Heavy mold inoculation was accomplished naturally by exposing the malt-agar and other materials overnight in a room maintained at 97% relative humidity and 80° F., and plentifully sup-

Table II. Relative Amounts of Mold Development[a] on Damp Test Materials Exposed to Vapors of Various Chemicals

		Material, Test, and Amount of Molding[a]												
	State at 80° F.[b]	Sole leather				Sapwood				Malt-agar				Tape, test D
Chemical		A	B	C	D	A	B	C	D	A	B	C	D	
m-Cresyl acetate (Cresatin)	L	0	0	0	H	L	VL	VL	M	0	VL	VL	...	0
Pentachloroethane	L	...	0	0	0	...	0	L	0	...	0	0	...	0
sym-Heptachloropropane	L	...	...	...	H	...	...	...	H	...	...	...	H	...
Hexachloropropene	L	...	...	...	H	...	...	...	H	...	...	...	H	...
Nonachloro-1-pentene	L	...	...	...	H	...	...	...	H	...	...	...	H	...
Octachloro-1,3-pentadiene	L	...	...	...	H	...	...	...	H	...	...	...	H	...
Trichloro-*tert*-butanol	S	...	0	0	L	...	L	0	L	0	L	VL	...	0
Paraformaldehyde	S	...	...	...	0	...	...	...	H	...	...	...	H	...
Benzaldehyde	L	0	0	0	0	0	0	0	0	...	0	0	...	0
Furfural	L	...	...	...	0	...	...	...	0	...	...	...	0	...
Ethyl mercuric chloride	S	...	...	...	0	...	...	...	VL	...	...	...	0	...
Ethyl mercuric phosphate (Ceresan)	S	...	L	L	M	...	M	M	H	...	0	0	...	L
o-Dichlorobenzene	L	0	0	0	0	0	0	VH	0	...	0	VH	...	0
m-Dichlorobenzene	L	0	0	0	VH	0	0	0	M	...	0	0	...	H
p-Dichlorobenzene	S	0	0	0	0	0	0	0	VL	0	0	0	...	VL
p-Dichlorobenzene (trial 2)	S	...	...	...	0	...	...	...	VL	...	...	...	0	...
1,2,3-Trichlorobenzene	S	0	0	0	VH	L	0	H	M	...	VL	L	...	M
1,2,4-Trichlorobenzene	L	0	0	0	M	0	M	0	L	...	0	0	...	L
Thymol	S	L	0	L	VH	H	L	VH	H	0	M	M	M	H
o-Chlorophenol	L	0	0	0	0	0	0	0	L	...	0	0	0	0
m-Chlorophenol	L	0	0	0	...	L	H	H	...	...	L	L	...	...
p-Chlorophenol	S	0	M	M	H	0	L	L	H	0	L	VL	...	0
2,4,6-Trichlorophenol	S	...	L	0	H	...	L	VL	M	0	L	L	...	M
o-Phenylphenol	S	H	L	M	...	M	VH	VH	...	...	M	M	...	...
m-Phenylphenol	S	VH	...	...	...	VH	...	...	...	...	...	...	...	...
2-Chloro-4-phenylphenol	S	VH	...	...	...	M	...	...	...	...	...	...	...	...
2-Chloro-6-phenylphenol	L	H	...	...	...	M	...	...	...	...	...	...	...	...
4-Chloro-6-phenylphenol	S	H	...	...	...	H	...	...	...	...	...	...	...	...
Monochloro-3-phenylphenol	L	VH	...	...	...	M	...	...	...	...	...	...	...	...
2,4-Dichloro-6-phenylphenol	S	VH	...	...	...	H	...	...	...	...	...	...	...	...
p-*tert*-Butylphenol	L	0	0	0	VH	0	H	H	VH	...	L	L	...	M
2-Chloro-4-*tert*-butylphenol	L	VH	...	...	...	H	...	...	...	...	...	...	...	...
2,6-Dichloro-4-nitrophenol	S	VH	...	...	...	H	...	...	...	...	...	...	...	...
2-Chloro-6-cyclohexylphenol	L	VH	...	...	...	VL	...	...	...	...	...	...	...	...
Butylcresol	L	0	H	H	VH	H	VH	VL	H	...	M	M	...	H
2-Chloro-5-hydroxytoluene	S	0	0	0	H	M	M	M	H	...	VL	L	...	M
Naphthalene	S	VL	L	L	...	0	VH	VH	...	0	M	H	...	...
α-Chloronaphthalene	L	0	0	0	...	H	0	0	...	...	VL	VL	...	...
α-Dichloronaphthalene	S	VH	...	...	...	L	...	...	...	...	...	...	...	...
α-Dibromonaphthalene	S	VH	...	...	...	H	...	...	...	...	...	...	...	...
2-Chlorodiphenyl	L	VH	...	...	...	H	...	...	...	...	...	...	...	...
4-Chlorodiphenyl	S	VH	...	...	...	H	...	...	...	...	...	...	...	...
Pyridine	L	0	0	0	0	0	0	0	0	...	0	0	...	0
2-Aminopyridine	L	...	...	...	VH	...	...	...	VH	...	...	...	VH	...
2-Chloropyridine	L	...	...	...	0	...	...	...	VL	...	...	...	0	...
Camphor (artificial)	S	0	L	L	VH	L	M	H	H	M	M	M	...	M
Insl-X Volatile Fungicide[c]	S	0	0	0	VL	0	0	0	L	0	0	0	0	0
None (control)		VH	VH	VH	VH	M	VH	VH	M-H	VH	VH	VH	H-VH	L

[a] 0 = no mold; VL = very light mold; L = light mold; M = medium mold; H = heavy mold; VH = very heavy mold.

[b] S = solid; L = liquid.

[c] Composition not specified by the manufacturer.

plied with molds and mold-carrying mites. Because of the large variety of mold species and strains brought into the test, inoculation in this way was considered preferable to working with any pure cultures that might be selected. Some of the molds that were prevalent at the time were identified as species of Aspergillus, Penicillium, Stachybotrytis, Stysanus, Chaetomium, Metarrhizium, and Memnoniella. The first two were most prominent on the material tested.

Tests A and B were made in this same room, and later tests in the laboratory; the molding tendencies subsequent to inoculation were practically the same in either location. The incubation temperature was between 75° and 80° F. Pertinent variables of the different tests are outlined in Table I.

With this general review of procedures in mind, the method of the preferred test, D, may be described in more detail. To aid in maintaining a continuously high relative humidity around the test specimens, a pad of cotton saturated with about 50 ml. of water was placed in the bottom of each jar. Three 50-ml. beakers were placed on this pad, one containing a $^1/_4$-inch layer of the chemical being tested, another containing two leather test strips standing in 10 ml. of distilled water, and the third containing 15 ml. of malt-agar medium with slanted surface. The sweet gum test strips were placed in groups of three directly on the cotton pad, with the top ends resting against the wall of the jar. The fourth test material, a strip of pressure tape, was attached at one end high on the wall of the jar and allowed to hang without touching the wet pad. All of the test materials were inoculated, as described above, before they were put in the jars. Where the chemical was ethyl mercuric chloride, the square of blotting paper containing it was taped at the corners to the wall of the jar, and the beaker otherwise used for chemical was omitted. The flat jar lids were finally taped in position, leaving a small opening (about $^1/_{25}$ inch) at one side.

RESULTS AND CONCLUSIONS

Mold occurrence is shown in Table II. The chemicals are grouped according to type of basic compound. Although most of the chemicals used are known to have considerable fungistatic action in solution, it is apparent that many of their vapors at ordinary partial pressures have comparatively slight effect on mold development. These deficiencies in mold suppression generally were most noticeable in the loosely covered containers, especially those with the larger capacity (test D) where there was less opportunity for development of maximum partial pressures. The latter result was expected; consequently chemicals that were definitely ineffective in test A were not tested further.

The most effective vapors are apparent from the data of Table II. To facilitate closer comparison among them, Table III is presented. As a basis of comparison only the heaviest molding in any test (usually test D) on each of the respective materials is listed. To aid further in appraising these chemicals, an index of evaporation rate is included for most of them.

Table III. Maximum Mold Occurrence Permitted by Most Effective Vapors as Tested

Chemical (in Order of Decreasing Over-all Effectiveness)	Evapn. Index[a]	Material and Amount of Mold[b] Leather	Sapwood	Malt-agar or tape
Benzaldehyde	48	0	0	0
Furfural	82	0	0	0
Pyridine	176	0	0	0
2-Chloropyridine	84	0	VL	0
Ethyl mercuric chloride[c]	<1	0	VL	0
o-Chorophenol	46	0	L	0
Pentachloroethane	213	0	L	0
p-Dichlorobenzene[c]	53	0	VL	VL
Insl-X Volatile Fungicide[c]	47	VL	L	0
α-Chloronaphthalene	..	0	H	VL
Trichloro-*tert*-butanol[c]	17	L	L	L
1,2,4-Trichlorobenzene[c]	13	M	M	L
m-Cresyl acetate (Cresatin)	5	H	M	VL
Paraformaldehyde[c]	11	0	H	H
o-Dichlorobenzene	60	0	VH	VH
Distilled water (control)	78	VH	VH	VH

[a] Figures given are 0.01 gram of chemical evaporated from a 10-ml. vial (18 mm. in diameter) in 11 days; evaporating atmosphere characterized by slow movement, 65% relative humidity, and a temperature of 80° F.

[b] Based on poorest result with each material: 0 = no mold; VL = very light mold; L = light mold; M = moderate mold; H = heavy mold; VH = very heavy mold.

[c] Chemical in solid state at test; other chemicals in liquid state.

From the combined standpoints of effectiveness against molding, a low to medium evaporation tendency, and a solid state at ordinary temperatures, *p*-dichlorobenzene, Insl-X Volatile Fungicide, and ethyl mercuric chloride seem to have considerable promise as mold inhibitors. It may be significant that *p*-dichlorobenzene has long been used extensively for the prevention of moth damage to stored woolens, and has more recently been successfully applied to the control of blue mold (*Peronospora tabacena*) of tobacco[1]. It has been effectively used at the Forest Products Laboratory for controlling mites in culture rooms, without apparent harm in intermittent dosages to cultures of wood-destroying fungi. It appears to be more fungistatic than fungicidal. Inhibition of mites would be a distinct aid to mold control, as mold spores are often carried to inaccessible places by the mites, and the dead mites furnish a favorable medium for mold development. This is said to be one of the major causes of mold development on optical glass in the tropics.

Several of the other chemicals would properly fall in the same or a higher class with respect to mold-inhibiting capacity, but their liquid state or higher volatilization tendencies would presumably place greater limitations on their range of usefulness. Of these, benzaldehyde and *o*-chlorophenol in particular might be worthy of further attention. Pyridine, 2-chloropyridine, furfural, and pentachloroethane presumably would be too volatile for any but rather specialized purposes involving very tight containers. Pyridine and, to a lesser extent, 2-chloropyridine have a pronounced objectionable odor.

Trichloro-*tert*-butanol and 1,2,4-trichlorobenzene, although apparently less effective than any of the preceding chemicals, may have compensating advantages in their solid state and relatively low volatilization tendency.

m-Cresyl acetate was not so effective as had been expected from reports of its present acceptance as a vapor inhibitor of molds. Possibly the material as distributed may vary somewhat in composition. It was, however, one of the slowest to volatilize of any of the chemicals tested and for this reason could be used in places of moderate mold hazard with less frequent replacement than the more volatile chemicals.

Combinations of different chemicals are frequently more effective than single compounds where a variety of fungi are to be controlled. Different species and strains of fungi tend to tolerate more of one chemical than another, especially if the chemicals are of different basic types. Consequently, a thorough consideration of vapor control of molding could profitably include trials of chemical mixtures. It might be most appropriate to do this, however, in connection with work on specific supplies or equipment and thus limit to some extent the kinds of fungi to be contended with.

In supplementary tests, vapors of none of the better chemicals tested noticeably affected the quality of Papreg (paper impregnated and laminated with phenol-formaldehyde resin). Those that appeared to promote corrosion of steel, aluminum, or brass were: benzaldehyde for steel; furfural for steel, aluminum, and brass; pentachloroethane for steel and aluminum; *m*-cresyl acetate for steel; and ethyl mercuric chloride for steel and aluminum.

The majority of the chemicals listed in Table II would probably be objectionable in the presence of foods. Such use of volatile fungicides, however, is not always excluded, as shown by the current commercial employment of diphenyl in paper wrappers for citrus fruits.

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[1] Clayton, E. E., Gains, J. G., Shaw, K. J., Smith, T. E., Foster, H. H., Sunn, W. M., and Graham, T. W., U. S. Dept. Agr., *Tech. Bull.* 799 (1942).

Methods of Producing Uniform Velocity Distribution

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This paper presents an elementary, theoretical quantitative treatment of two well known methods of smoothing velocity distributions in open and closed channels and ducts. The derived equations, while subject to limitations, are believed to possess an accuracy in keeping with that required in the design and operation of certain types of process equipment.

A UNIFORM distribution of fluid velocity through certain engineering process equipment is necessary for maximum capacity and efficiency of operation. This is particularly true in installations for making mechanical separations such as skimming and settling basins or chambers, elutriation columns, and electrical precipitators. However, in the actual construction of such installations, cost and the limitation of space usually make sharp bends and sudden enlargements in the connecting channels or duct work necessary. Consequently a nonuniform velocity profile will often exist at the inlet and outlet of the structure, and will prevail in between unless specific corrective measures are taken. Methods of smoothing out these irregular velocity distributions will be analyzed; although the methods in themselves are well known, their quantitative nature is not always appreciated.

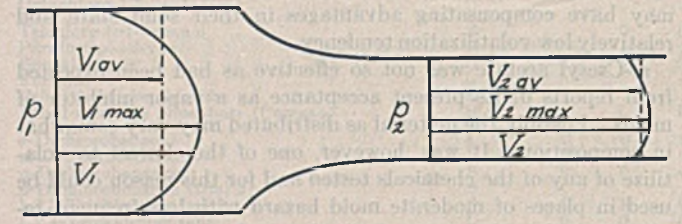

Figure 1. Smoothing a Velocity Distribution by Reducing the Flow Cross Section

Basically, there are two methods of making a velocity profile more uniform: (1) increasing the average velocity by reducing the cross-sectional area of flow, such as with a rounded converging transition (Figure 1); and (2) adding a uniform resistance across the flow area in the form of a homogeneous screen, grid work of baffles, perforated plate, etc. (Figure 2). Both methods are characterized by a drop in the static head of the fluid. In the case of method 1 there is little energy loss, and consequently the static head drop is almost completely compensated by the increased velocity head. With the second method the drop in static head corresponds to a loss in energy of the fluid stream in passing through the resistance.

Guide vanes, or turning vanes, are not analyzed here since their principal application is to lessen the energy loss of fast-moving streams while flowing around sharp bends and through diverging transitions by maintaining an already more or less uniform velocity distribution. For this purpose they can be used to good advantage. However, guide vanes are not particularly practical for smoothing an uneven profile, because a considerable amount of experimental cutting and trying of their arrangement is usually necessary before the desired uniformity is attained. Also, if a subsequent structural change is made upstream from the vanes, the vanes will generally have to be readjusted.

To simplify the notation, the flow in each case will be assumed horizontal and two dimensional. Thus, both Figures 1 and 2 lie in a horizontal plane.

METHOD 1

With a rounded converging transition, as indicated by Figure 1, the energy loss and fluid mixing will be slight and Bernoulli's equation of energy along any given flow line, not in the immediate vicinity of the solid boundaries, is expressed very well by:

$$\frac{p_1}{w} + \frac{V_1^2}{2g} = \frac{p_2}{w} + \frac{V_2^2}{2g} \tag{1}$$

or

$$V_2^2 - V_1^2 = \frac{2g}{w}(p_1 - p_2) \tag{2}$$

Since, according to Equation 2, all flow lines experience an equal gain in kinetic energy in passing through the transition, it is apparent that the velocity profile must be smoothed. Furthermore, if the differential equation for continuity is combined with Equation 2, it is possible, theoretically at least, to determine the downstream velocity distribution from the upstream distribution and the pressure drop.

The energy equation along the fluid filament of maximum velocity is:

$$V_{2max}^2 - V_{1max}^2 = \frac{2g}{w}(p_1 - p_2) \tag{3}$$

In the case of a flow line which possesses the average velocity upstream, the energy equation is

$$V'^2_{2av} - V^2_{1av} = \frac{2g}{w}(p_1 - p_2) \tag{4}$$

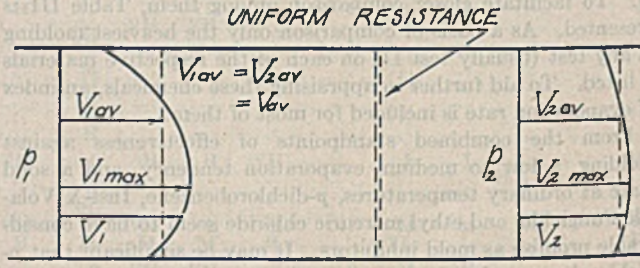

Figure 2. Smoothing a Velocity Distribution by Adding a Homogeneous Resistance across the Flow Area

It is to be noted here that downstream from the transition the velocity along this flow line will not, in general, be the average downstream velocity, V_{2av}. Let the fractional deviation of $V_2'_{av}$ from V_{2av} be designated by δ. That is,

$$\delta = \frac{V_{2av} - V'_{2av}}{V_{2av}} \tag{5}$$

Since it is reasonable to assume that the pressure does not vary across the flow, Equation 4 can be combined with Equation 3 to give:

$$V_{2av}^2\,(1-\delta)^2 - V_{1av}^2 = V_{2max}^2 - V_{1max}^2 \qquad (6)$$

With the aid of the over-all continuity equation,

$$A_1V_{1av} = A_2V_{2av} \qquad (7)$$

it follows that Equation 6 can be expressed as

$$\frac{V_{2max}}{V_{2av}} = \sqrt{1 + \left(\frac{A_2}{A_1}\right)^2\left[\left(\frac{V_{1max}}{V_{1av}}\right)^2 - 1\right] - 2\delta + \delta^2} \qquad (8)$$

Fortunately, the last two terms under the radical are frequently small enough so that a good approximation results, even if they are neglected. For purposes of determining the effect of δ in Equation 8, we assume that the upstream velocity and pressure drop through the transition is given. Then, from the equation of continuity in differential form, which is

$$V_1da_1 = V_2da_2 \qquad (9)$$

the downstream cross-sectional area of flow can be expressed by

$$A_2 = \int\limits_{\text{over } A_2} da_2 = \int\limits_{\text{over } A_1} \frac{V_1}{V_2}\,da_1 \qquad (10)$$

where V_2 is defined by Equation 2. The average downstream velocity, V_{2av}, is thus obtainable from Equations 10 and 7 which, with Equation 4 for expressing $V_2'{}_{av}$, give the necessary means for evaluating δ. The quantities in Table I were calculated in this manner for the particular case of V_1 having a two-dimensional triangular distribution.

Although the case just chosen is a special one, it is a rather severe distribution and thereby serves to magnify the influence of δ. Even so, the maximum error due to omitting δ from Equation 8, as indicated in Table I, is only 6%. This error is on the conservative side; that is, one would expect the actual downstream velocity profile to be slightly more uniform than is indicated by Equation 8, with δ considered equal to zero.

METHOD 2

The flow through a homogeneous resistance in a duct of uniform cross section is indicated in Figure 2. Here the average velocity upstream and downstream are the same and will be designated by V_{av}. Such a flow is accompanied by a certain amount of mixing, and consequently the flow lines tend to lose their identity in the process. For this reason it is not possible to write the energy equation for every arbitrary flow line. However, in the immediate vicinity of the fluid filament of maximum velocity, the flow lines are essentially identical in regard to energy. In spite of any slight shuffling of the lines due to the resistance, it is permissible to write:

$$\frac{p_1}{w} + \frac{V_{1max}^2}{2g} = \frac{p_2}{w} + \frac{V_{2max}^2}{2g} + K\,\frac{V_{2max}^2}{2g} \qquad (11)$$

or

$$(1+K)\,V_{2max}^2 - V_{1max}^2 = \frac{2g}{w}\,(p_1 - p_2) \qquad (12)$$

where the resistance energy-loss coefficient, K, can usually be defined by

$$\frac{p_1 - p_2}{w} = K\,\frac{V_{av}^2}{2g} \qquad (13)$$

Thus

$$(1+K)\,V_{2max}^2 - V_{1max}^2 = KV_{av}^2 \qquad (14)$$

Table I. Influence of δ in Equation 8 for the Special Case of V_1 Having a Two-Dimensional Triangular Distribution ($V_{1max}/V_{1av} = 2.0$)

$\dfrac{V_{1max}}{\sqrt{\frac{2g}{w}(p_1 - p_2)}}$	$\dfrac{A_2}{A_1}$	δ	Equation 8 with δ Neglected	Equation 8	% Error with δ Neglected
0.00	0.000	0.000	1.000	1.000	0.0
0.25	0.123	0.008	1.023	1.015	0.8
0.50	0.236	0.029	1.080	1.053	2.5
1.00	0.414	0.076	1.23	1.17	4.9
2.00	0.618	0.126	1.46	1.38	5.5
3.00	0.721	0.133	1.60	1.52	5.0
5.00	0.820	0.117	1.74	1.67	4.0
∞	1.000	0.000	2.00	2.00	0.0

and

$$\frac{V_{2max}}{V_{av}} = \sqrt{\frac{\left(\frac{V_{1max}}{V_{av}}\right)^2 + K}{1+K}} \qquad (15)$$

However, there is the objection to Equation 13 that the value of K thus defined depends upon the velocity distribution; consequently, K in Equations 11 and 12 is not equal, in general, to K in Equation 13. A more valid equation for defining K is:

$$\frac{p_1}{w} + \alpha_1\,\frac{V_{av}^2}{2g} = \frac{p_2}{w} + \alpha_2\,\frac{V_{av}^2}{2g} + \alpha_2\,K\,\frac{V_{av}^2}{2g} \qquad (16)$$

Here the kinetic energy coefficient, α, is given by

$$\alpha = \frac{(V^2)_{av}}{V_{av}^2} \qquad (17)$$

By combining Equations 11 and 16, it follows that

$$\frac{V_{2max}}{V_{av}} = \sqrt{\frac{\left(\frac{V_{1max}}{V_{av}}\right)^2 + \alpha_2 - \alpha_1 + \alpha_2K}{1+K}} \qquad (18)$$

Since it is usually desirable, in the type of equipment mentioned earlier, to have the downstream velocity profile fairly uniform, α_2 should consequently be only a few per cent greater than unity. If this is true, the value given by Equation 18 will be at most only slightly larger than that according to Equation 15. For example, if enough resistance is used to make α_2 equal to, say, 1.1, then the value defined by Equation 18 cannot be more than 5% greater than that defined by Equation 15. Incidentally, to help appreciate the significance of $\alpha_2 = 1.1$, one recalls that $\alpha = 1.05$ to 1.10, and $V_{max}/V_{av} = 1.1$ to 1.2 are fairly typical of the velocity distribution in long straight ducts. Needless to say, viscous or laminar flow is not considered in any of the preceding discussion.

APPLICATIONS

The type of process equipment mentioned in the first paragraph ordinarily handles large volumes at low velocities. Consequently, smoothing these velocity profiles by method 1 is not practical, owing to the fact that the ducts or channels would have to be larger than the equipment itself, which is already relatively large. There are, however, applications in other fields for this method. One notable example is in wind tunnels where a uniform high velocity is required. Also, the method is employed to advantage in providing a region of uniform velocity for calibrating velocity meters. In each of these applications the velocity is usually fairly uniform before the rounded transition is reached; consequently, Equation 8, with δ neglected, would be expected to be quite accurate.

On the other hand, method 2 does have application for the types of installations in question. With the low velocities the energy loss through the resistance will be small, which is important owing to the large flow volumes involved. In practice, the velocity through this type of equipment seldom exceeds 10 feet per second for gases and possibly not more than 2 feet per second for liquids. With K as large as 10, this would only amount to 16.5 and 0.6 foot of fluid, if the fluid were a gas or a liquid, respectively. If the gas were air at ordinary conditions, the above loss would correspond to only 0.25 inch of water.

The value of K for a resistance, such as a perforated plate or grid work of baffles, depends upon the ratio of the combined area of the distributed openings to the total flow area. If the openings are considered as submerged orifices of discharge coefficient C and combined area A_0, the relationship between K and the area ratio can be estimated for large K values by:

$$CA_0 \sqrt{\frac{2g}{w}(p_1 - p_2)} = AV_{av}$$

and

$$K \frac{V^2_{av}}{2g} = \sqrt{\frac{p_1 - p_2}{w}}$$

Thus

$$K = \left(\frac{A}{A_0}\right)^2 \frac{1}{C^2}$$

A value of $K = 10$, if C is assumed to be 0.6, corresponds to

$$\frac{A}{A_0} = \sqrt{10 \times 0.6^2} = 1.9$$

In other words, for $K = 10$, the combined area of the uniformly distributed openings should comprise approximately half the total cross-sectional area. It is assumed, of course, that the flow through the openings is in the turbulent region.

Obviously, in the choice of the kind of resistance it is essential to consider the possibility of fouling. The reason is not so much that the energy loss might become excessive, but rather that uneven build-up or coating on the resistance might actually aggravate rather than correct an already maldistribution. In some applications fouling will occur eventually, regardless of the resistance design, but it is often feasible to provide means of cleaning the resistance by brushing, rapping, or fluid jet lancing.

In each of the two methods described, it must be realized that the downstream station designated by subscript 2 is immediately after the transition in method 1 and immediately following the resistance in method 2. Thus, station 2 is not situated far enough downstream for wall friction to have produced any important influence on the velocity profile. In this regard, however, a downstream distance equal to several channel widths is usually required to establish the normal distribution due to wall friction.

In the preceding derivations it is tacitly assumed that the flow is rectilinear and parallel to the channel axis. Actually, for a very irregular distribution and particularly for one that is extremely asymmetrical, there will be some cross flow and mixing of the fluid before reaching and while passing through the transition or resistance. This will cast some doubt on the accuracy of Equation 1 and can conceivably alter the effective value of K over portions of the otherwise uniform resistance. Attention is also called to the fact that the distribution ahead of either the transition or the resistance will be influenced somewhat by the presence of these structures themselves. But even under drastic conditions the equations should, at least, serve as fair approximations.

NOMENCLATURE

p = static pressure in fluid, lb./sq. ft.
V = velocity of flow, ft./sec.
V'_{2av} = downstream velocity corresponding to V_{1ar} (Equation 4), ft./sec.
δ = velocity ratio defined by Equation 5, dimensionless
A = cross-sectional area of flow, sq. ft.
da = differential cross-sectional area of flow, sq. ft.
g = acceleration due to gravity, ft./sec./sec.
w = weight density of fluid, lb./cu. ft.
K = energy-loss coefficient due to resistance, dimensionless
α = kinetic energy coefficient (Equation 17), dimensionless

Subscripts
1, 2 = upstream and downstream conditions, respectively
av, *max* = average and maximum values

Benzoic Acid from Phosgene and Benzene

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IN CONNECTION with the insect and rodent control program of the armed forces during the war, several esters of benzoic acid, particularly benzyl benzoate, were found to be valuable as miticides. Consequently, an ambitious production schedule for benzyl benzoate was planned. This program was of such proportion that production methods for starting materials such as benzyl chloride and benzoic acid which did not depend upon toluene as the basic chemical had to be investigated.

In this connection the Chemical Warfare Service undertook an exploratory laboratory study of the aluminum chloride–catalyzed reaction between benzene and phosgene with the view of obtaining benzoic acid. A specific advantage of the process lies in the fact that chlorine-free benzoic acid is necessarily formed:

$$C_6H_6 + COCl_2.AlCl_3 \longrightarrow C_6H_5COCl.AlCl_3 + HCl \text{ (gaseous)}$$
$$C_6H_5COCl.AlCl_3 + 8H_2O \longrightarrow C_6H_5COOH + Al(H_2O)_6^{+++} + H_3O^+ + 4Cl^-$$

Although there are several references in the early published chemical literature on the liquid-phase reaction between phosgene and benzene in the presence of aluminum chloride (*2*), it remained for Wilson and Fuller (*3*) to point out the feasibility of this process for the production of benzoic acid. Wilson and Fuller discovered that, when benzene is added slowly to a cold mixture of phosgene, carbon disulfide, and aluminum chloride, the major reaction product formed is benzoyl chloride along with a smaller amount of benzophenone. Under the reaction conditions employed, the benzoyl chloride formed was hydrolyzed and subsequently isolated as benzoic acid.

The data of Wilson and Fuller indicate that carbon disulfide is an essential diluent in the reaction mixture. In the absence of carbon disulfide, these authors report a very low yield of benzoic acid, the major product being benzophenone. The process employing carbon disulfide as reaction solvent was later patented by Norris and Fuller (*1*), who also claimed that hydrocarbons, free of olefins, may be substituted for carbon disulfide.

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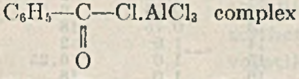
The preparation of benzoic acid through the aluminum chloride–catalyzed reaction between benzene and an excess of liquid phosgene was found to be superior to the previously known reaction between these reagents in such inert reaction solvents as carbon disulfide. The yields of benzoic acid, in the process here described, are dependent upon the reaction time and the molar ratios of aluminum chloride to benzene and phosgene to benzene, respectively. For a molar relation of phosgene to benzene to aluminum chloride equal to 3 to 1 to 1, a maximum yield of benzoic acid of 55–58% of theory, based on benzene, is obtained after a reaction period of 16–18 hours at 3–8° C. The by-product of the reaction is benzophenone. An increase of the aluminum chloride–benzene molar ratio above unity accelerates the reaction but does not increase the over-all yield of benzoic acid. A decrease of the phosgene–benzene molar ratio below 3 to 1 reduces the yield of benzoic acid and increases the yield of benzophenone. The reaction between phosgene and benzene produces a grade of benzoic acid which is free of nuclear chlorine.

That carbon disulfide, or some other inert diluent, had to be present in the reaction mixture was explained by Wilson, Fuller, and Norris in the following way: A slow addition of benzene to a cold mixture of carbon disulfide, aluminum chloride, and phosgene formed predominantly the  $C_6H_5\text{—}\underset{\underset{O}{\|}}{C}\text{—}Cl.AlCl_3$ complex which was insoluble in carbon disulfide. Thus, carbon disulfide served to remove the desired complex from the reaction medium as an insoluble solid, so that the complex, once formed, was denied the opportunity of reacting with more benzene to form the undesired benzophenone.

The present authors checked the work of Wilson and Fuller and found, in addition to the undesirability of introducing carbon disulfide into the reaction mixture, that the presence of this diluent contaminates the benzoic acid product with a small amount of a sulfur-containing impurity of highly obnoxious odor. When hexane was tried in place of carbon disulfide, no benzoic acid was obtained.

It was found that these difficulties could easily be obviated by conducting the reaction in an excess of liquid phosgene and omitting carbon disulfide or any other foreign diluent from the reaction mixture. In general, the results obtained by this method are more reproducible and, what is more important, the elimination of carbon disulfide leads to purer products. Yields for both procedures are of the same order of magnitude.

GENERAL PROCEDURE

A desired quantity of phosgene (ranging from 1.0 to 6.0 moles) was condensed in a tared 500-ml., three-neck, round-bottom flask by immersing the flask in an ice water bath. After the proper amount of liquid phosgene had been weighed into the flask, the flask was equipped with a mercury-seal stirrer, a thermometer, a dropping funnel, and a gas escape tube terminating in a calcium chloride trap. After being mounted the reactor flask was immersed in a 4-pint Dewar flask which was charged with an ice water mixture. The temperature of the phosgene was thus maintained at 3–8° C. A desired quantity of aluminum chloride, depending upon the run made (Table I), was added to the liquid phosgene with stirring. After addition of all the aluminum chloride, benzene was allowed to drop into the reaction medium at a slow rate, indicated in more detail in Table I. The entire reaction mixture was then stirred at 3–8° C. for a previously determined length of time.

At the end of the reaction period, the contents of the reaction flask were poured onto about 1 to 1.5 liters of cracked ice. This step served to hydrolyze the aluminum chloride complex and thus liberate benzoyl chloride. In those runs where an excess of aluminum chloride was used with respect to benzene (i.e., a mole ratio of aluminum chloride to benzene greater than 1), it was observed that the hydrolysis went directly to benzoic acid and left but little unhydrolyzed benzoyl chloride.

After the hydrolyzed reaction product had reached room temperature and all of the excess phosgene had either been decomposed or evaporated off, the organic layer was separated and the aqueous layer was extracted twice using about 75-ml. of diethyl ether in each extraction.

The combined organic product–extract layers were poured into 750 to 1000 ml. of approximately 7–8% aqueous sodium hydroxide and warmed. The ether was expelled, and any residual benzoyl chloride was transformed into sodium benzoate. After cooling, the solution was filtered free of benzophenone. To the filtrate a quantity of concentrated hydrochloric acid sufficient to precipitate all of the benzoic acid was added with stir-

Table I. Data on Reaction of Phosgene with Benzene

Expt. No.	$COCl_2$, Moles	$AlCl_3$, Moles	C_6H_6, Moles	Addition of C_6H_6		Reaction after Adding C_6H_6		Yield of Benzoic Acid			Benzophenone Formed		Benzene Accounted For in Products	
				Time, min.	Temp., ° C.	Time, hr.	Temp., ° C.	Grams	Mole	% of theory	Grams	Mole	Mole	% of total
1	2.0	0.5	0.5	10	4–5	2	4–5	9.5	0.080	15.6	..	...	...	..
2	2.0	0.5	0.5	10	4–5	4	4–6	20.0	0.164	32.8	..	...	...	..
3	2.0	0.5	0.5	10	3–6	8	5–6	25.6	0.210	41.9	..	...	...	..
4	2.0	0.5	0.5	15	4–9	10	4–6	22.4	0.183	36.7[a]	..	...	...	..
5	2.0	0.5	0.5	10	3–7	12.5	3–5	29.2	0.239	47.8	..	...	...	..
6	2.0	0.5	0.5	15	4–8	16	3–5	26.5	0.217	43.4[b]	..	...	...	..
7	2.0	0.5	0.5	15	3–8	20	4–6	32.9	0.269	53.9	12.5	0.069	0.338	67.6
8	2.0	0.5	0.5	20	4–5	20	5–6	30.4	0.249	49.8[b]	16.4	0.090	0.339	67.8
9	3.0	0.5	0.5	55	4–5	20	5–6	34.6	0.283	56.7	..	...	...	..
10	2.0	0.5	0.5	15	3–4	24	4–6	34.8	0.285	57.0	..	...	...	..
11	2.0	0.75	0.5	20	4–5	2	4–5	18.0	0.147	29.5	10.9	0.060	0.207	41.4
12	2.0	0.75	0.5	32	4–5	6.5	4–5	32.3	0.264	52.9	15.6	0.086	0.350	70.0
13	2.0	0.75	0.5	25	4–5	18	4–7	35.5	0.291	58.1	19.9	0.109	0.400	80.0
14	2.0	1.0	0.5	32	4–5	2	4–5	25.6	0.210	41.9	12.3	0.068	0.278	55.6
15	2.0	1.0	0.5	20	4–5	6.25	4–6	35.1	0.287	57.5	14.6	0.080	0.367	73.4
16	2.0	1.0	0.5	30	4–6	18	4–8	35.3	0.289	57.8	21.3	0.117	0.406	81.2
17	1.5	0.75	0.5	20	4–5	6	4–6	35.1	0.287	57.5	18.5	0.102	0.389	77.8
18	1.0	0.75	0.5	27	4–5	6	4–6	29.5	0.242	48.3	23.9	0.131	0.373	74.6
19	1.5	1.0	1.0	47	4–8	6	4–6	51.3	0.420	42.0	43.8	0.240	0.660	66.0
20	1.5	1.5	1.0	31	5–6	6	5–7	46.2	0.378	38.7	49.3	0.271	0.649	64.9
21	1.0	1.0	1.0	28	4–5	6	5–8	41.8	0.342	34.2	52.5	0.288	0.630	63.0

[a] Slight loss due to alternate method of separation.
[b] Small mechanical losses during handling of product.

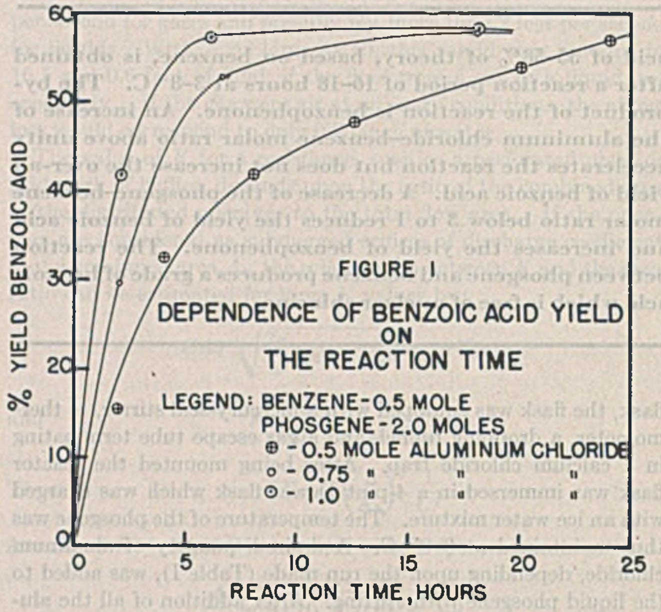


FIGURE 1
DEPENDENCE OF BENZOIC ACID YIELD ON THE REACTION TIME

ring. The precipitated acid-brine mixture was cooled to about 5–10° C., and subsequently the benzoic acid was filtered off with suction and dried in air. When dry its weight was determined.

In the procedure described, the initial crude reaction product was separated immediately from the aqueous layer containing dissolved aluminum chloride. A more troublesome procedure for the isolation of benzoic acid, leading, however, to slightly lower yields as compared with the procedure just described, took advantage of the amphoteric property of hydrated aluminum salts. After the crude reaction mixture was poured onto ice and the hydrated reaction mixture had reached room temperature, sufficient 40–50% aqueous sodium hydroxide solution was added to convert all the aluminum to the soluble aluminate, and sufficient (an excess) to convert benzoic acid and benzoyl chloride to sodium benzoate. The solution was filtered free of benzophenone and the filtrate was acidified as before with concentrated hydrochloric acid. At this point sodium aluminate was again transformed into gelatinous aluminum hydroxide together with the precipitation of free benzoic acid from sodium benzoate. An excess of hydrochloric acid again dissolved the aluminum hydroxide as its chloride, and left benzoic acid ready for suction filtration as before. The necessity of using many more times the quantities of sodium hydroxide and hydrochloric acid as compared with the first procedure made this latter method less desirable. Another disadvantage was the likelihood of obtaining solid sodium chloride, particularly if insufficient quantities of water were employed, and thus necessitating purification of the crude benzoic acid obtained. In the runs of Table I the first procedure for the isolation of benzoic acid was followed throughout, except in run 4 where the latter method was employed.

Although no attempts were made in this investigation to recover unused excess phosgene, it is believed that this can be accomplished with the aid of proper refrigeration equipment.

The results of twenty-one runs, together with specific reaction conditions in each, are compiled in Table I.

ANALYSIS OF DATA

The data in Table I reveal the fact that the reaction between phosgene and benzene is dependent upon three main factors: reaction time, molar ratio of aluminum chloride to benzene, and molar ratio of phosgene to benzene.

For a molar ratio of aluminum chloride to benzene of 1 to 1, the reaction occurs at a slow rate, reaching the 50% conversion point only after 16 to 18 hours:

Expt. No.[a]	Reaction Time, Hours	Yield of Benzoic Acid, %	Expt. No.[a]	Reaction Time, Hours	Yield of Benzoic Acid, %
1	2	15.6	5	12.5	47.8
2	4	32.8	7	20	53.9
3	8	41.9	10	24	57.0

[a] Reagents used: 0.5 mole benzene, 0.5 mole aluminum chloride, 2.0 moles phosgene.

If the molar ratio of aluminum chloride to benzene is increased to a value greater than unity, the rate of reaction is markedly enhanced (Figure 1). There is, however, no increase in over-all yield. The following results also show that the yield of benzophenone increases slightly as the aluminum chloride–benzene ratio is raised:

Expt. No.[a]	$AlCl_3$, Moles	Reaction Time, Hours	Yield of Benzoic Acid		Yield of Benzophenone, Grams
			Grams	%	
1	0.5	2	9.5	15.6	..
3	0.5	8	25.6	41.9	..
7	0.5	20	32.9	53.9	12.5
11	0.75	2	18.0	29.5	10.9
12	0.75	6.5	32.3	52.9	15.6
13	0.75	18	35.5	58.1	19.9
14	1.0	2	25.6	41.9	12.3
15	1.0	6.25	35.1	57.5	14.6
16	1.0	18	35.3	57.8	21.3

[a] Reagents used: 0.5 mole benzene, 2.0 moles phosgene.

From the standpoint of economics, as little phosgene as practicable should be used in this reaction. The effect of varying molar ratios of benzene to phosgene on the yield of benzoic acid follow:

Expt. No.[a]	$AlCl_3$, Mole	$COCl_2$, Moles	Yield of Benzoic Acid		Yield of Benzophenone, Grams
			Grams	%	
21	0.5	0.5	20.9	34.2	26.3
19	0.5	0.75	25.7	42.0	21.9
20	0.75	0.75	23.1	38.7	24.7
18	0.75	1.0	29.5	48.3	23.9
17	0.75	1.5	35.1	57.5	18.5
12	0.75	2.0	32.3	52.9	15.6

[a] 0.5 mole of benzene used in each experiment. The reaction period was 6 hours except in experiment 12, where it was 6.5 hours.

The data indicate that the amount of benzophenone increases as the molar ratio of aluminum chloride to benzene is increased. Experiment 17 shows that the molar ratio of phosgene to benzene should not be less than 3 to 1. Experiment 9 (Table I) shows that increasing the amount of phosgene from 2 to 3 moles per 0.5 mole of aluminum chloride and benzene each has but little effect on the total yield of benzoic acid produced; that is, the yield of acid is not increased above the 57% value which appears to be easily attainable under more economic conditions (experiments 13 and 17, Table I).

The combined effects of aluminum chloride and phosgene concentrations as given in the two preceding tables point to the conclusions that molar ratios of phosgene to aluminum chloride to benzene of 3 to 1.5 to 1 are probably best suited for this process. These ratios give the maximum obtainable yield of benzoic acid in a reasonably short time.

The reaction between phosgene and benzene produces a grade of benzoic acid which is highly pure and free of chlorine, with a minimum effort in purification. The products described in this report were entirely free of chlorine (less than 0.01%) after one recrystallization from water.

Attempts to use catalysts other than aluminum chloride were without success. The reaction has not yet been studied in pilot plant equipment.

LITERATURE CITED

(1) Norris, J. F., and Fuller, E. W., U. S. Patent 1,542,264 (1925).
(2) Thomas, C. A., "Anhydrous Aluminum Chloride in Organic Chemistry", pp. 233–4, New York, Reinhold Pub. Corp., 1941.
(3) Wilson, R. E., and Fuller, E. W., J. Ind. Eng. Chem., 14, 406 (1922).

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CHEMICAL PROPELLANTS

Analytical Studies and Characteristics of the System Hydrogen Peroxide-Permanganate

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Physical and chemical constants of hydrogen peroxide and permanganate have been collected from various sources, along with values determined by the authors. The densities and viscosities of aqueous calcium permanganate from 10° to 40° C. and the freezing points of solutions containing from 5 to 52% MnO_4^- are also given, along with two points on the sodium permanganate curve. Certain special analytical techniques were developed to handle the concentrated peroxide and permanganate solutions. Where these techniques differ from accepted analytical practice, they are described here. For the peroxide the method of assay for H_2O_2, nonvolatile matter, total acid, and pH are given. For permanganates, methods are described for determination of MnO_4^-, Ca, Na, Fe, SO_4^{--}, and pH. Analysis of captured German peroxide, indicating high total solids content, and also "summer" and "winter" permanganates are given.

RELIABLE values for the physical and chemical constants of hydrogen peroxide and permanganate were needed in studying this system as a chemical propellant (*1*). Some of the data were gathered from various sources, and others were determined in the course of the investigation. Table I lists physical properties of pure hydrogen peroxide taken from various handbooks and International Critical Tables.

Maass and co-workers are the source of a considerable amount of precise data relative to exceedingly pure hydrogen peroxide. The vapor pressures of the pure material (Table II) from room temperature up to 90° C. were taken from the work of Maass and Hiebert (*7*). These data are plotted in Figure 1, along with the vapor pressures of water at the corresponding temperatures for comparison. Table II also gives the densities and viscosities of the pure material at several temperatures.

Table III lists the densities and viscosities of aqueous peroxide solutions at 18° C. from the data of Maass and Hatcher (*5*) and at 25° C. from our own measurements. These values are plotted in Figure 2.

Table IV and Figure 3 present the freezing points of aqueous peroxide solutions, taken from Maass and Herzberg (*6*). Freezing point was an important consideration in the field use of hydrogen peroxide. The steep slope of the curve in the range between 80 and 100% peroxide permitted the use of a lower concentration without serious loss of power in climates where the higher concentrations would have frozen or become too viscous to flow through pipes.

Table V and Figure 4 present the densities and viscosities of aqueous calcium permanganate solutions from 20 to 51.9% MnO_4^- and from 10° to 40° C. Table VI and Figure 5 show the freezing points of calcium permanganate solutions over the range from 5 to 52% MnO_4^-. Table VI also gives two points on the sodium permanganate curve.

In dealing with these unusual concentrated solutions of peroxide and calcium and sodium permanganates, special methods and techniques were necessary. Whenever possible, standard recognized procedures were used and are not listed here.

HYDROGEN PEROXIDE

ASSAY. All glassware was cleaned by soaking for 30 minutes or longer in concentrated nitric acid, well rinsed with distilled water, and oven-dried before use.

A 0.25–0.35 gram sample of 90% hydrogen peroxide or a proportionately larger sample of a more dilute solution was transferred into a small weighing bottle by a medicine dropper and weighed. The weighing bottle was then carefully dropped into a 600-ml. beaker containing approximately 300 ml. of distilled water. After stirring, 8 ml. of 10 *M* sulfuric acid were added, and the mixture was titrated at once with 0.5 *N* potassium permanganate. The latter was standardized against National Bureau of Standards sodium oxalate in the usual manner. This method has a precision of 1 part per thousand.

Samples of hydrogen peroxide were also measured out in a calibrated 0.1-ml. pipet and, after dilution as above, titrated with 0.5 *N* potassium permanganate solution. Although subject to greater error (precision about 10 parts per thousand), the method proved useful in following the larger changes in peroxide concentration in some of the more extended stability series.

NONVOLATILE MATTER. The 90% hydrogen peroxide was checked as received for nonvolatile residue (at 110° C.). The solutions of such high concentration cannot be safely evaporated to dryness in platinum unless the sample is added in many small increments over a period of several hours. This method is time consuming and subject to mechanical loss due to spray. The method used was to add a previously diluted sample (100 grams peroxide plus 100 ml. of water) from a specially designed separatory funnel (Figure 6) to a 150-ml. platinum dish containing about 20 ml. of water. The dish was placed on a steam bath and the separatory funnel supported so that the capillary tip extended to just above the water level. The dish was covered with a Fisher Speedy-Vap watch glass. The pressure regulator was inserted far enough in the separatory funnel to ensure a flow rate of not more than 3–5 ml. per minute when the stopcock was fully open. At this rate the peroxide decomposed rapidly but smoothly and required no attention. After the entire sample had been added and the funnel rinsed, the mixture was evaporated until bubbling due to decomposition of peroxide had ceased. It was then transferred to a tared 50-ml. platinum dish, evaporated to dryness, dried at 110° C., and weighed.

TOTAL ACID (AS H_2SO_4). Twenty grams of 90% hydrogen

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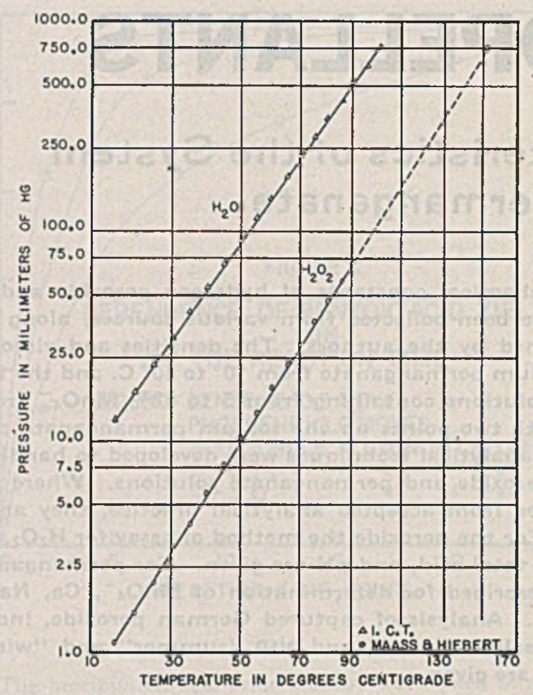

Figure 1. Vapor Pressure of Water and Hydrogen Peroxide

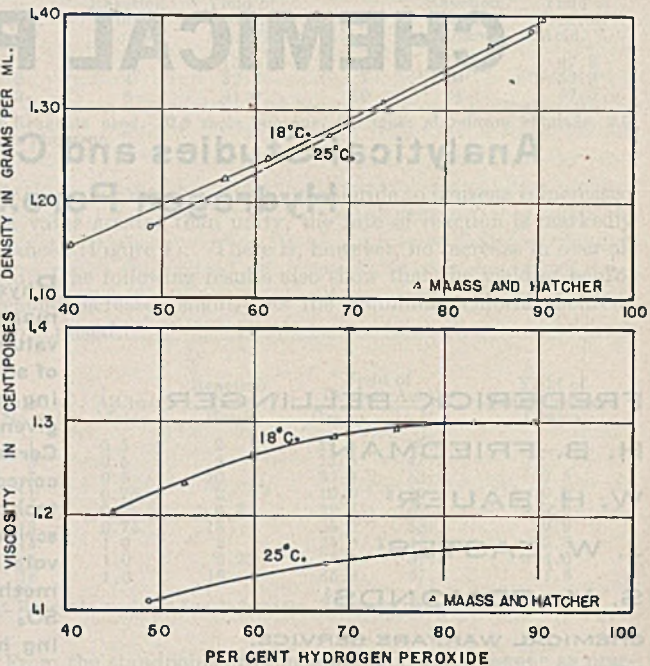

Figure 2. Density and Viscosity of Concentrated Hydrogen Peroxide Solutions

TABLE I. PHYSICAL PROPERTIES OF 100% HYDROGEN PEROXIDE

Freezing point, ° C.	−1.70
Boiling point (estd.), ° C.	151.4
Approx. explosion temperature (*8*), ° C.	151
Density of liquid at 18° C., g./cc.	1.444
Density of solid at −7.5° C., g./cc.	1.644
Mean coefficient of expansion, −10° to +20° C.	0.00107
Specific heat of liquid (0–18° C.), cal./g.	0.579
Specific heat of solid, cal./g.	0.470
Latent heat of vaporization (estd.), cal./g.	326
Latent heat of fusion, cal./g.	74
Surface tension at 20° C., dynes/cm.	75.7
Viscosity at 18° C., centipoises	1.307
Refractive index, n_D^{22}	1.4139
Heat of decomposition (*8*)[a], cal.	−23,450
Ionization constant at 20° C. with glass electrode (*3*)	1.55×10^{-12}
Dielectric constant at 0° C. (*4*)	93.7

[a] For H_2O_2 (liquid) = H_2O (liquid) + $^1/_2O_2$ (gas, 1 atm.)

TABLE II. VAPOR PRESSURE, DENSITY, AND VISCOSITY OF 100% HYDROGEN PEROXIDE AT VARIOUS TEMPERATURES

Vapor Pressure (*7*)				Density[a]		Viscosity (*5*)	
t° C.	Mm. Hg.	t° C.	Mm. Hg	t° C.	G./cc.	t° C.	Centipoises
15	1.1	55	13.8	−10	1.475	0.04	1.828
20	1.5	60	18.1	− 5	1.4685	11.90	1.456
25	2.1	65	23.3	0	1.4649[b]	12.20	1.447
30	2.75	70	29.65	5	1.4575	19.60	1.272
35	4.0	75	37.6	10	1.452		
40	5.7	80	47.4	15	1.447		
45	7.8	85	59.1	20	1.442		
50	10.4	90	71.5				

[a] Estimated from the curve of Maass and Hatcher (*5*).
[b] This value taken from Cuthbertson, Matheson, and Maass (*2*).

TABLE III. DENSITY AND VISCOSITY OF CONCENTRATED HYDROGEN PEROXIDE SOLUTIONS

H_2O_2, %	Density, G./Cc. 18° C. (*5*)	Density, G./Cc. 25° C.	H_2O_2, %	Viscosity, Centipoises 18° C. (*5*)	Viscosity, Centipoises 25° C.
100.0	1.444	...	89.5	1.301	..
98.9	1.440	...	89.2	...	1.17
90.4	1.396	...	83.2	1.300	..
89.2	...	1.383	75.0	1.292	..
84.9	1.366	...	68.5	1.285	..
73.4	1.307	...	67.7	...	1.15
67.7	...	1.272	59.6	1.266	..
61.2	1.247	...	52.5	1.236	..
56.7	1.227	...	48.9	...	1.11
48.9	...	1.186	44.8	1.204	..
40.1	1.155	...			

TABLE IV. FREEZING POINTS OF HYDROGEN PEROXIDE SOLUTIONS (*6*)

% H_2O_2	F.P., ° C.	% H_2O_2	F.P., ° C.	% H_2O_2	F.P., ° C.
4.9	− 3.4	46.2	−51.8	63.1	−50.0
10.0	− 6.1	47.0	−50.8	65.4	−45.5
15.9	−11.1	49.8	−51.7	67.4	−41.5
22.5	−17.0	53.7	−52.5	69.2	−39.0
27.7	−23.4	55.1	−53.6	74.0	−32.5
32.0	−28.5	56.2	−54.3	80.5	−22.7
36.5	−35.7	58.8	−54.5	86.0	−14.0
37.8	−38.0	61.1	−52.5	96.7	− 4.0
42.0	−46.3			99.9	− 1.7

TABLE V. DENSITIES AND VISCOSITIES OF CALCIUM PERMANGANATE SOLUTIONS[a]

MnO_4^-, %	Density, G./Cc.			Viscosity, Centipoises		
	10° C.	25° C.	40° C.	10° C.	25° C.	40° C.
20	1.209	1.201	1.187	1.667	1.181	0.886
30	1.347	1.336	1.324	1.704	1.542	1.175
40	1.506	1.493	1.479	3.23	2.31	1.877
51.9[b]	1.750	1.734	1.719	9.36	6.27	4.52

[a] Prepared from lot No. C-60-61, Carus Chemical Company.
[b] The analysis of this calcium permanganate (labeled 76.7% by Carus) follows:

MnO_4^-, %	51.9	pH (1–10 diln.)	6.4
$Ca(MnO_4)_2$, %	59.5	MnO_4^-, calcd. as $Ca(MnO_4)_2 \cdot (H_2O)_4$	76.4
$NaMnO_4$, %	1.2		
Mg, %	Trace (< 0.1)		

TABLE VI. FREEZING POINTS[a] OF CALCIUM PERMANGANATE[b] AND OF SODIUM PERMANGANATE SOLUTIONS

MnO_4^-, %	Freezing Point, ° C. Ca permanganate	Freezing Point, ° C. Na permanganate
5	− 1	..
15	− 4.5	..
25	−10	− 9
35	−22	..
41	..	−15
42	−37	..
45	−53	..
52	−49	..

[a] These points represent temperatures at which, after seeding, appreciable crystal formation takes place.
[b] Prepared from Carus Chemical Company's lot No. C-60-61. Table V gives analysis of the 52% stock solution.

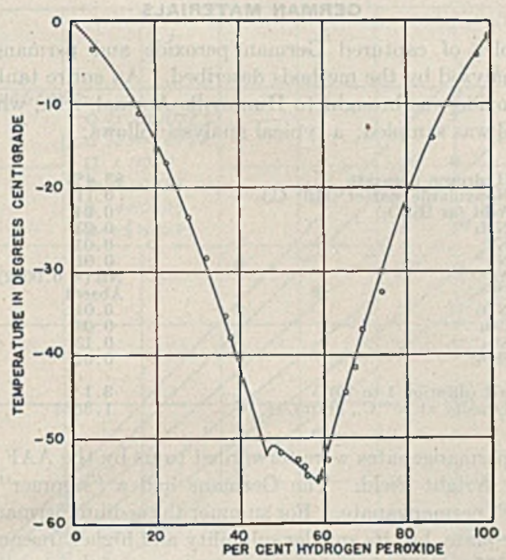

Figure 3. Freezing Point of Hydrogen Peroxide Solutions (5)

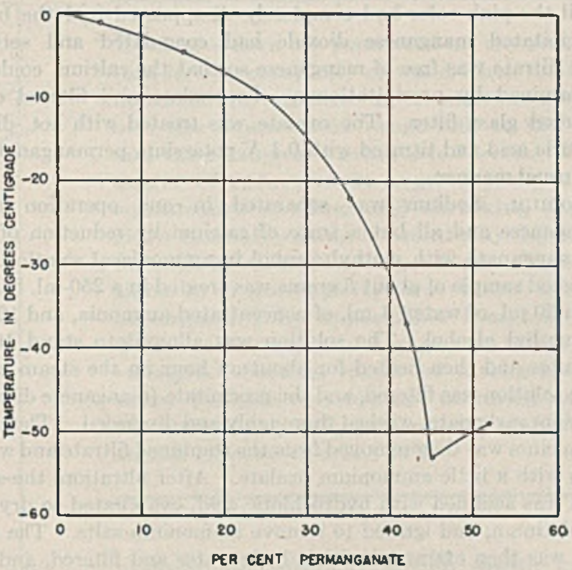

Figure 5. Freezing Point of Calcium Permanganate Solutions

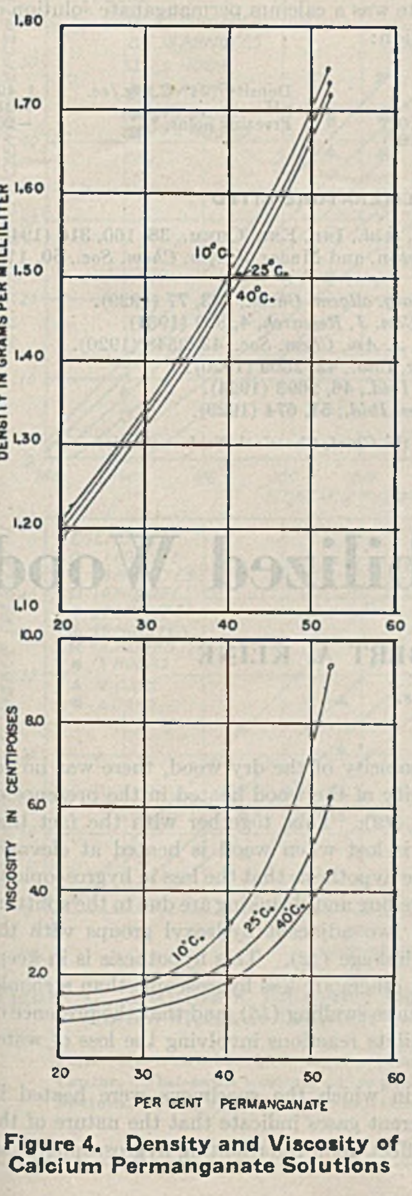

Figure 4. Density and Viscosity of Calcium Permanganate Solutions

peroxide were diluted with 100 ml. of carbon dioxide-free water and titrated with carbon dioxide-free, 0.01 *N* sodium hydroxide, using methyl red as indicator. A blank was also run and any correction subtracted from the titer.

Hydrogen Ion Concentration. The 90% peroxide was diluted 1:10 with freshly distilled water (pH 6.1–6.3), and the pH of the mixture was determined with a glass electrode and a Coleman pH electrometer.

CALCIUM PERMANGANATE

A direct permanganate determination was used to evaluate concentration changes in the stability tests and to check solution strength of the materials used in the thrust motor experiments. Complete qualitative and quantitative analyses were made of original samples of calcium and sodium permanganates procured for this work, of materials synthesized, and of captured German permanganates. The high percentage of permanganate present in those samples complicated the methods for the determination of some of the elements sought and necessitated the development of special methods. These are described in the following paragraphs.

Permanganate. A weighed sample equivalent to about 30–40 ml. of 0.5 *N* ferrous sulfate was diluted with a few milliliters of water and then slowly poured into a mixture of exactly 50.00 ml. of 0.5 *N* ferrous sulfate to which had been added 150 ml. of water and 20 ml. of 10 *M* sulfuric acid. After complete transfer, the excess ferrous sulfate was back-titrated with standard 0.5 *N* potassium permanganate. The ferrous sulfate solution was checked daily in the usual manner against the standard potassium permanganate.

Calcium. A weighed sample equivalent to about 50–60 mg. of calcium was treated in a 250-ml. beaker with 15 ml. of 6 *M* nitric acid. The beaker was covered with a watch glass and placed on a steam bath. There was usually some effervescence at the start as the permanganate decomposed to form manganese dioxide. After about 15 minutes the watch glass and walls of the beaker were washed down with a little water. Heating was continued

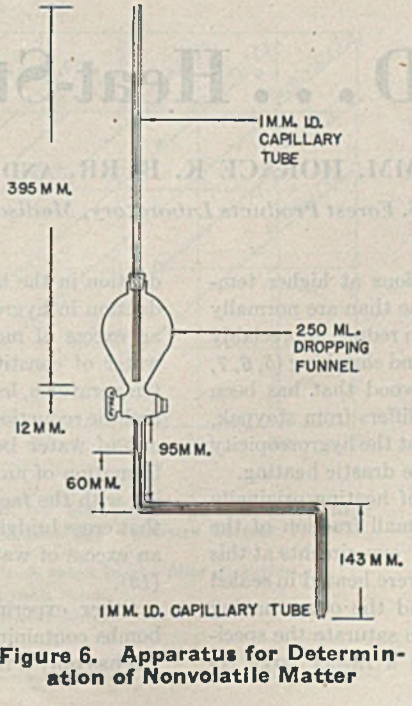

Figure 6. Apparatus for Determination of Nonvolatile Matter

until the pink color had completely disappeared and the black precipitated manganese dioxide had coagulated and settled. The filtrate was free of manganese so that the calcium could be determined by precipitation as the oxalate and filtered on a sintered glass filter. The oxalate was treated with hot, dilute sulfuric acid and titrated with 0.1 *N* potassium permanganate in the usual manner.

Sodium. Sodium was separated in one operation from manganese and all but a trace of calcium by reduction of the permanganate with methyl alcohol in ammoniacal solution. A weighed sample of about 5 grams was treated in a 250-ml. beaker with 50 ml. of water, 1 ml. of concentrated ammonia, and 10 ml. of methyl alcohol. The solution was allowed to stand 10–15 minutes and then heated for about an hour on the steam bath. The solution was filtered, and the precipitate (manganese dioxide, calcium carbonate) washed thoroughly and discarded. The trace of calcium was then removed from the combined filtrate and washings with a little ammonium oxalate. After filtration, the solution was acidified with hydrochloric acid, evaporated to dryness in platinum, and ignited to remove ammonium salts. The residue was then extracted with a little water and filtered, and the filtrate collected in a small tared platinum dish. The solution was treated with a few drops of hydrochloric acid, evaporated to dryness, and ignited below a red heat, and the weight of residue (sodium chloride) was obtained.

Iron. Iron was determined colorimetrically as ferric thiocyanate with a Fisher photoelectric colorimeter. Manganese was first removed by the nitric acid treatment described under calcium. From 8 to 10 grams of sample were used.

Sulfate. Since permanganate badly contaminates the barium sulfate precipitate, prior reduction of the permanganate ion is necessary. A weighed sample of about 5 grams was treated with 100 ml. of water and 10 ml. of concentrated hydrochloric acid. The mixture was heated until the pink color was discharged and the manganese dioxide had coagulated. It was then filtered, and the filtrate was neutralized with ammonia and made slightly acid with hydrochloric acid. Barium sulfate was then precipitated in the conventional way.

Hydrogen Ion Concentration. The calcium or sodium permanganate solutions were diluted to approximately 30% permanganate ion with freshly distilled water of pH 6.1–6.3, and the pH was determined using a glass electrode and the Coleman pH electrometer.

GERMAN MATERIALS

Samples of captured German peroxide and permanganates were analyzed by the methods described. An entire tank car of the peroxide was brought to Huntsville Arsenal, Ala., where the material was sampled; a typical analysis follows:

Hydrogen peroxide	83.4%
Nonvolatile matter (110° C.)	0.11
Acid (as H_2SO_4)	0.24
NH_4^+	0.03
K^+	0.01
Na^+	0.01
Al^{+++}	Nil (< 0.0002)
Cl^-	Absent
NO_3^-	0.01
PO_4^{---}	0.03
SO_4^{--}	0.13
SiO_2	0.01
pH (dilution 1 to 10)	3.1
Density at 25° C., grams/cc.	1.3533

The permanganates were forwarded to us by the AAF Supply Officer, Wright Field. The Germans had a "summer" and a "winter" permanganate. For summer the sodium permanganate was adequate, but its smaller solubility and higher freezing point made it unsuitable for winter temperatures; therefore the much more soluble calcium permanganate was employed.

Summer permanganate was found to be a solution containing 42.11% of sodium permanganate. Both potassium and calcium were absent. The density of the solution at 24° C. was 1.396 grams per cc.; its pH was 7.05 and its freezing point −15° C.

Winter permanganate was a calcium permanganate solution of the following composition:

$Ca(MnO_4)_2$	38.60%	Density (24° C.), g./cc.	1.406
$NaMnO_4$	1.75	pH	4.91
Mg^{++}	Trace (0.01)	Freezing point, ° C.	−20
SO_4^{--}	Trace (0.01)		
K^+	Absent		

LITERATURE CITED

(1) Bellinger, Friedman, *et al.*, Ind. Eng. Chem., 38, 160, 310 (1946).
(2) Cuthbertson, Matheson, and Maass, *J. Am. Chem. Soc.*, 50, 1120 (1928).
(3) Kargin, V. A., *Z. anorg. allgem. Chem.*, 183, 77 (1929).
(4) Linton and Maass, *Can. J. Research*, 4, 322 (1931).
(5) Maass and Hatcher, *J. Am. Chem. Soc.*, 42, 2548 (1920).
(6) Maass and Herzberg, *Ibid.*, 42, 2569 (1920).
(7) Maass and Hiebert, *Ibid.*, 46, 2693 (1924).
(8) Matheson and Maass, *Ibid.*, 51, 674 (1929).

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STAYBWOOD . . . Heat-Stabilized Wood

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HEATING wood under drying conditions at higher temperatures or for longer periods of time than are normally encountered in kiln drying has been shown to reduce appreciably the hygroscopicity and subsequent swelling and shrinking (*5*, *6*, *7*, *10*, *12*, *16*). Staybwood is uncompressed wood that has been dimensionally stabilized by heat alone. It differs from staypak, a heat-stabilized compressed wood (*8*), in that the hygroscopicity of the wood is reduced as a result of the more drastic heating.

The importance to antishrink efficiency of heating originally dry wood, or green wood that dries in a small fraction of the total heating time, has been demonstrated by experiments at this laboratory. Matched dry-wood specimens were heated in sealed bombs, one containing no free moisture and the other having more than enough free water in the bomb to saturate the specimen. Under heating conditions that gave a rather large reduction in the hygroscopicity of the dry wood, there was no reduction in hygroscopicity of the wood heated in the presence of an excess of moisture (*12*). This, together with the fact that water of constitution is lost when wood is heated at elevated temperatures, led to the hypothesis that the loss in hygroscopicity and the reduction in swelling and shrinking are due to the splitting out of water between two adjacent hydroxyl groups with the formation of an ether linkage (*12*). This hypothesis is in keeping with the facts that ethers are less hygroscopic than alcohols, that cross bridging reduces swelling (*15*), and that the presence of an excess of water inhibits reactions involving the loss of water (*12*).

Other experiments in which the specimens were heated in bombs containing different gases indicate that the nature of the gas has only a minor effect upon the resulting hygroscopicity, an

Extensive data are presented on the reduction in hygroscopicity of wood when heated beneath the surface of a molten metal over the temperature range 120° to 320° C. and time range of 1 minute to 1 week. The degree of reduction in hygroscopicity and equilibrium swelling and shrinking for a given time of heating is practically doubled for each 10° C. rise in temperature. Reductions in hygroscopicity are shown to be accompanied by appreciable increases in decay resistance and significant losses in strength. Serious losses in strength for many possible uses are not obtained until the reductions in hygroscopicity and antishrink efficiency exceed 50%.

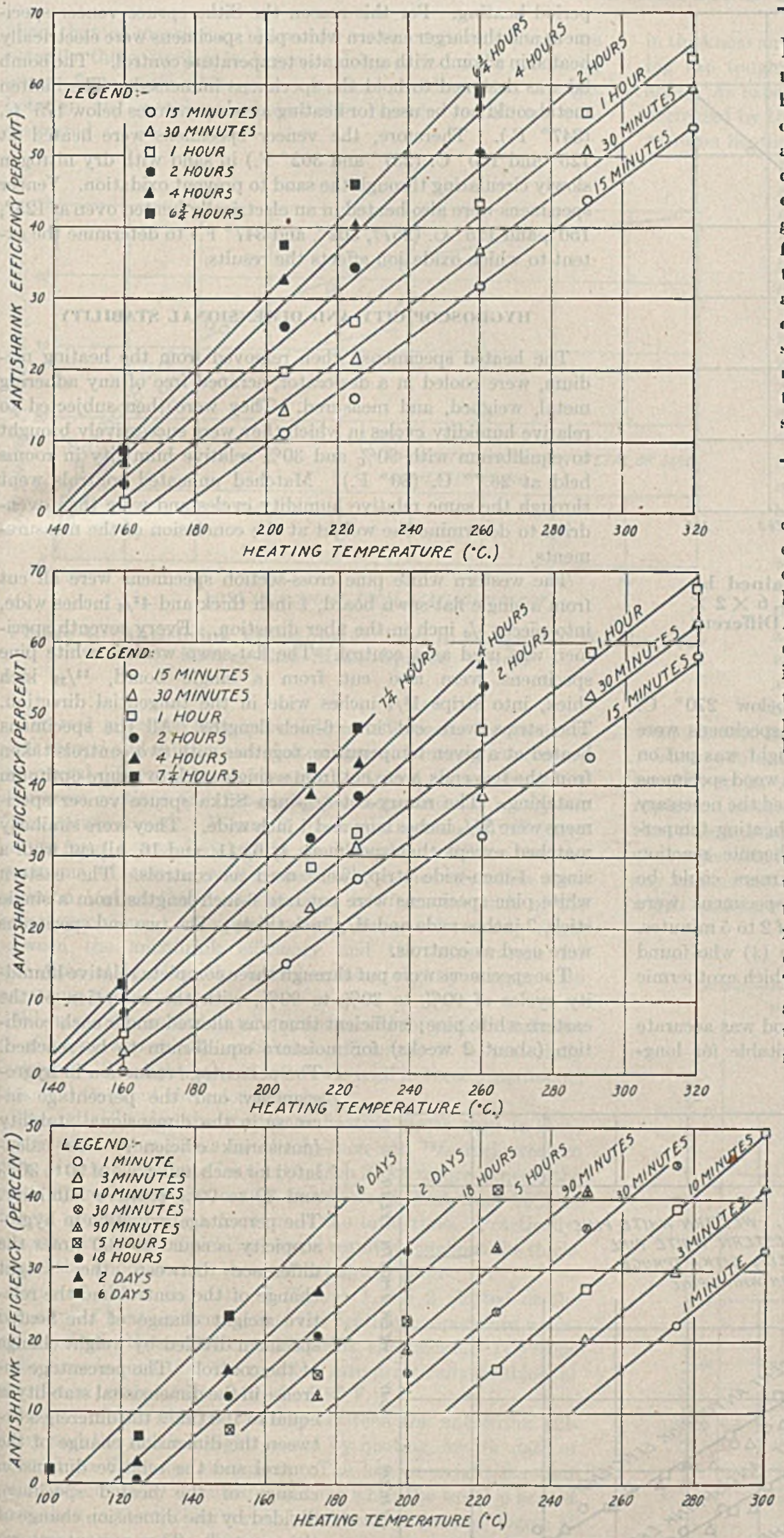

Figure 1. Antishrink Efficiency Obtained by Heating Specimens under Molten Metal at Different Temperatures for Various Times

Top. **Western white pine cross sections, 1/2 inch thick in the fiber direction.**
Center. **Flat-sawn western white pine, 13/32 inch thick.**
Bottom. **Sitka spruce rotary-cut veneer, 1/16 inch thick.**

oxidizing atmosphere being only slightly more effective than a reducing atmosphere. Previous data also show that the effect of heat upon the hygroscopicity of wood is permanent (*10, 12*). After an initial humidification-dehumidification cycle or soaking-drying cycle subsequent to heating, no gain in hygroscopicity occurs within the time or number of cycles tested. The phenomenon thus cannot be explained on the basis of a hysteresis effect.

HEATING IN MOLTEN METAL

It seemed desirable to extend heating measurements over a much broader range of heating temperatures and times in order to analyze the nature of the phenomenon better and to determine the practicability of such a process for commercially stabilizing the dimensions of wood. To minimize oxidation and its effect on strength and to make possible rapid heat transfer so as to avoid making corrections for the length of time required to attain the desired temperature in high temperature–short time combinations, a method of heating wood beneath the surface of molten metal was adopted (*10*). A lead-tin-cadmium alloy (approximately 50% tin, 30% lead, and 20% cadmium) with a melting point of about 150° C. (302° F.) was used. This alloy had but little tendency to stick to the specimens when they were removed from the bath except when used at temperatures only slightly above its melting point. Any small amount of adhering metal was readily scraped off with a steel spatula. In later work Wood's metal was tried in order to determine if it could be used at lower temperatures. This metal tended to stick to the wood sections and hence its use was abandoned.

The experiments with western white pine were made by heating the wood in an iron pan containing the molten metal with a steel weight having an insulated handle for holding the specimens immersed. The pan was heated with two Bunsen burners. The bath, with the weight immersed, was heated to about 2° C. (3.6° F.)

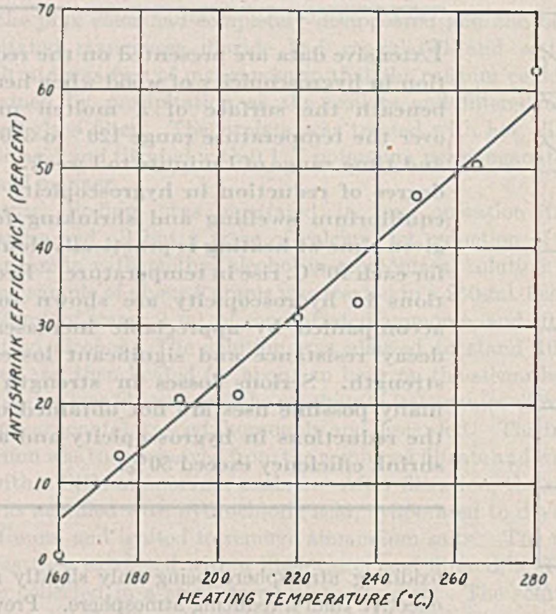

Figure 2. Antishrink Efficiency Obtained by Heating Eastern White Pine Specimens, 6 × 2 × 15/16 Inch, under Molten Metal at Different Temperatures for 2 Hours

above the desired point for temperatures below 270° C. (518° F.). The weight was rapidly lifted, the specimens were placed on the molten-metal surface, and the weight was put on them to immerse them in the molten metal. The wood specimens cooled the bath by about 2° C. and thus minimized the necessary manual adjustment of the burners. When the heating temperature was above 270° C. (518° F.) the exothermic reaction was sufficiently great so that one of the burners could be removed, slightly before or at the time the specimens were put into the bath, and not replaced for a period of 2 to 5 minutes. This agrees with the findings of Kobe and Goin (*4*) who found 273° C. (523° F.) to be the temperature at which exothermic decomposition of wood becomes appreciable.

The temperature control by this manual method was accurate to only 2–5° C. (3.6–9.0° F.). It was not suitable for long-period heating. For this reason the Sitka spruce veneer specimens and the larger eastern white pine specimens were electrically heated in a bomb with automatic temperature control. The bomb lid was designed to hold the specimens immersed. The molten metal could not be used for heating at temperatures below 175° C. (347° F.). Therefore, the veneer specimens were heated at 125° and 150° C. (257° and 302° F.) in sand with dry nitrogen slowly circulating through the sand to prevent oxidation. Veneer specimens were also heated in an electrically heated oven at 125°, 150°, and 175° C. (257°, 302°, and 347° F.) to determine the extent to which oxidation affects the results.

HYGROSCOPICITY AND DIMENSIONAL STABILITY

The heated specimens, when removed from the heating medium, were cooled in a desiccator, scraped free of any adhering metal, weighed, and measured. They were then subjected to relative humidity cycles in which they were successively brought to equilibrium with 90% and 30% relative humidity in rooms held at 26.7° C. (80° F.). Matched unheated controls went through the same relative humidity cycles and were then oven-dried to determine the weight at the conclusion of the measurements.

The western white pine cross-section specimens were all cut from a single flat-sawn board, 1 inch thick and $4^{3}/_{8}$ inches wide, into pieces $^{1}/_{2}$ inch in the fiber direction. Every seventh specimen was used as a control. The flat-sawn western white pine specimens were also cut from a single board, $^{13}/_{32}$ inch thick, into strips $1^{1}/_{4}$ inches wide in the tangential direction. The strips were cut into 6-inch lengths. All the specimens heated at a given temperature, together with two controls taken from the two ends, were cut from a single stick to assure optimum matching. The rotary-cut $^{1}/_{16}$-inch Sitka spruce veneer specimens were $5^{7}/_{8}$ inches long and 1 inch wide. They were similarly matched except that specimens 1, 6, 11, and 16, all cut from a single 1-inch-wide strip, were used as controls. The eastern white pine specimens were cut into 6-inch lengths from a single stick, 2 inches wide and $^{15}/_{16}$ inch thick. The two end specimens were used as controls.

The specimens were put through three complete relative humidity cycles of 90% to 30% to 90%, with the exception of the eastern white pine; sufficient time was allowed under each condition (about 2 weeks) for moisture equilibrium to be reached.

The percentage reduction in hygroscopicity and the percentage increase in the dimensional stability (antishrink efficiency) was calculated for each half cycle of 90 to 30% and 30 to 90% relative humidity. The percentage reduction in hygroscopicity is equal to 100 times the difference between the weight change of the control and the relative weight change of the heated specimen divided by weight change of the control. The percentage increase in the dimensional stability is equal to 100 times the difference between the dimension change of the control and the relative dimension change of the heated specimen, divided by the dimension change of the control. The percentage reduction in hygroscopicity and the antishrink efficiency are practically equal under the experimental conditions of this research. In view of this equality and inasmuch as the accuracy of weighing is greater

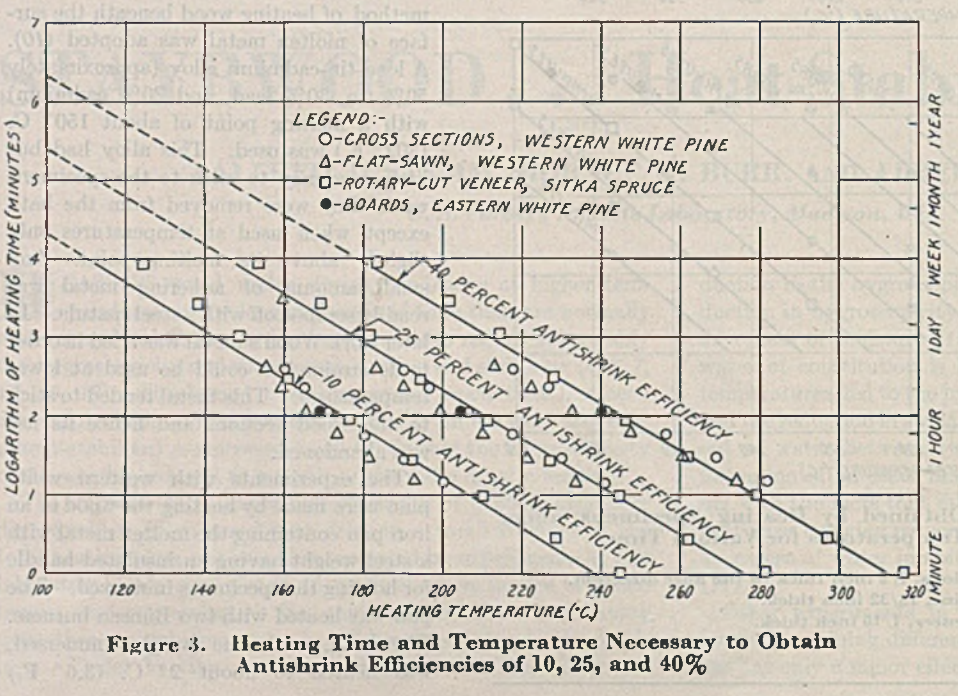

Figure 3. Heating Time and Temperature Necessary to Obtain Antishrink Efficiencies of 10, 25, and 40%

than that of measuring, the values recorded in this paper are actually the reduction in hygroscopicity as found by weighing, except for eastern white pine. In this case dimension changes between the water-soaked and the oven-dry condition were measured.

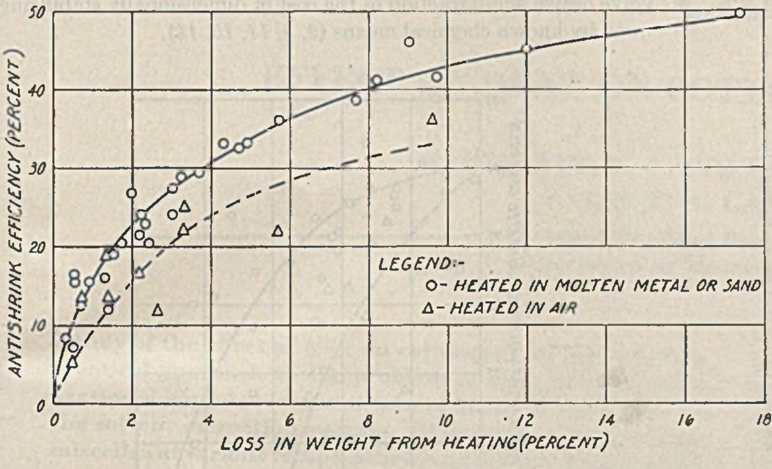

Figure 4. Antishrink Efficiency vs. Loss in Weight on Heating, for Rotary-Cut Sitka Spruce Veneer

Figure 1 gives the average antishrink efficiencies for the complete second and third cycles plotted against heating temperature for several different times of heating, obtained on western white pine cross sections and flat-sawn specimens and the rotary-cut Sitka spruce veneer. Figure 2 shows the antishrink efficiency values from a water-soaked to an oven-dry condition for the specimens of eastern white pine. These measurements were made on $^1/_8$-inch-thick cross sections cut from the ends of the larger specimens. An approximately linear relationship exists between the antishrink efficiency and the temperature for each time of heating, the lines becoming slightly steeper with increasing time.

When wood is heated at temperatures and for periods sufficient to give an appreciable antishrink efficiency, it is materially darkened. The light-colored softwoods used in these experiments darkened to about the color of walnut.

Theoretically, for the minimum heating times used in these experiments (15 minutes for the $^1/_2$-inch and $^{13}/_{32}$-inch western white pine and 1 minute for the $^1/_{16}$-inch Sitka spruce veneer) the temperature rise at the center of the wood is at least 95% of that at the surface in a fraction of the total time. Practically, uniform antishrink efficiencies should result throughout the thickness of the wood, even in these short heating times.

Figure 3 shows the data of Figures 1 and 2 plotted as the logarithm of heating time against the heating temperature necessary to obtain three different antishrink efficiencies. The slope of the lines is such that the reaction rate practically doubles for each rise in temperature of 10° C. (18° F.).

Figure 4 shows the relationship between the antishrink efficiency and the loss in weight caused by heating, for the data of Figure 1 on Sitka spruce veneer. The loss in weight per unit antishrink efficiency obtained is greater when the wood is heated in air than in the molten metal. Evidently a greater degree of oxidation occurs in air; this contributes less, if at all, to the antishrink efficiency than the postulated ether-linkage formation.

Figure 5 gives the relationship between toughness and antishrink efficiency of the flat-sawn western white pine specimens in equilibrium with 30% relative humidity. The measurements were made on the Forest Products Laboratory toughness machine (*1*), using a 4-inch span. The toughness values are for the actual cross section of the specimens corrected, for the slight variation in thickness and width, to an area of 0.53 square inch by considering the toughness directly proportional to the cross-sectional area. As expected, the toughness of the wood was appreciably decreased by the heat treatment. The reduction in toughness of wood on heating is not attributable to the reduced moisture content at test which results from the reduced hygroscopicity of the wood. The variation in toughness of wood with changes in moisture content is small compared to the loss in toughness obtained on heating. The loss in toughness must thus be due to embrittlement of the fiber itself.

Figure 6 shows the relationship between the face hardness and antishrink efficiency of the eastern white pine specimens as determined by the A.S.T.M. method, in which the load required to embed a 0.444-inch diameter ball to half its diameter is measured. The specimens were preconditioned at 65% relative humidity. The hardness is reduced significantly at the higher degrees of heating, but not so much as the toughness.

Figure 7 shows the relationship between the antishrink efficiency of spruce veneer and the modulus of rupture in equilibrium with 30% relative humidity. The measurements were made on a cantilever-beam stiffness tester (*3*, *17*). The veneer heated in the molten metal showed a much smaller decrease in modulus with increase in antishrink efficiency than did the veneer heated in air.

The modulus of elasticity is also decreased by the heating process, but to an appreciably lesser degree than the modulus of rupture. Heating in air again causes a greater loss in strength than does heating beneath the surface of molten metal. It is thus of considerable importance to heat wood in the absence of air in any commercial operation aimed at stabilizing wood for uses in which moderate strength is important.

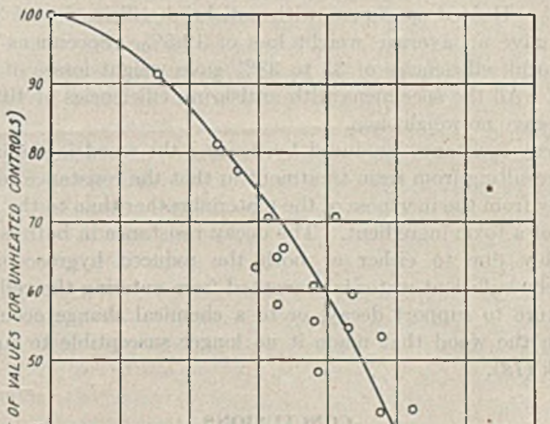

Figure 5. Toughness vs. Antishrink Efficiency Obtained by Heating Flat-Sawn Western White Pine Specimens as Indicated in Figure 1

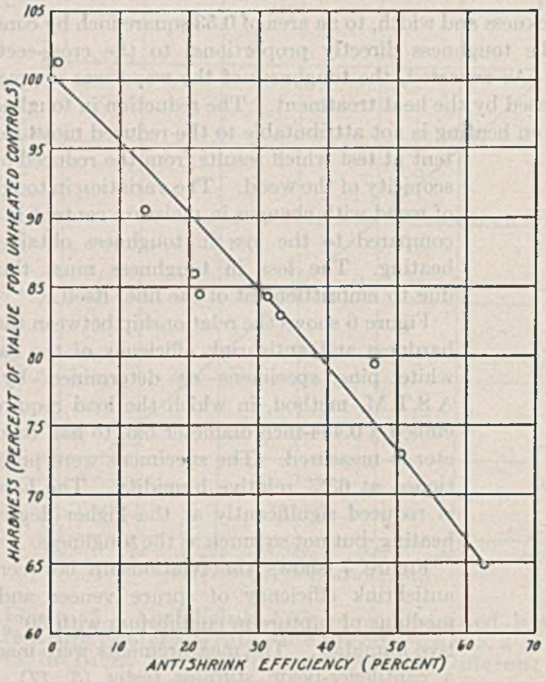

Figure 6. Hardness *vs.* Antishrink Efficiency Obtained by Heating Eastern White Pine Specimens as Indicated in Figure 2

A few preliminary pure-culture decay tests were made on the flat-sawn western white pine specimens. Both the heated specimens and controls were cut into 2-inch lengths, oven-dried, weighed, and placed in jars containing a good growth of the wood-destroying fungus, *Trametes serialis.* The jars were held under favorable growth conditions for 2 months. The fungus grew over the surface of all the specimens. This growth was carefully removed and the specimens were again oven-dried and weighed. The controls sustained an average weight loss of 28.4%. Heated specimens with antishrink efficiencies of 30 to 33% gave an average weight loss of 12.5%. Specimens with antishrink efficiencies of 33 to 38% gave weight losses of 0 to 4.5%. All the specimens with antishrink efficiencies of 40% or more gave no weight loss.

Decay resistance produced by heating the wood is similar to that resulting from resin treatment in that the resistance results largely from the inertness of the material rather than to the presence of a toxic ingredient. The decay resistance in both is presumably due to either or both the reduced hygroscopicity, whereby sufficient water is prevented from entering the cell-wall structure to support decay, or to a chemical change occurring within the wood that made it no longer susceptible to fungus attack (*12*).

CONCLUSIONS

It appears feasible to impart an appreciable degree of stabilization of dimensions and decay resistance to wood commercially by means of a simple heat treatment which materially reduces the hygroscopicity. Such a heat treatment causes a loss in strength properties varying from a rather large loss in toughness to a small loss in modulus of elasticity in bending. It appears that the practical limitations on the degree of dimensional stabilization obtainable will, in large measure, be controlled by the acceptable loss in toughness. In general, it is felt that an antishrink efficiency of 40 to 50% is as high as is practical. Under these conditions the toughness is less than half that of the original wood, according to data thus far obtained.

In the strength properties tested, the loss in strength per unit antishrink efficiency obtained is greater when the wood is heated in the presence of air than when air is excluded by heating under a molten metal. This suggests that lumber might be fed through a trough of electrically heated molten metal under a series of rollers to convey it through the trough. The process could be made rapid for half-inch or thinner stock, and need not be prohibitively long for 1-inch or somewhat thicker stock (*11*). If the trough were well insulated, the energy consumption would involve only a small fraction of the cost of dimensionally stabilizing wood by known chemical means (*2, 9, 11, 13, 14*).

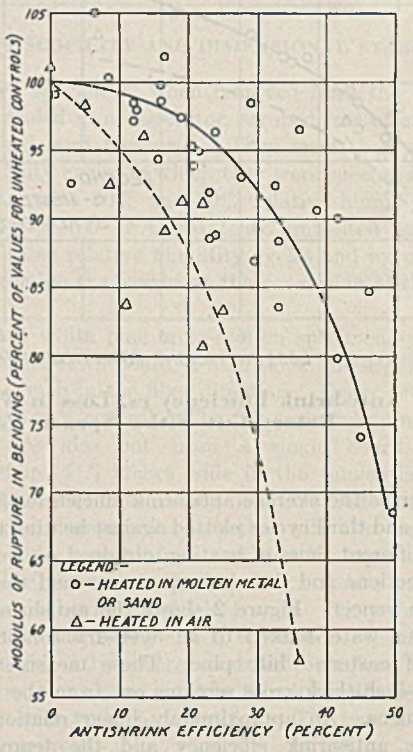

Figure 7. Modulus of Rupture in Bending *vs.* Antishrink Efficiency Obtained by Heating Rotary-Cut Sitka Spruce Veneer Specimens as Indicated in Figure 1

Before any large-scale tests are undertaken, further work should be done to determine the abrasion resistance and other strength properties and also the gluing and painting qualities of heat-stabilized wood. Additional species should also be studied.

LITERATURE CITED

(1) Forest Products Lab., *Rept.* 1308 (1941).
(2) *Ibid.*, R1277 (1943).
(3) Jungmann, E. C., Turner, H. D., and Burr, H. K., *Ibid.*, 1388 (1944).
(4) Kobe, K. A., and Goin, T. L., Ind. Eng. Chem., 31, 1171 (1939).
(5) Koehler, A., and Pillow, M. Y., *Southern Lumberman*, Dec. 19, 1925, 219.
(6) Merritt, R. W., and White, A. A., Ind. Eng. Chem., 35, 297 (1943).
(7) Pillow, M. Y., *Wood Working Ind.*, Oct., 1929, 8.
(8) Seborg, R. M., Millett, M. A., and Stamm, A. J., *Mech. Eng.*, 67, 25 (1945).
(9) Stamm, A. J., Ind. Eng. Chem., 29, 833 (1937).
(10) Stamm, A. J., U. S. Patent 2,296,316 (1942).
(11) Stamm, A. J., and Hansen, L. A., Ind. Eng. Chem., 27, 1480 (1935).
(12) *Ibid.*, 29, 831 (1937).
(13) Stamm, A. J., and Seborg, R. M., *Ibid.*, 31, 897 (1939).
(14) Stamm, A. J., and Seborg, R. M., *Trans. Am. Inst. Chem. Engrs.*, 37, 385 (1941).
(15) Staudinger, H., *Trans. Faraday Soc.*, 32, 323 (1936).
(16) Tiemann, H. D., *Lumber World Rev.*, 28 (7), 10 (1915).
(17) Tinius Olsen Testing Machine Co., *Bull.* 11.

Solvent Extraction of Cottonseed and Peanut Oil

EFFECT OF HEAT ON COTTONSEED OIL MISCELLAS

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Study of the effect of heat on cottonseed oil miscella in a practical approach to the problem of objectionable color fixation during heating and solvent removal operations in the solvent extraction process. Heating of cottonseed oil miscellas at various temperatures and definite time periods under appropriate reduced pressures was carried out to determine the effect of heat on the resulting refined and bleached oils. Color fixation became objectionable between 150° and 180° F., and beyond 180° increased rapidly. Properly prepared solvent-extracted cottonseed oils from a prime lot of seed were successfully refined by slightly modified official A.O.C.S. refining methods which yielded oils of prime quality with low refining losses. The finished oils were equal in quality to high-grade hydraulic-pressed oils. Results have yielded necessary engineering information useful for design and operation of pilot plant equipment and for processing operations. Absorption spectra curves ranging through the visible and ultraviolet are reproduced as examples of applicability of this technique for studying solvent-extracted cottonseed oils.

MANY attempts have been made in the United States to apply the solvent extraction process to cottonseed. There is considerable activity in this field at present, but only a few publications have appeared (*7, 8*). The early commercial efforts (*16, 18, 19*) to produce an industrially useful oil from cottonseed by solvent extraction were abandoned largely because of the dark color of the resulting oil.

Cottonseed pigments, such as gossypol and related substances, extracted with the oil from the cottonseed flakes or meal by organic solvents, impart to the miscella its characteristic color (*1–5, 7, 9, 10*). It is claimed that an aliphatic hydrocarbon such as hexane dissolves only a small portion of gossypol present in uncooked flakes or meal (*4, 7, 9*). Some investigators report (*6; 9, 11, 12, 15*) that the gossypol content of cottonseed oil reduces the alkali refining loss. Podol'skaya and Tobler (*12*) claim that with increasing gossypol concentration the color of the oil is greatly intensified; similar color effect is produced on the resulting soapstock.

The effect of temperature on color fixation during solvent removal has already been investigated. It was pointed out (*9*) that high temperatures must be avoided to prevent color fixation in the final oil. Rosenthal (*14*) reports that cottonseed oil miscella from liquefied butane or propane extraction of cottonseed meats, when filtered and solvent-removed at temperatures not exceeding 210° F. under vacuum, produces a cooking oil of prime quality or lighter after the usual refining procedure with caustic. Thurman (*17*) claims that color fixation occurs in crude cottonseed oil if heated to 300° F., which prohibits bleaching by fuller's earth or by other methods ordinarily employed. No systematic investigation, however, has been reported on the effect of such variables as temperature and time of heating during solvent removal on color fixation and quality.

The work here described was undertaken primarily to obtain engineering information required for the design and operation of equipment and for processes in solvent extraction installations; it is a practical effort to evaluate the effect of temperature and time of heating during processing operations upon the fixation of objectionable coloring matter in miscella obtained by extraction of uncooked cottonseed flakes with commercial hexane. The results reported were obtained from work on one lot of prime cottonseed. Further work is necessary on miscella from seeds not only of different varieties but also in different stages of deterioration. Cottonseed oil miscellas were heated over a range of temperatures from 140° to 240° F. during definite heating intervals under appropriate reduced pressures. The temperatures and reduced pressures needed for concentrating and removing solvent from the miscellas were obtained from the boiling point curves established in the first paper of this series (*13*). The properly prepared solvent-extracted oils from the prime lot of cottonseed were refined by slightly modified official American Oil Chemists' Society (A.O.C.S.) refining methods, which yielded oils equal in quality to high-grade hydraulic-pressed oils. Because of the differences in the characteristics of solvent-extracted cottonseed oil and of hydraulic-pressed oil, it is apparent that additional refining studies are necessary.

The present investigation falls into three series of experiments: (1) preliminary heating and refining; (2) refining experiments, growing out of the preliminary series, for the purpose of determining the most advantageous preparatory procedures; and (3) a systematic study of the effect of heat on solvent-extracted cottonseed oil. The conditions required for the third series were established from results of the other two.

PREPARATION OF MISCELLA

A prime lot of East Texas cottonseed was carefully cleaned, delinted, hulled, and flaked in pilot plant processing equipment. Percentage analyses of the seed and flakes follow:

	Moisture (Original)	Lipides (As-Is Basis)	Nitrogen (As-Is Basis)
Seed	9.75	19.12	3.27
Flakes	7.47	32.90	5.12

The average thickness of the flakes was 0.010 to 0.014 inch; the oil from the flakes had a free fatty acid content of 1.2% and an iodine value of 105.6.

The solvent for the extraction was a commercial hexane (Skellysolve B) with the following specifications: gravity at

60° F., 74.4° A.P.I.; boiling range, 140–160° F.; Reid vapor pressure at 100° F., 5.1 pounds per square inch; evaporation residue by weight, 0.0016%; and color, water-white. The reasons for choosing this solvent were its negligible tendency to rupture pigment glands during normal extraction periods (*4*), its negligible solvent action for extracting coloring matter from hulls, its low cost, and its general use in industrial solvent extraction installations.

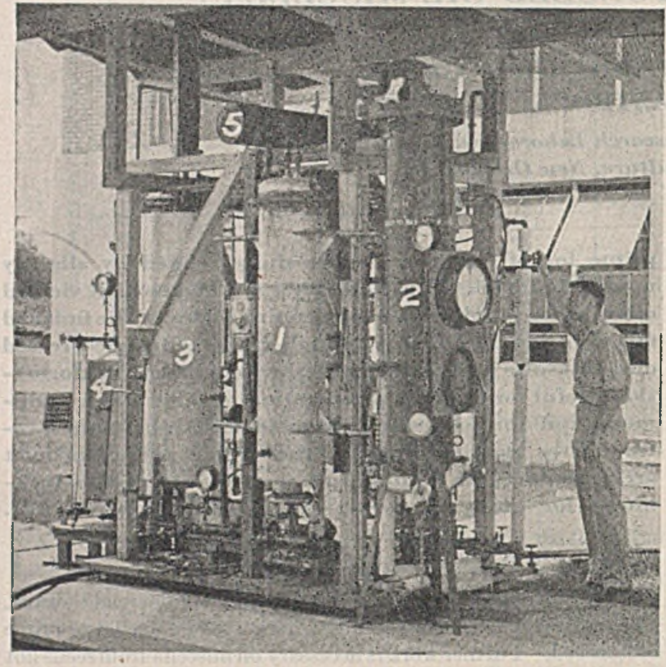

Figure 1. Pilot Plant Batch Extraction Unit

1. Extractor, 120-pound capacity
2. Evaporator
3. Solvent storage tank
4. Solvent condensate tank
5. Condensers

A single-cell extractor (Figure 1), of 120-pound capacity and with necessary auxiliaries, was used in the extraction and concentration of the miscella. A sufficient quantity of flaked meats was prepared, and extraction was started immediately to minimize any increase in the free fatty acid of the extracted oil. The solvent, at 70° F., was pumped in an upward path through the extractor at a rate of 1.5 pounds of solvent per pound of flakes per hour for a total extraction time of 4.5 hours. An oil extraction efficiency of 98% was attained. During extraction, solvent was distilled from the miscella in the evaporator under a reduced pressure of 20 inches of vacuum, at a temperature not exceeding 105° F. The liquid level of the miscella in the evaporator was maintained above the heating coil to prevent the possibility of overheating the oil film during concentration. At intervals of 1.5 hours the partly concentrated miscella (30–40% oil by weight) was drained from the evaporator to prevent excessive heating. Approximately 20 gallons of dilute miscella were collected from each extraction, and at the end of the extraction period the miscella was concentrated in the evaporator in 1.5 hours under 24 inches of vacuum until the boiling temperature reached 120° F. Thus approximately 6 gallons of miscella containing 90% oil by weight were obtained from each extraction. This concentrated miscella was filtered to remove any meal particles, as these have a tendency to increase the free fatty acid of the oil upon aging. Free fatty acid values averaged 1.4–1.5% for properly prepared miscellas. A mixture of miscella from several extractions as described above constituted a batch of miscella for each of the three series of experiments.

The experimental work to determine the effect of each set of heating conditions consisted of the following steps: heating the miscella (exclusive of control runs); stripping the solvent from heat-treated miscella; de-emulsifying the stripped oil; and refining, bleaching, and color determinations on the oil.

HEATING PROCEDURE IN SERIES 3

The method consisted essentially of heating the miscella (90% oil by weight) to the desired temperature for a required time interval in the equipment described in previous work (*13*). This temperature was maintained by boiling the miscella under controlled reduced pressure and total reflux for the specified period. At completion of the heating period the miscella was immediately removed from the boiler and cooled to room temperature in an ice bath. Table I shows operating data for series 3 conducted at 150°, 180°, 210°, and 240° F. for $\frac{1}{4}$, 1, and 3 hours; Figure 2 gives the time-temperature curves for representative experiments (5, 8, 11, and 15, Table I). These curves show the time required for heating to desired temperatures, the periods of heating, and the time required for cooling.

LOW-TEMPERATURE STEAM STRIPPING

The solvent was removed from the concentrated and heat-treated miscellas by low-temperature steam stripping under reduced pressure in a column 36 inches high and $3\frac{5}{8}$ inches in diameter, packed with $\frac{3}{8}$-inch Raschig rings. A low temperature was chosen for this work to prevent color fixation of the oil. Figure 3 shows the column and its auxiliary equipment. Water at 4° C. was recirculated through the condensers of the system. The pressure in the system was reduced to 65 mm. (absolute), and the column heated to 105–110° F. with steam introduced at the bottom before the miscella was fed. The miscella feed preheated to 110° F. was introduced at a point 6 inches below the top of the column at an average rate of 30 ml. per minute. All

Table I. Operating Data for Heating Cottonseed Oil Miscella, Series 3

Expt. No.[a]	Time for Heating Oil from Room Temp. (80° F.), Min.	Heating Temp., ° F.	Heating Time, Hr.	Time to Cool to Room Temp., Min.	Temp. Difference between Oil Bath & Boiler, ° F.	Abs. Pressure, Mm.		Miscella			
								Volume, ml.		Sp. gr.[b] after heating, g./cc.	% oil by wt. after heating[c]
						Atmospheric	In system	Before heating	After heating		
3	40	150	$\frac{1}{4}$	25	45	761	217	3300	3110	0.8890	92.0
4	40	150	1	25	38	766	216	3300	3120	0.8890	92.0
5	40	150	3	25	27	766	216	3000	2820	0.8925	93.2
6	50	180	$\frac{1}{4}$	30	36	765	368	3000	2890	0.8893	92.1
7	50	180	1	30	38	762	363	3000	2900	0.8885	91.9
8	50	180	3	30	32	761	357	3000	2865	0.8920	93.0
9	60	210	$\frac{1}{4}$	30	27	763	586	3000	2870	0.8898	92.4
10	60	210	1	30	27	758	587	3000	2860	0.8898	92.4
11	60	210	3	30	29	759	590	3000	2865	0.8825	91.5
12	70	240	0	30	36	763	763	3300	3120	0.8932	93.3
13	70	240	$\frac{1}{4}$	30	31	764	764	3000	2870	0.8910	92.7
14	70	240	1	30	32	763	763	3000	2840	0.8915	92.8
15	70	240	3	30	32	762	762	3000	2855	0.8910	92.7

[a] Experiments 1 and 2 were controls: de-emulsification by vacuum drying and de-emulsification by centrifuging.
[b] Specific gravity before heating was 0.8856.
[c] % oil by weight before heating was 90.7.

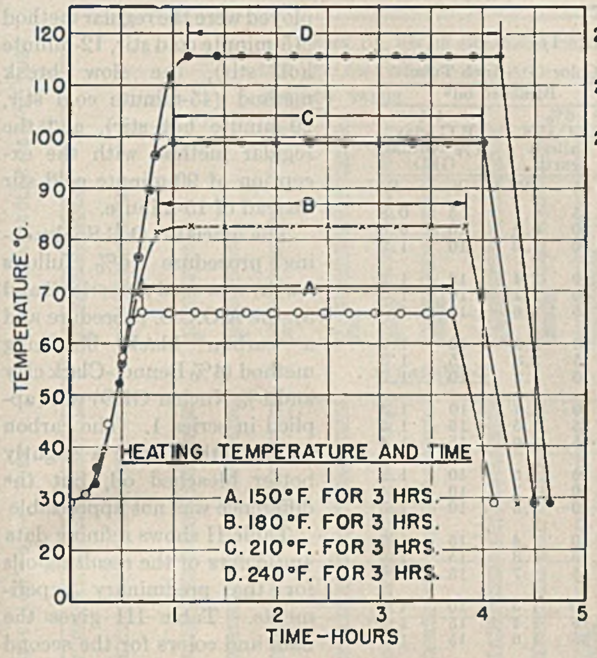

Figure 2. Time-Temperature Curves for Heating Crude Cottonseed Oil Miscella (90.7% Oil by Weight)

miscellas were stripped so that at no point in the apparatus was the oil hotter than 110° F. At this temperature the condensation of steam which takes place results in a partial oil-water emulsion, containing about 20 parts oil to 1 part water, which was collected in a jacketed flask at the bottom of the column.

DE-EMULSIFICATION OF STRIPPED OIL

Three methods of breaking the oil-water emulsion formed during the stripping operation were investigated—salting out, centrifugation, and vacuum drying.

For the salting-out procedure, a saturated solution of sodium chloride proved most satisfactory, after trials with several different salts and concentrations. The salt solution was added to the oil-water mixture in a separatory funnel, thoroughly shaken, and allowed to stand overnight. The consistent appearance of soft foots during refining of the resulting oil indicated that other methods of breaking the emulsion might prove more advantageous.

For the centrifugation method of breaking the emulsion, a laboratory supercentrifuge was used. The bowl had an inside diameter of 1.75 inches and rotated at 48,000 r.p.m.

Vacuum drying was accomplished in the heating apparatus (*13*) by applying a reduced pressure of 20 mm. (absolute) to the system and then heating the oil-water mixture to 110° F. The temperature was gradually increased to 125° F. and the pressure to 60 mm. (absolute) to minimize excessive foaming. A volume of 1200 ml. of stripped oil required approximately 1 hour to remove 60 ml. of water; the resulting oil contained only 0.1 to 0.2% moisture.

For salted-out oils the average moisture content was 0.28%. Some centrifuged oils contained 0.34% moisture, though in subsequent samples it was less than 0.1%. The moisture content for vacuum-dried oils averaged 0.15%. The oils de-emulsified by all three methods had a specific gravity of 0.9112–0.9116 (Westphal balance), indicating for practical purposes a 100% oil.

All three de-emulsification methods were applied to the second series of experiments (refining and de-emulsification); salting-out alone was used for the first (preliminary) series; and vacuum drying for the third series (heating experiments).

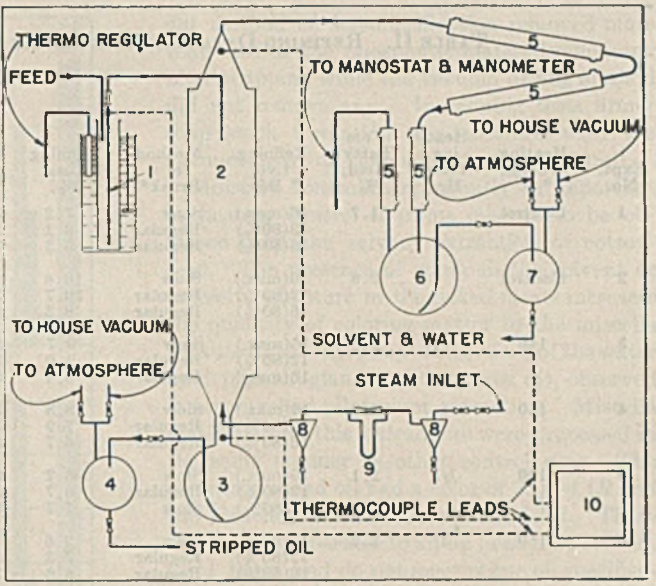

Figure 3. Apparatus for Stripping Cottonseed Oil Miscella under Reduced Pressures

1. Miscella feed with constant temperature controlled bath (2000 ml.)
2. Jacketed stripping column
3. Jacketed flask for collecting stripped oil (5000 ml.)
4. Trap flask for stripped oil from 3 (1000 ml.)
5. Solvent and water condensers
6. Ice-jacketed flask for collecting condensate (5000 ml.)
7. Trap flask for condensate from 6 (1000 ml.)
8. Steam traps
9. Venturi and manometer
10. Recording potentiometer

REFINING, BLEACHING, AND COLOR DETERMINATION

The refining methods applied to the solvent-extracted cottonseed oil were modifications of the official A.O.C.S. methods for hydraulic pressed oils. Shrader (*16*) suggested that modified methods of refining benzene-extracted cottonseed oil were necessary; and Olcott (*9*) indicated that refining methods now used for hydraulic oils would undoubtedly have to be modified for solvent-extracted cottonseed oils, partly because of the presence of gossypol which is said to be beneficial to soap stock formation.

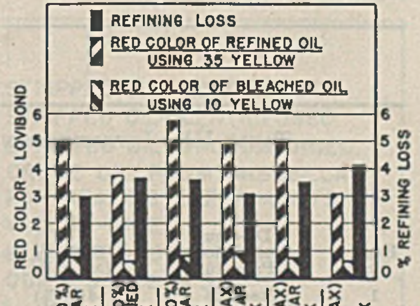

Figure 4. Investigation of Refining Loss Method

Although in this study the amount of alkali added to the crude solvent-extracted oil was the amount specified for hydraulic oils by the official A.O.C.S. method, the concentrations of the alkali and the methods of break in the present procedure were varied: that is, when the official method called for a 14° (80%) lye for a 1.4% free fatty acid oil, in the modified procedure the various concentrations of alkalies used were calculated to contain solid sodium hydroxide equivalent to the solid sodium hydroxide content of the 14° (80%) lye. The following lye concentrations were investigated: 12° (80%), 14° (80%), 16° (80%), 14° (maximum), and 16° (maximum); the methods of break employed were the regular method (15-minute cold stir, 12-minute hot stir), the slow break method (45-minute cold stir, 20-minute hot stir), and the regular method with the exception of 90-minute cold stir instead of 15-minute.

The official A.O.C.S. bleaching procedure (6% fuller's earth) was used for series 2 and 3; the A.O.C.S. procedure and a carbon black bleaching method (4% Bennet-Clark clay and 1% Nuchar GFO) were applied in series 1. The carbon black method gave a slightly better bleached oil, but the difference was not appreciable

Table II shows refining data and colors of the resulting oils for the preliminary experiments. Table III gives the data and colors for the second series of refining studies in which the oil-water mixtures were de-emulsified by salting out, vacuum drying, and centrifuging. Figure 4 is a bar graph of the data given in Table III; the colors and refining losses shown are the average values of the three different de-emulsified oils for each refining method employed. This graph indicates that 14° (80%) lye and 16° (maximum) lye are preferred to the 12° (80%) lye, and that the regular refining method with the 90-minute cold stirring period gives better refining results than either the straight regular break or the slow break method.

Table II. Refining Data for Preliminary Work (Series 1)

Expt. No.	Heating Temp., ° F.	Heating Time, Hr.	Free Fatty Acid, %	Refining Lye, ° Bé.	Method of Break[a]	Refining Loss, %	Lovibond Color (5¼-Inch Tube)					
							Refined oil		Bleached oil[b]			
									6% A.O.C.S. fuller's earth		4% B.C. clay, 1% Nuchar GFO	
							Y	R	Y	R	Y	R
1	Control		1.7	16(max.)	Slow	7.2	35	4.4	5	0.7	5	0.8
				12(80%)	Regular	6.1	35	5.7	10	0.9	10	0.8
				16(80%)	Regular	5.3	35	4.7	10	1.2	10	1.2
2	Control		2.8	16(max.)	Slow	10.6	35	5.1	10	1.4	10	1.2
				12(80%)	Regular	10.7	35	6.8	10	1.2	10	1.3
				16(80%)	Regular	8.3	35	5.9	15	1.6	15	1.5
3	140	¼	2.3	16(max.)	Slow	9.7	35	5.1	10	1.2	10	1.2
				12(80%)	Regular	9.0	35	6.1	15	1.3	15	1.3
				16(max.)	Regular	8.4	35	5.0	10	1.2	10	1.2
4	140	1	2.2	16(max.)	Slow	8.8	35	5.2	10	1.4	10	1.3
				12(80%)	Regular	7.9	35	6.7	15	1.5	15	1.5
				16(80%)	Regular	6.7	35	6.1	15	1.6	15	1.4
5	160	¼	2.1	16(max.)	Slow	8.2	35	4.9	10	1.6	10	1.2
				12(80%)	Regular	6.7	35	6.8	10	1.3	10	1.4
				12(80%)	Slow	7.7	35	5.9	10	1.5	10	1.3
6	160	1	2.2	16(max.)	Slow	8.6	35	5.1	10	1.4	15	1.3
				12(80%)	Regular	7.3	35	7.8	15	1.3	15	1.4
				16(80%)	Regular	6.6	35	6.7	15	1.7	15	1.6
7	180	¼	2.2	16(max.)	Slow	8.6	35	5.1	10	1.3	10	1.2
				12(80%)	Regular	7.4	35	6.7	15	1.4	15	1.4
				16(80%)	Regular	6.4	35	5.6	15	1.6	15	1.5
8	180	1	2.3	16(max.)	Slow	9.1	35	6.0	15	1.8	20	1.8
				12(80%)	Regular	8.7	35	8.1	20	2.0	20	2.3
				16(max.)	Regular	8.1	35	6.2	15	1.8	20	2.0
9[c]	180	1	2.1	16(max.)	Slow	8.5	35	5.8	10	1.9	15	1.8
				12(80%)	Regular	8.7	35	7.7	20	1.9	20	2.0
				16(80%)	Regular	7.2	35	7.0	20	2.3	20	2.3
10[c]	180	3	2.1	16(max.)	Slow	8.4	35	6.2	15	2.1	20	2.0
				12(80%)	Regular	7.3	35	8.5	20	2.3	20	2.3
				16(max.)	Regular	6.9	35	7.3	20	2.1	20	2.3
11	210	1	2.2	16(max.)	Slow	8.1	35	7.0	20	2.3		
				12(80%)	Regular	6.5	35	9.5	20	3.1		
				26[d]	Regular	8.3	35	6.0	20	1.8		
12	240	1	2.1	16(max.)	Slow	8.4	35	10.3	35	4.8		
				12(80%)	Regular	6.7	35	16.7	35	6.2		
				26[d]	Regular	10.6	35	8.4	35	3.3		
13	240	3	2.1	16(max.)	Slow	9.6	35	20.3	35	11.3		
				12(80%)	Regular	7.8	35	30.9	35	14.8		
				26[d]	Regular	11.8	35	12.0	35	7.0		

[a] Firm soap stock formed, except for a precipitate-like material suspended over the firm layer; one or two remelts were required for total firm foots.

[b] 200-gram samples handled according to official A.O.C.S. methods.

[c] 50 grams of iron filings added to miscella prior to heating had no effect on color of resulting refined and bleached oil.

[d] Weight of 26° lye calculated to contain solid NaOH equivalent to solid NaOH content of 16° maximum lye required.

Table III. Investigation of Modified Refining Methods for Solvent-Extracted Cottonseed Oils (1.4% Free Fatty Acid Content), Series 2

Expt. No.	De-emulsification Procedure	Refining Lye, ° Bé.	Method of Break	Refining Loss, %	Type of Soap Stock Formed[a]	Lovibond Color (5.25-In. Tube)			
						Refined oil		Bleached oil, 6% A.O.C.S. fuller's earth	
						Y	R	Y	R
1	Salted-out	14(80%)	Regular	2.8	Very small suspended layer over firm layer	35	5.5	10	0.8
	Vacuum-dried	14(80%)	Regular	3.0	Single firm layer	35	5.9	10	0.9
	Centrifuged	14(80%)	Regular	3.0		35	5.7	10	0.8
2	Salted-out	12(80%)	Regular	2.9	Fair sized suspended layer over firm layer	35	4.7	10	0.7
	Vacuum-dried	12(80%)	Regular	3.1	Very small suspended layer over firm layer	35	5.2	10	0.8
	Centrifuged	12(80%)	Regular	2.9		35	4.8	10	0.7
3	Salted-out	12(80%)	Regular[b]	3.7	Small suspended layer over firm layer	35	3.6	10	0.6
	Vacuum-dried	12(80%)	Regular[b]	3.7	Single firm layer	35	3.9	10	0.7
	Centrifuged	12(80%)	Regular[b]	3.7		35	3.9	10	0.6
4	Salted-out	16(max.)	Regular	3.5	Small suspended layer over firm layer	35	4.6	10	0.7
	Vacuum-dried	16(max.)	Regular	3.4	Single firm layer	35	5.1	10	0.7
	Centrifuged	16(max.)	Regular	3.6		35	4.8	10	0.6
5	Salted-out	16(max.)	Slow	3.9	Small suspended layer over firm layer	35	3.1	10	0.4
	Vacuum-dried	16(max.)	Slow	4.0		35	3.2	10	0.5
	Centrifuged	16(max.)	Slow	4.4		35	3.1	10	0.5
6	Salted-out	14(max.)	Regular	3.1	Small suspended layer over firm layer	35	5.0	10	0.8
	Vacuum-dried	14(max.)	Regular	3.0	Very small suspended layer over firm layer	35	4.9	10	0.9
	Centrifuged	14(max.)	Regular	3.7	Single firm layer	35	4.8	10	0.8

[a] All soap stock contained large quantities of orange pigment which rapidly became purple on exposure to sunlight.

[b] Regular refining procedure modified by stirring 90 minutes in cold bath following addition of alkali.

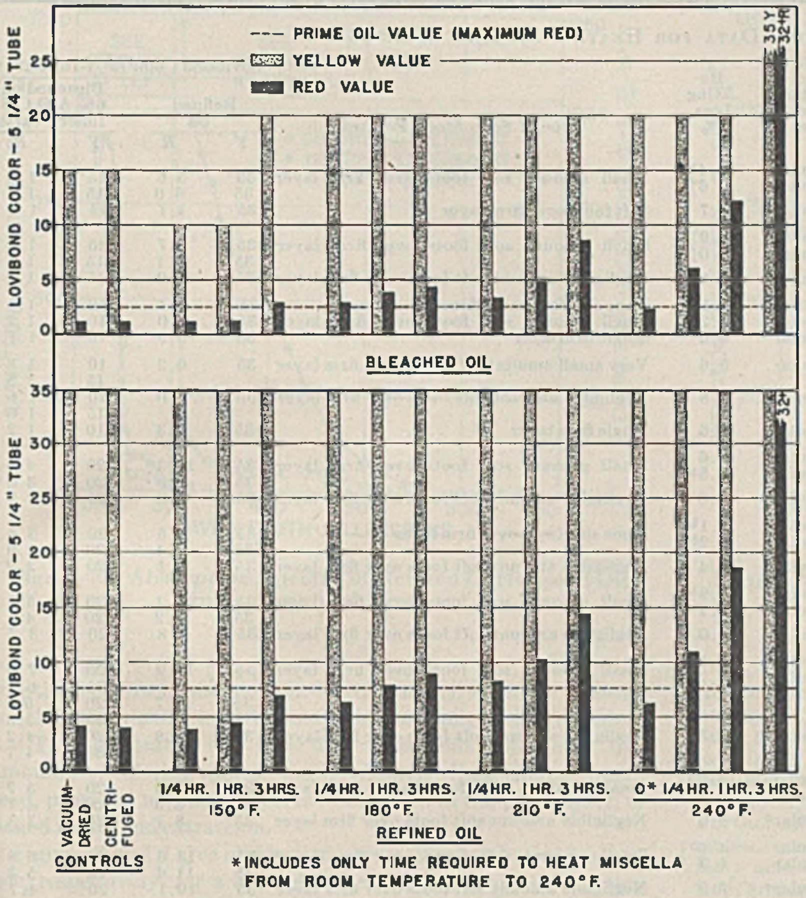

Figure 5. Effect of Heat on Color of Refined and Bleached Solvent-Extracted Cottonseed Oil

Table IV shows the refining data and colors of the resulting oils for series 3, for which operational data are recorded in Table I. The concentrations of alkali and methods of break were based on information obtained from series 1 and 2. These data illustrate that the colors of both refined and bleached oils increase from the control run to the oil sample heat-treated at 240° F., the rise being gradual at low temperatures and very rapid at higher temperatures. A substantial increase in color is likewise noted when the time of heating for each temperature is increased from 15 minutes to 3 hours. These results are shown more vividly in a bar graph (Figure 5) in which the 16° (maximum) lye samples, regular break with 90-minute cold stirring, were plotted. The critical temperatures and periods of heating at which objectionable color fixation takes place, to the extent that the oil no longer meets prime oil specifications, are around 180° F. for 1 hour and 210° for 15 minutes. The sample heated at 150° F. for 3 hours gave a refined oil that approaches the limits of a prime oil, and a bleached oil that is slightly past the prime stage.

Refining data on the hydraulic-pressed oils from the same lot of prime cottonseed used for the solvent extraction are given in Table V. The hydraulic-pressed oils were refined and bleached according to the official A.O.C.S. methods. The refining losses of the hydraulic-pressed oils are comparable to all refining losses of solvent-extracted oils, in both the control runs and the heating experiments; the colors of the refined and bleached hydraulic-pressed oils are comparable to the colors of the solvent-extraction control runs and heating experiments at 150° F. up to 1 hour.

Phosphorus determinations of various solvent-extracted cottonseed oils indicated that heating had no quantitative effect upon the amount of the phosphatic material present; that stripping of the miscella with steam under reduced pressure removed approximately half of the phosphatic material; and that the salting-out method of de-emulsification removed more than half of the phosphatic material remaining after stripping while the vacuum drying method did not remove any. In refining tests firmer soap stock formation was obtained with the vacuum-dried oil than with the salted-out oil.

Moisture control is apparently as important as heating control if prime oils are to be obtained from the solvent extraction of cottonseed. The presence of water in the solvent or excessive moisture in the flaked meats increases the quantity of coloring matter in the miscella because of the rapid rupturing effect of the water upon pigment glands in cottonseed (*4*), observed in a controlled pilot-plant extraction. Miscella and oil from this extraction were processed in the same manner as other control runs. The resulting refined oil had a color of 35*Y*–8.1*R* and the bleached oil a color of 15*Y*–3.5*R*. These colors are comparable to an oil heated at 180° F. for 1 hour, and do not meet prime oil specifications. It is probable that any heating of this oil would result in rapid and excessive color fixation.

Excess moisture in a crude de-emulsified solvent-extracted cottonseed oil increases the free fatty acid appreciably, as shown by data obtained after 31 days of aging:

Sample No.	Moisture, %	Free Fatty Acid, %	
		Original	After 31-day "aging"
1	0.11	1.43	1.47
2	0.28	1.40	1.62
3	0.34	1.40	2.21

The effect of aging on the free fatty acid content of a carefully prepared miscella is considered negligible. This is shown in an experiment where the free fatty acid of a sample (90% oil by weight) increased from 1.41 to 1.47% in 58 days. The effect of aging on color of bleached oils from heat-treated runs was noted as follows: A bleached oil with an original color of 10*Y*–1.3*R*

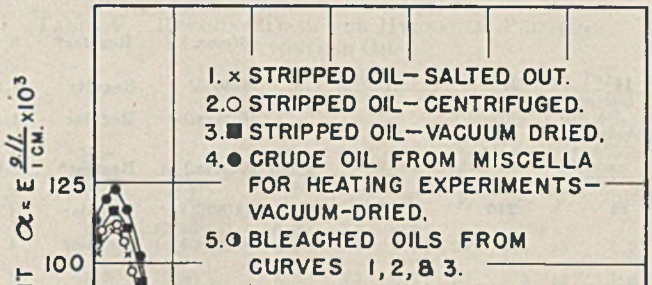

Figure 6. Absorption Spectra of Crude Solvent-Extracted Cottonseed Oil (in Commercial Hexane)

Table IV. Refining Data for Heating Studies, Series 3

Expt. No.	Heating Temp., ° F.	Heating Time, Hr.	Free Fatty Acid, %	Refining Lye, ° Bé.	Method of Break	Refining Loss, %	Type of Soap Stock Formed	Lovibond Color (5¹/₄-In. Tube): Refined oil, Y	Refined oil, R	Bleached oil, 6% A.O.C.S. fuller's earth, Y	Bleached oil, R
1	Control, vacuum-dried		1.5	14(80%)	Regular	4.4	Small amount soft foots over firm layer	35	5.6	15	1.8
				16(max.)	Regular	4.6		35	5.0	15	1.4
				16(max.)	Regular^a	4.7	Soft foots over firm layer	35	4.1	15	1.2
2	Control, centrifuged		1.4	14(80%)	Regular	3.9	Small amount soft foots over firm layer	35	5.7	15	1.9
				16(max.)	Regular	4.0		35	5.1	15	1.5
				16(max.)	Regular^a	5.2	Negligible amount soft foots over firm layer	35	4.0	15	1.2
3	150	¹/₄	1.5	14(80%)	Regular	4.1	Some soft foots over firm layer	35	5.4	10	1.5
				16(max.)	Regular	4.2	Small amount soft foots over firm layer	35	5.0	10	1.2
				16(max.)	Regular^a	6.0	Single firm layer	35	3.9	10	1.1
4	150		1.4	14(80%)	Regular	3.6	Very small amount soft foots over firm layer	35	6.2	10	1.8
										15	1.8
				16(max.)	Regular	3.8	Negligible amount soft foots over firm layer	35	6.0	10	1.6
										15	1.6
				16(max.)	Regular^a	5.6	Single firm layer	35	4.3	10	1.2
5	150	3	1.4	14(80%)	Regular	4.6	Small amount soft foots over firm layer	35	10.3	20	4.6
				16(max.)	Regular	4.8^b		35	7.8	20	3.6
				16(max.)	Regular^a	6.0	Negligible amount soft foots over firm layer	35	6.9	20	2.9
6	180	¹/₄	1.8	14(80%)	Regular	5.1^b	Some soft foots over firm layer	35	9.5	20	3.6
				16(max.)	Regular	5.2^b		35	7.4	20	2.9
				16(max.)	Regular^a	6.4	Negligible amount soft foots over firm layer	35	6.1	20	2.9
7	180	1	1.4	14(80%)	Regular	4.9^b	Small amount soft foots over firm layer	35	10.2	20	5.2
				16(max.)	Regular	5.1		35	9.2	20	4.1
				16(max.)	Regular^a	6.0	Negligible amount soft foots over firm layer	35	7.8	20	3.7
8	180	3	1.5	14(80%)	Regular	4.5	Small amount soft foots over firm layer	35	11.9	20	7.0
										35	6.7
				16(max.)	Regular	4.7^b		35	11.7	20	5.4
										35	5.3
				16(max.)	Regular^a	6.3	Negligible amount soft foots over firm layer	35	8.8	20	4.2
										35	4.1
9	210	¹/₄	1.4	14(80%)	Regular	4.6^b	Small amount soft foots over firm layer	35	10.5	20	5.2
				16(max.)	Regular	5.1		35	8.3	20	4.1
				16(max.)	Regular^a	6.0	Negligible amount soft foots over firm layer	35	8.1	20	3.3
10	210	1	1.4	14(80%)	Regular	4.6^b	Small amount soft foots over firm layer	35	13.6	20	6.8
				16(max.)	Regular	4.9		35	11.6	20	5.3
				16(max.)	Regular^a	5.9	Negligible amount soft foots over firm layer	35	10.1	20	4.7
11	210	3	1.4	14(80%)	Regular	4.5	Small amount soft foots over firm layer	35	20.9	20	12.4
										35	12.2
				16(max.)	Regular	4.7^b		35	19.3	20	10.8
										35	10.4
				16(max.)	Regular^a	5.9	Negligible amount soft foots over firm layer	35	14.3	20	8.6
										35	8.6
12	240	0	1.4	Filtered							
				14(80%)	Regular	3.3	Large amount soft foots over firm layer	35	9.6	20	3.5
				14(80%)	Regular	4.3	Small amount soft foots over firm layer	35	9.4	20	3.6
				16(max.)	Regular	4.5		35	8.2	20	3.2
				16(max.)	Regular^a	5.5	Single firm layer	35	6.1	20	2.3
13	240	¹/₄	1.5	14(80%)	Regular	4.6^b	Small amount soft foots over firm layer	35	15.8	20	8.4
										35	8.2
				16(max.)	Regular	5.0^b		35	12.9	20	7.0
										35	7.0
				16(max.)	Regular^a	6.0	Negligible amount soft foots over firm layer	35	10.9	20	6.0
										35	5.8
14	240	1	1.5	14(80%)	Regular	4.6	Small amount soft foots over firm layer	35	29.0	20	16.2
										35	16.4
				16(max.)	Regular	4.8^b		35	23.2	20	14.2
										35	14.3
				16(max.)	Regular^a	6.0	Negligible amount soft foots over firm layer	35	18.5	20	12.1
										35	12.0
15	240	3	1.5	14(80%)	Regular	4.9	Small amount soft foots over firm layer	35	9.1^c	20	6.4^c
										35	6.1^c
				16(max.)	Regular	4.9		35	9.0^c	20	6.1^c
										35	6.0^c
				16(max.)	Regular^a	6.1	Negligible amount soft foots over firm layer	35	7.4^c	20	5.2^c
										35	5.0^c

[a] Regular refining procedure modified by stirring 90 minutes in cold bath following addition of alkali.
[b] Oil cloudy, containing jelly-like material; sample remelted without decanting; all remelts produced firm foots with no jelly-like matter.
[c] Color measurements made in 1-inch color tubes; readings for standard 5.25-inch tube were beyond the scale of the colorimeter (32 *R*).

decreased to 10*Y*–0.7*R* after standing 145 days, and a second sample decreased from 20*Y*–3.1*R* to 20*Y*–2.0*R* after standing 100 days.

An experiment on a sample having a characteristic odor showed that solvent-extracted cottonseed oil can be satisfactorily deodorized.

Examination of absorption spectra of solvent-extracted cottonseed oil (Figures 6, 7, and 8) suggests the possibility of using absorption-spectrum curves as an indication for the amount of coloring matter present in a certain lot of seed or miscella. This type of data would make it possible to predict, within a certain range, the color of the finished oil, provided the oils are processed under comparable conditions.

Figure 6 shows absorption spectra curves in the visible range for solvent-extracted crude cottonseed oils. Curves 1, 2, and 3, representing the crude oils from the three de-emulsification procedures, indicate a slight difference in absorption spectra. Curve 5 shows that the absorption spectra of the bleached oils from these three crude oils are coincident and negligible, an indication of almost colorless oils. Curve 4, representing the ab-

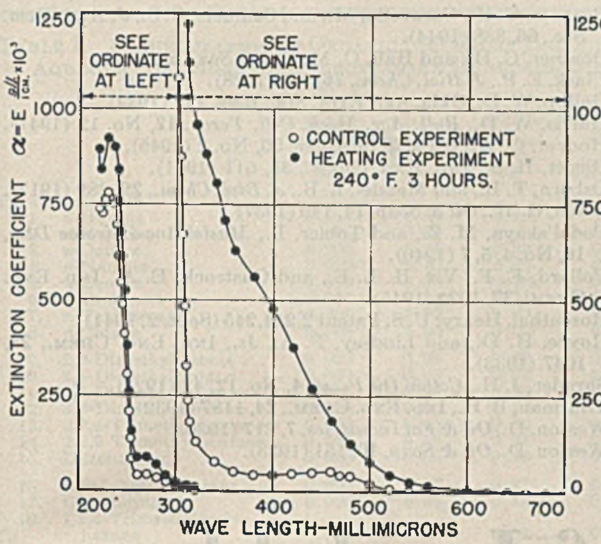

Figure 7. Absorption Spectra of Refined Cottonseed Oil (in Commercial Hexane)

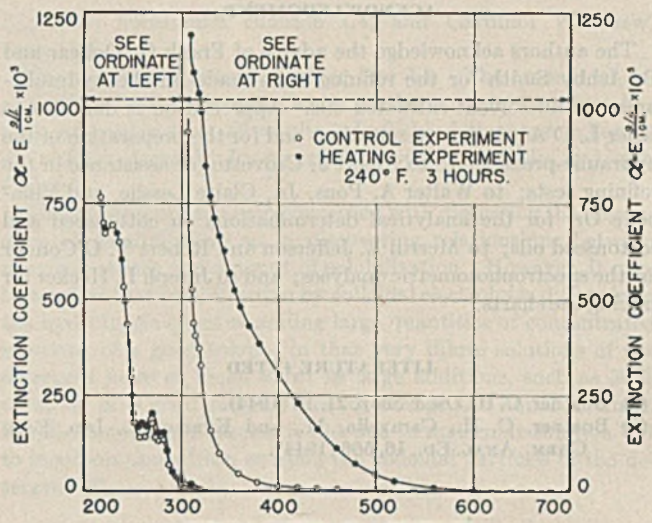

Figure 8. Absorption Spectra of Bleached Cottonseed Oil (in Commercial Hexane)

sorption spectra of the vacuum-dried crude oil from the miscella for the final heating experiments, is almost congruent with curve 3. This illustrates the fact that crude oils containing like amounts of coloring matter can be obtained from similar lots of seed, provided normal control is maintained in the preparation of flaked meats and extraction.

Figures 7 and 8 give absorption curves of refined and bleached oils, respectively, for a control run and for the highest heating experiment (240° F. for 3 hours). The wide differences in the visible range between the absorption spectra of both the refined and bleached oils from the control and heat-treated runs indicate the amount of color fixation caused by heat. The absorption spectra for the ultraviolet range is also included.

SUMMARY AND CONCLUSIONS

Results of preliminary experiments determined the heating time and temperature range required for demonstrating the effects of heat on solvent-extracted cottonseed oils obtained by low-temperature steam stripping. The data indicated that de-emulsification methods other than salting out should be investigated, and that the official A.O.C.S. refining methods needed modification for solvent-extracted cottonseed oil. A second series of experiments was conducted, therefore, for the purpose of obtaining suitable de-emulsification and refining procedures. Results from the first and second series served as a basis for establishing conditions required for a third series in which a systematic study was made of the effect of heat on solvent-extracted cottonseed oil.

Color fixation became objectionable for miscella from prime cottonseed oil as follows:

Miscella Heating Time	Temperature Range, ° F.	
	Refined oil	Bleached oil
15 min.	180–210	150–180
1 hr.	150–180	150–180
3 hr.	150–180	Under 150

No appreciable difference was noted in the refining losses of the various heat-treated runs, although the control samples showed approximately 1% less refining loss.

An examination of absorption spectra of solvent-extracted cottonseed oil suggests the possibility of using absorption-spectrum curves to indicate the amount of coloring matter.

The following generalizations can be made in regard to the refining and bleaching of the solvent-extracted cottonseed oils investigated: In all samples of refined oil a firm layer of soap stock was obtained, although present over this layer in most cases was a suspension of flocculent foots ranging from a negligible amount to 5% of the total weight of the soap stock. The regular break method with the 90-minute period of cold stirring after the addition of alkali tended to give better soap stock formation, a clearer unfiltered oil, an oil that filters rapidly, and a lighter colored refined and bleached oil; these advantages compensate, possibly, for higher refining losses. The vacuum-drying and centrifugation methods of de-emulsification, both giving better soap stock formation, were more satisfactory than the salting-out procedure. Further advantages of the vacuum-drying procedure were low moisture content which prevented appreciable increase in free fatty acid of the oil on aging, a shorter period for de-emulsification, and no loss of oil or phosphatic material. Yet refining losses and colors obtained with vacuum drying were comparable to those obtained with the other two methods, with an apparently negligible fixation of objectionable coloring matter.

Solvent extraction of one prime lot of cottonseed produced a refined and bleached oil equivalent in quality to high-grade hydraulic-pressed cottonseed oils.

The data obtained supply necessary engineering information for designing, installing, and operating solvent-extraction processes.

Table V. Refining Data for Hydraulic-Pressed Cottonseed Oil

Expt. No.	Free Fatty Acid, %	Refining Lye, ° Bé.	Refining Loss, %	Lovibond Color (5¼-Inch Tube)					
				Refined oil		Bleached oil, 6% A.O.C.S. fuller's earth[a]		Bleached oil, 4% B.C. clay + 1% Nuchar GFO[a]	
				Y	R	Y	R	Y	R
1	1.4	12(80%)	5.3	35	6.8	20	2.3	15	1.7
		14(80%)	5.7	35	6.7				
2	1.3	12(80%)	5.3	35	6.7	20	1.9	15	1.6
		14(80%)	5.7	35	6.8				
3	1.7	12(80%)	6.0[b]	35	10.6	20	2.4	15	1.6
		16(max.)	7.0[b]	35	8.6				
		16(80%)[c]	6.9[b]	35	12.8				
4	1.3	12(80%)	4.4	35	6.9	20	1.7	15	1.5
		14(80%)	4.4	35	8.0				
5	1.1	12(80%)	4.4	35	6.7	15	1.5	15	1.4
		14(80%)	4.8	35	6.1				
6	1.2	12(80%)	4.1	35	6.2	15	1.6	15	1.5
		14(80%)	4.5	35	6.4				
7	1.0	12(80%)	4.2	35	8.6	20	1.8	15	1.4
		14(80%)	4.2	35	8.5				
8	1.0	12(80%)	5.0	35	8.1	20	2.0	15	1.4
		14(80%)	4.7	35	8.0				

[a] 200-gram samples handled according to official A.O.C.S. methods.
[b] Refined oils contained gelatinous soaps.
[c] Refined by slow breaking method.

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LITERATURE CITED

(1) Boatner, C. H., *Oil & Soap*, 21, 10 (1944).
(2) Boatner, C. H., Caravella, M., and Kyame, L., Ind. Eng. Chem., Anal. Ed., 16, 566 (1944).
(3) Boatner, C. H., Caravella, M., and Samuels, C. S., *J. Am. Chem. Soc.*, 66, 838 (1944).
(4) Boatner, C. H., and Hall, C. M., *Oil & Soap*, in press.
(5) Clark, E. P., *J. Biol. Chem.*, 76, 229 (1928).
(6) Gallup, W. D., Okla. Agr. Expt. Sta., *Rept.* 177 (1934).
(7) Harris, W. D., *Bull. Agr. Mech. Coll. Texas*, 12, No. 12 (1941).
(8) Hoover, C. W., *Oil Mill Gazetteer*, 50, No. 2 (1945).
(9) Olcott, H. S., Ind. Eng. Chem., 33, 611 (1941).
(10) Osborn, T. B., and Mendel, L. B., *J. Biol. Chem.*, 29, 289 (1917).
(11) Owen, G. W., *Oil & Soap*, 14, 149 (1937).
(12) Podol'skaya, M. Z., and Tobler, L., *Maslobolno-Zhirovoe Delo*, 16, No. 4, 5, 7 (1940).
(13) Pollard, E. F., Vix, H. L. E., and Gastrock, E. A., Ind. Eng. Chem., 37, 1022 (1945).
(14) Rosenthal, Henry, U.S. Patent 2,254,245 (Sept. 2, 1941).
(15) Royce, H. D., and Lindsey, F. A., Jr., Ind. Eng. Chem., 25, 1047 (1933).
(16) Shrader, J. H., *Cotton Oil Press*, 4, No. 12, 42 (1921).
(17) Thurman, B. H., Ind. Eng. Chem., 24, 1187 (1932).
(18) Wesson, D., *Oil & Fat Industries*, 7, 217 (1930).
(19) Wesson, D., *Oil & Soap*, 10, 151 (1933).

Solubilization of Insoluble Organic Liquids by Detergents

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Solubilization is attributed to incorporation of the insoluble substance within and upon the colloidal particles or micelles of the soap or detergent. Although many instances of this action have been reported, this is the first attempt at a systematic investigation of the characteristics of an insoluble organic substance that determine the extent to which it is solubilized. A number of cation-active and anion-active detergents have been used with a series of aliphatic and aromatic hydrocarbons, in addition to a number of polar compounds. Substances of very low molecular weight are freely solubilized, but the extent of solubilization falls off rapidly with increase in molecular weight or molar volume. Polar compounds are more readily solubilized than hydrocarbons. Although, in general, the various detergents show parallel behavior, merely differing in degree of solubilizing power, and the cation-active detergents are generally better solubilizers than the anion-active detergents, there are numerous specificities and influences of structure, both of the detergent and of the material being solubilized. Soaps and detergents that have in common the twelve-carbon paraffin chain differ greatly in solubilizing power, each favoring particular classes of chemical substances.

THE remarkable phenomenon of solubilization (*3*) consists in the taking up, by even very dilute solutions of soaps and detergents, substances which are otherwise insoluble or very slightly soluble in the solvent medium. Indeed, it is probable that any substance can be made soluble in any medium by the use of a suitable solubilizing agent.

The solubilized material is in solution in the sense that it is not present as suspended or protected particles or emulsified droplets, but is incorporated in the colloidal particles of the detergent itself. It is therefore in solution in the same sense that the soap itself is in solution. At least a portion of the solubilized material has been shown by x-ray examination (*1*, *2*, *5*) to be present in layers within the lamellar micelles of the detergent. As soon as the saturation value for solubilization is exceeded, any excess of the solubilized material appears as suspended particles or droplets of emulsion and causes a steep rise in turbidity. At the suggestion of one of the authors (Richards), this point of sharp increase in turbidity has been used as an indicator for the maximum amount of a given material that can be solubilized by a given detergent solution at a given temperature and concentration.

This communication contains the first systematic survey of the amount of solubilization of different organic liquids as depending upon such factors as molecular weight and structural and chemical composition. Decinormal aqueous solutions of sodium oleate, potassium laurate, and cation-active dodecylamine hydrochloride have been used with all the organic liquids. A number of measurements with other synthetic detergents, Gardinol WA new, concentrated (containing sodium lauryl sulfate and salts), and the cation-active Emulsol 607L and cetyl pyridinium chloride have also been included. Most of the results follow general rules, but a few specific relations also appear.

MATERIALS AND METHOD

Dodecylamine hydrochloride was prepared from a fairly pure dodecylamine obtained from Armour & Company, and was twice recrystallized from ethyl alcohol and washed with ether. Sodium oleate was prepared from Kahlbaum's "pure" oleic acid, and a 10% solution in acetone was cooled to −20° C. to precipitate out linoleic acid. Oleic acid was recovered from the filtrate and converted by carbonate-free sodium hydroxide to sodium oleate. Potassium laurate was a Kahlbaum preparation, rectified and purified by M. E. L. McBain. Emulsol 607L was a purified specimen and was the lauryl ester of α-alanine hydrochloride supplied by the Emulsol Corporation. Cetyl pyridinium chloride was used as purified and supplied by the Wm. S. Merrell Company. Gardinol WA new, conc., was used as supplied by the National Aniline & Chemical Company; unlike the others, the active substance, sodium lauryl sulfate, may be only one third of the total weight, and salts are present.

Table I. Solubilization of Organic Liquids by Decinormal Aqueous Solutions of Dodecylamine Hydrochloride at 25° C.

	Soly. in Water, G./100 Cc.	Total in Solution, Ml./100 Cc.	Amount Solubilized: Grams/100 Cc.	Amount Solubilized: Mole/mole detergent
Paraffinic liquids				
1. *n*-Hexane	0.014	1.00	0.64	0.75
2. *n*-Heptane	0.005	0.80	0.54	0.54
3. *n*-Octane	0.002	0.48	0.33	0.29
4. *n*-Nonane	0.000	0.40	0.29	0.22
5. *n*-Decane	0.000	0.24	0.18	0.13
6. *n*-Dodecane	0.000	0.14	0.11	0.06
7. *n*-Tetradecane	0.000	0.02	0.02	0.01
8. *n*-Cetane	0.000	0.00	0.00	0.00
9. 2,2-Dimethylbutane	0.000	0.96	0.63	0.73
10. 2,3-Dimethylbutane	0.000	0.98	0.64	0.75
11. 2,3-Dimethylpentane	0.000	0.90	0.63	0.62
12. 3,3-Dimethylpentane	0.000	0.80	0.55	0.55
13. 2,2,4-Trimethylpentane	0.000	0.44	0.30	0.27
14. 2,2,3-Trimethylpentane	0.000	0.48	0.34	0.30
15. Diisobutylene	0.000	0.66	0.48	0.43
16. Methylcyclopentane	0.000	0.50	0.37	0.40
17. Cyclohexane	0.000	0.98	0.73	0.87
18. 1,2,4-Trimethylcyclohexane	0.000	0.03	0.02	0.02
Aromatic liquids				
19. Benzene	0.070	0.66	0.51	0.65
20. Toluene	0.049	0.58	0.45	0.49
21. Nitrobenzene	0.190	0.60	0.53	0.43
22. Ethylbenzene	0.014	0.48	0.40	0.38
23. *p*-Xylene	0.013	0.44	0.36	0.34
24. Amylbenzene	0.000	0.20	0.17	0.12
25. *p*-Cymene	0.000	0.30	0.26	0.19
Polar compounds				
26. Methyl *tert*-butyl ether	5.126	9.30	1.80	2.05
27. Methyl isobutyl ketone	1.820	4.50	1.78	1.78
28. Amyl acetate	0.173	2.14	1.69	1.45
29. Isopropyl *tert*-butyl ether	0.050	0.90	0.62	0.53
30. Octylamine	0.020	0.24	0.17	0.13
31. *n*-Octyl alcohol	0.059	0.36	0.24	0.18
32. 2-Ethylhexanol	0.013	0.58	0.47	0.36
33. Lauryl alcohol	0.000	0.10	0.08	0.05
34. Oleic acid	0.000	0.08	0.07	0.02
35. Tributyrin	0.000	0.66	0.68	0.22
36. Triolein	0.000	0.00	0.00	[a]

[a] Immeasurable.

The thirty-six organic compounds used were the purest obtainable. Some of them were specially supplied by Shell Development Company. They comprise eighteen aliphatic hydrocarbons, seven aromatic hydrocarbons, and a number of polar compounds.

A series of 10-cc. samples of soap solution were measured into small glass bottles with plastic caps lined with platinum foil, and known amounts of the organic compound were added from a microburet reading to 0.001 cc. They were placed on a gentle shaker overnight. Thereupon the turbidity was measured in a Barnes turbidimeter (*4*). This instrument, designed in the laboratories of the American Cyanamid Company, measures the turbidity or scattered light as a percentage of the total light passed through a 1-cm.-thick plane-parallel cell. The percentage turbidity of the detergent solution remains practically constant until a saturation value for solubility is just exceeded, whereupon the turbidity rises sharply and careful inspection reveals the presence of emulsified droplets.

All the experiments when not otherwise stated were conducted at 25° C. in an air thermostat which also contained the shaker. Decinormal solutions of detergent were employed. From 3 to 5 hours were necessary to reach the equilibrium point, and thereafter the results did not change. The turbidities of the decinormal solution without admixture were: dodecylamine hydrochloride 1.2, sodium oleate 4.9, potassium laurate 1.2, cetyl pyridinium chloride 1.4, and Gardinol WA new, conc., 1.8.

The results are listed in Tables I to VI. The amount of organic liquid soluble in pure water at the same temperature has been subtracted from all results. In Table I the organic liquids are numbered serially for comparison with later tables and with Figure 1.

This paper is not so much concerned with discussing the mechanism of solubilization as in discovering relationships between chemical nature and amount of solubilization. However, it may be recalled that solubilization by colloidal electrolytes differs from the hydrotropic effect of adding large quantities of concentrated solutions of a good solvent in that very dilute solutions of the detergent have as much effect as large additions, such as 30% or more, of a good solvent used to change the liquid medium. Furthermore, solubilization is not due to molecular solution but to incorporation within or upon the colloidal particles of the detergent (*6*).

COMPARISON OF LIQUIDS SOLUBILIZED BY ONE SOAP

The outstanding result of this investigation is the finding that increase in molecular weight within any homologous series mili-

Table II. Solubilization of Organic Liquids by Decinormal Aqueous Solutions of Sodium Oleate and of Potassium Laurate at 25° C.

Liquid No.	Sodium Oleate: Total in solution, ml./100 cc.	Sodium Oleate: Amount solubilized: G./100 cc.	Sodium Oleate: Amount solubilized: Mole/mole detergent	Potassium Laurate: Total in solution, ml./100 cc.	Potassium Laurate: Amount solubilized: G./100 cc.	Potassium Laurate: Amount solubilized: Mole/mole detergent
1	0.6	0.398	0.46	0.26	0.156	0.18
2	0.5	0.340	0.34	0.18	0.117	0.12
3	0.3	0.210	0.18	0.14	0.096	0.08
4	0.2	0.142	0.11	0.10	0.071	0.06
5	1	0.047	0.05	0.06	0.045	0.03
6	0.02	0.015	0.01	0.01	0.008	0.005
7	0.00	0.000	0.00	0.00	0.000	0.00
8	...	...	...	...	...	...
9	0.60	0.386	0.45	0.18	0.116	0.13
10	0.60	0.394	0.46	0.20	0.121	0.14
11	0.50	0.350	0.35	0.16	0.110	0.11
12	0.45	0.312	0.31	0.14	0.097	0.10
13	0.26	0.178	0.16	0.08	0.055	0.05
14	0.28	0.205	0.18	0.14	0.110	0.09
15	0.60	0.428	0.38	0.16	0.114	0.10
16	0.32	0.244	0.26	0.04	0.030	0.32
17	0.60	0.465	0.56	0.26	0.194	0.23
18	0.02	0.014	0.012	0.02	0.015	0.012
19	0.70	0.594	0.76	0.28	0.226	0.29
20	0.60	0.466	0.51	0.25	0.116	0.13
21	0.80	0.768	0.62	0.27	0.183	0.18
22	0.50	0.419	0.40	0.30	0.214	0.20
23	0.46	0.383	0.36	0.26	0.210	0.20
24	0.30	0.257	0.17	0.06	0.051	0.04
25	0.40	0.342	0.26	0.12	0.103	0.08
26	9.50	1.936	2.20	7.50	1.460	1.66
27	4.55	1.820	1.82	4.00	1.200	1.20
28	2.70	1.990	1.71	1.20	1.038	0.89
29	1.22	0.858	0.73	0.24	0.166	0.14
30	0.14	0.088	0.07	0.014	0.088	0.07
31	1.00	0.764	0.59	0.54	0.385	0.29
32	0.75	0.610	0.47	0.10	0.083	0.064
33	0.25	0.206	0.13	0.06	0.049	0.03
34	0.16	0.137	0.05	0.06	0.051	0.018
35	1.10	1.124	0.37	0.32	0.327	0.11
36	0.00	0.000	0.00	...	...	...

Table III. Solubilization of Organic Liquids by Decinormal Aqueous Solutions of Emulsol 607L, Cetyl Pyridinium Chloride, and Gardinol WA New, Conc.

Liquid No.	Emulsol 607L: Total in solution, ml./100 cc.	Emulsol 607L: Amount solubilized: Grams/100 cc.	Emulsol 607L: Amount solubilized: Mole/mole detergent	Cetyl Pyridinium Chloride: Total in solution, ml./100 cc.	Cetyl Pyridinium Chloride: Amount solubilized: Grams/100 cc.	Cetyl Pyridinium Chloride: Amount solubilized: Mole/mole detergent	Gardinol WA New, Conc.: Total in solution, ml./100 cc.	Gardinol WA New, Conc.: Grams solubilized per 100 cc.
1	0.38	0.235	0.27	0.66	0.418	0.49	0.34	0.209
5	0.12	0.089	0.062	0.25	0.193	0.14	...	...
19	0.70	0.540	0.69	0.74	0.577	0.74	0.30	0.192
20	0.70	0.534	0.58	0.74	0.588	0.64	...	...
30	0.35	0.252	0.20	2.60	2.00	1.55	0.08	0.042
31	0.95	0.723	0.56	1.10	0.855	0.66	...	...
34	0.04	0.034	0.012	0.22	0.188	0.065	...	...

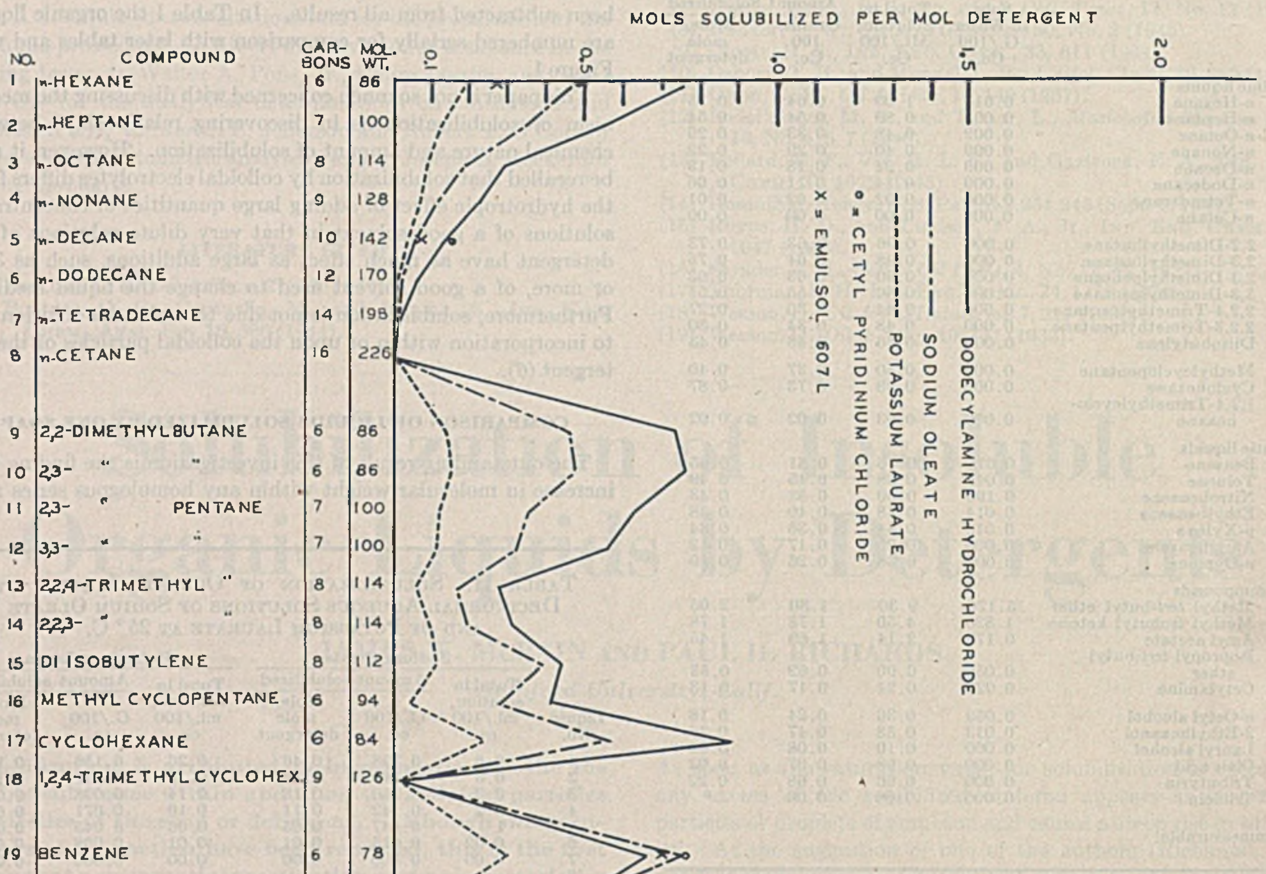

Figure 1. Solubilization of Thirty-five Organic Liquids by Aqueous Solutions of Five Soaps and Detergents (Two Anion-active and Three Cation-active)

The data are incomplete for two of the detergents, and only the experimental points are indicated. The solubilization is expressed in gram moles solubilized per gram equivalent of detergent. Molecular weight and the number of carbon atoms are given for each compound.

Table IV. Comparison of Number of Moles of Organic Liquid Solubilized per Mole of Detergent[a]

Liquid No.	No. of Atoms	$C_{12}HCl$	NaC_{18}	KC_{12}	Emulsol	CePy
1	6	0.75	0.46	0.18	0.27	0.49
2	7	0.54	0.34	0.12	...	...
3	8	0.29	0.18	0.08	...	...
4	9	0.22	0.11	0.06	...	...
5	10	0.13	0.052	0.03	0.063	0.14
6	12	0.063	0.009	0.005	...	...
7	14	0.008	0.000	...	...	...
8	16	0.000	...	...	...	...
9	6	0.73	0.45	0.13	...	...
10	6	0.75	0.46	0.14	...	...
11	7	0.62	0.35	0.11	...	...
12	7	0.55	0.31	0.10	...	...
13	8	0.27	0.16	0.05	...	...
14	8	0.30	0.18	0.09	...	...
15	8	0.43	0.38	0.10	...	...
16	6	0.40	0.26	0.032	...	...
17	6	0.87	0.56	0.23	...	...
18	9	0.019	0.012	0.012	...	...
19	6	0.65	0.76	0.29	0.69	0.74
20	7	0.49	0.51	0.13	0.58	0.64
21	6 (1 N)	0.43	0.62	0.18	...	...
22	8	0.38	0.40	0.20	...	...
23	8	0.34	0.36	0.20	...	...
24	11	0.12	0.17	0.04	...	...
25	10	0.19	0.26	0.08	...	...
26	5 (1 O)	2.05	2.20	1.66	...	...
27	6 (1 O)	1.78	1.82	1.20	...	...
28	6 (3 O)	1.45	1.71	0.89	...	...
29	7 (1 O)	0.53	0.73	0.14	...	...
30	8 (1 N)	0.13	0.07	0.07	0.20	1.55
31	8 (1 O)	0.18	0.59	0.29	0.56	0.66
32	8 (1 O)	0.36	0.47	0.064	...	...
33	12 (1 O)	0.052	0.13	0.03	...	...
34	18 (2 O)	0.024	0.05	0.018	0.012	0.065
35	15 (6 O)	0.22	0.37	0.11	...	...
36	57 (6 O)	0.00	0.00	...	...	...

[a] $C_{12}HCl$ = dodecylamine hydrochloride, NaC_{18} = sodium oleate, KC_{12} = potassium laurate, emulsol = Emulsol 607L, CePy = cetyl pyridinium chloride.

tates strongly against solubilization. Substances of high molecular weight are scarcely solubilized; whereas all the compounds of low molecular weight so far investigated are freely solubilized.

As an example, dodecylamine hydrochloride solubilizes the hydrocarbons with six carbon atoms to the extent of 0.75 mole of hydrocarbon per mole of detergent; methylcyclopentane differs in being as low as 0.40 while cyclohexane is high, 0.87 mole per mole, an indication that configuration likewise has a decided influence. Steric effects must interfere with close packing. Similarly the results for the hydrocarbons with eight carbon atoms, whether paraffinic, branched-chain, or aromatic, all range between 0.27 and 0.43 mole per mole, the highest being diisobutylene and the lowest the less symmetrical 2,2,4-trimethylpentane.

Table V. Effect of Molecular Weight and of Molar Volume on Solubilization

No.	Compound	Molecular Weight	Molar Volume	$C_{12}HCl$	NaC_{18}	KC_{12}
1	*n*-Hexane	86.1	131.3	0.75	0.46	0.18
9	2,2-Dimethylbutane	86.1	133.7	0.73	0.44	0.13
10	2,3-Dimethylbutane	86.1	131.1	0.75	0.45	0.14
2	*n*-Heptane	100.2	147.1	0.54	0.34	0.12
11	2,3-Dimethylpentane	100.2	144.1	0.62	0.35	0.11
12	3,3-Dimethylpentane	100.2	145.1	0.55	0.31	0.10
3	*n*-Octane	114.23	163.3	0.29	0.18	0.08
13	2,2,4-Trimethylpentane	114.23	165.7	0.27	0.16	0.05
14	2,2,3-Trimethylpentane	114.23	160.4	0.30	0.18	0.09

The results are given in Figure 1, where the number of moles of organic liquids solubilized by five detergents are graphed. The series for normal hydrocarbons shows the effect of increasing molecular weight in lowering the value for *n*-hexane from 0.75 down to practically 0 for *n*-hexadecane. This important effect of increasing molecular weight is plotted for each of the detergents.

The second outstanding generalization is that the polar compounds are much more extensively solubilized than the hydrocarbons. (There is a negative effect for nitrogen-containing compounds.) This is especially marked for those of low molecular weight, such as methyl *tert*-butyl ether, methyl isobutyl ketone, and amyl acetate. However, here, too, differences in configuration are important. Two compounds with eight carbon atoms and one oxygen are 2-ethylhexanol and *n*-octyl alcohol, and of these the former is solubilized to twice the extent of the latter. These numbers have been, perhaps arbitrarily, corrected for natural solubility in water.

No simple relation has yet appeared between any single property of solubilized material and the extent to which it is solubilized by a given detergent. Solubilization appears to fall off at first linearly with molar volume and then to fall more slowly and asymtotically to zero for the higher members. However, closer examination shows that molecular volume may exert more influence than molecular weight. This is illustrated in Table V where hydrocarbons of identical molecular weight but different structure are compared. It is evident that a branched chain can be solubilized to a greater extent than the straight chain of the same molecular weight.

However, molecular volume of itself does not determine solubilization. Table VI compares groups of substances of similar molecular volume and shows that their degree of solubilization may differ greatly. The extent of solubilization of an organic chemical depends not only upon low molecular weight, upon molecular volume, upon structure, and upon the presence or nature or position of any polar groups, but also sometimes upon a direct interaction with the detergent. This must operate in the formation of certain acid soaps from fatty acid and soap; but in the present work a good example is found in the interaction between octyl amine and cetyl pyridinium chloride. This results in the abnormally high mole/mole ratio of 1.55 and is evidenced in a color change to a different tone of yellow observed in this solution.

Table VI. Comparison of Solubilization of Groups of Substances of Similar Molecular Volume by Dodecylamine Hydrochloride, Sodium Oleate, and Potassium Laurate

No.	Compound	Molar Volume	Mole/Mole Ratio		
			$C_{12}HCl$	NaC_{18}	KC_{12}
17	Cyclohexane	108.5	0.87	0.56	0.23
20	Toluene	106.7	0.49	0.51	0.13
26	Methyl *tert*-butyl ether	118	2.05	2.20	1.66
22	Ethylbenzene	122.5	0.38	0.40	0.20
27	Methyl isobutyl ketone	125.0	1.78	1.82	1.20
1	*n*-Hexane	131.3	0.75	0.46	0.18
28	Amyl acetate	134.1	1.45	1.71	0.89
25	*p*-Cymene	156.5	0.19	0.26	0.08
29	Isopropyl *tert*-butyl ether	157.3	0.53	0.73	0.14
31	*n*-Octyl alcohol	157.8	0.18	0.59	0.29
3	*n*-Octane	163.3	0.29	0.18	0.08
13	2,2,4-Trimethylpentane	165.7	0.27	0.16	0.05
18	1,2,4-Trimethylcyclohexane	164.9	0.019	0.012	0.012
30	Octylamine	166.0	0.13	0.07	0.07
24	Amylbenzene	172.7	0.12	0.17	0.04
5	*n*-Decane	191.4	0.13	0.05	0.03
33	Lauryl alcohol	191.7	0.052	0.13	0.03
8	*n*-Cetane	293.5	0.00	0.00	0.00
34	Oleic acid	339.6	0.024	0.05	0.018
35	Tributyrin	295.7	0.22	0.37	0.11

COMPARISON OF DETERGENTS

Five of the detergents are compared in Table IV. The data show the number of moles of organic liquid solubilized by one mole of each of the detergents. Figure 1 likewise shows relative solubilizing power by the position of the lines connecting the volumes solubilized by the respective detergents. In general, the curves for the different detergents show a definite parallelism.

However, it is striking that they differ in solvent power. Dodecylamine hydrochloride, potassium laurate, and Emulsol 607L have the same twelve-carbon chain in common, but for hydrocarbons and many other liquids, potassium laurate possesses only a small fraction of the solubilizing power of dodecylamine hydrochloride. The cation-active detergents are better solubilizers than the anion-active detergents, although there are distinct differences within each group.

Cetyl pyridinium chloride is rather like dodecylamine hydrochloride in spite of its sixteen-carbon chain, but is usually more effective in solubilizing. In some cases it is equaled by the twelve-carbon Emulsol 607L, but usually the latter is far less effective and in one case falls even below the laurate.

Sodium oleate, with eighteen carbon atoms, exhibits intermediate values for the paraffinic and cyclic hydrocarbons but excels in solubilizing aromatic and polar compounds.

It is therefore clear that neither the carbon atom chain of the detergent nor its polar groups alone determine the solubilizing power, but that certain favorable and unfavorable combinations, as well as occasional specificities, overlie the general regularities observed.

LITERATURE CITED

(1) Harkins, W. D., Mattoon, R. W., and Corrin, M. L., *J. Colloid Sci.*, 1, 105 (1946).

(2) Hughes, E. W., Sawyer, W. M., and Vinograd, J. R., *J. Chem. Phys.*, 13, 131 (1945).

(3) McBain, J. W., "Advances in Colloid Science", Vol. I, pp. 99–142, New York, Interscience Publishers, 1942.

(4) McBain, J. W., and Stamberg, O. E., Rept. to Master Brewers' Assoc. of Am., 1942.

(5) Ross, Sydney, and McBain, J. W., *J. Am. Chem. Soc.*, 68, 296 (1946).

(6) Smith, E. L., *J. Phys. Chem.*, 36, 1401, 1672, 2455 (1932).

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Material or Heat Transfer between a Granular Solid and Flowing Fluid

PRESENT STATUS OF THE THEORY

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This paper is a review of the work so far reported on the computation of the transfer of material (or heat) when a fluid (liquid or gas) is passed through a bed of granular solid, as in the decolorization of liquids, the recovery of volatile solvents, regenerators on furnaces, gas masks, chromatography, etc. For the transfer of a single material, where equilibrium between fluid and solid can be assumed, the problem has been completely solved, and some progress has been made for multiple transfer of materials. For the transfer of a single material where the rate of approach to equilibrium is finite, numerous special cases have been solved, but for more than one material transferred little has been done. At present the need is for a better experimental basis.

AN OPERATION which recurs in many branches of chemical engineering is that in which a fluid—gas or liquid—is passed through a bed of granular solid for the purpose of removing something from, or adding something to, the fluid (or both). In the oil and sugar industries, oils or sirups are passed through beds of adsorbents to remove impurities causing color and other undesired effects. In the recovery of volatile solvents, air charged with solvent vapor is passed over solid adsorbents. In leaching, liquids are passed through beds of solids to remove some constituent of the solids. In heat recovery in regenerators, air or other gas is passed through checker work in order to transfer heat first from one gas to the checker work and then to another gas.

There is no generally accepted term for this broad class of operations; the term "percolation" seems convenient and suitable, though not free from objection. The unit operation of percolation has been but little discussed in chemical engineering texts. Nevertheless, for the last quarter century, material for a theory of the operation has been accumulating, and progress has been especially rapid in the last few years. The object of this paper is not to make additions to the theory, but to direct attention to the scattered literature and to summarize the results so far obtained, without reproducing the derivations and proofs. It does not cover experimental work. A review at this time seems especially desirable since a considerable amount of work has been repeated, later investigators being unacquainted with what was done earlier.

It will be understood that percolation is here considered as a chemical engineering operation. There is a large amount of literature on the physical chemistry of adsorption, some of which furnishes a necessary background to percolation as applied to adsorption. But the calculation of the behavior of a gas mask, for example, requires something more, just as the design of a heat exchanger requires something more than knowledge of the conductivity, specific heat, and viscosity of the fluid employed. It is this "something more" which constitutes the chemical engineering theory.

In the interests of conciseness, some terms need to be defined. A substance which passes from the fluid to the solid, or vice versa, will be called a "solute". The equation or curve which defines the concentration of a solute in the solid as a function of the corresponding equilibrium concentration in the fluid will be called an "isotherm". The direction of flow of the fluid will be assumed to be downward. Further, practically all authors assume that the solid is contained in a vessel of uniform cross section, and that at any cross section at a given time the concentrations in solid and fluid are uniform, so that there is no loss in generality in basing all formulas on unit cross section. So far no author has taken into account the heat effects which accompany adsorption, so that a uniform temperature is assumed (except where heat is the thing transferred). Various cases of differing degrees of complexity have been investigated.

So far, nearly all the successful mathematical development has concerned the transfer of a single substance (or heat) to or from the solid. This is of practical importance in such cases as the recovery of volatile solvents and must also form the basis of any more elaborate theory.

SINGLE SOLUTE, EQUILIBRIUM ASSUMED

The simplest assumption we can make is that at all times at every point the distribution of the solute between fluid and solid is given by the isotherm; that is, equilibrium prevails at all points. This case was discussed by DeVault (*6*), Weiss (*27*), Wilson (*29*), and Wicke (*28*), who all assumed that diffusion is negligible in the vertical direction. The treatment by DeVault is the most satisfactory.

Let V = volume of solution poured into column since initial time

Since the cross section is unity, we may imagine that the column is only partly full of solid, and that all the fluid (assumed to be a liquid) was initially put in the column above the solid at the initial time. Then V will be the distance the level of liquid has descended since the initial time. (If the fluid is a gas, we may imagine it to be confined by a descending piston.)

Let x = distance of any point in column under consideration from top of solid
c = amount of solute per unit volume of solution, as a function of solution passed and position in column
M = amount of granular solid per unit volume of column
b = amount of solute adsorbed on unit amount of solid, as a function of solution passed and position in column
$b = f(c)$ be the isotherm of system under consideration; f, the functional relation, may be expressible algebraically or graphically
α = pore volume per unit bulk volume of granular solid; that is, fraction of volume not occupied by solid itself

Then DeVault showed that:

$$(dV/dx)_c = \alpha + Mf'(c) \qquad (1)$$

where $f'(c)$ = derivative of $f(c)$ with respect to c

If the isotherm is expressed by a curve, $f'(c)$ is the slope of the tangent at the value of c in question.

The right-hand side of Equation 1 may be looked upon as the derivative with respect to c of the quantity $\alpha c + Mb$, which gives the total solute in unit volume of the column, including both that adsorbed on the solid and that in the fluid in the interstices. It is a function of c, and the curve for it will in general be similar in character to the curve for the isotherm as defined above. Then Equation 1 may be expressed in words as follows: The rate of descent of the level in the column, where the fluid has the concentration c, is to the rate of descent of the fluid in the empty space above the column as the rate of increase in the solute concentration in unit volume of fluid is to the rate of concentration increase in unit volume of fluid plus solid, when the solute concentration in the fluid is c, and equilibrium prevails.

As an example of the application of the equation, we may take the case of an adsorbent and liquid in which Freundlich's equation is obeyed for a solute. Let the isotherm (for concreteness) be $b = c^{1/2}$, and let the solute be uniformly distributed through the solid at the start, the concentration being one in both solid and liquid. Let the column be washed with pure liquid. Then the behavior of the column is shown in Figure 1. At the start there will be a discontinuity at the top of the column, where the value of c will pass from 0 to 1 in an infinitesimal space. Since for an isotherm of the Freundlich type, the slope is greater for low concentrations of c, it follows that the high concentrations will descend the column faster than the low concentrations. The result is a distribution of concentrations, as Figure 1 shows.

If we now consider the reverse case, where the solid is free from solute at the start and is percolated with a solution containing solute, obeying Freundlich's equation, a difficulty is encountered. As before, at the start all concentrations between 0 and 1 will exist in an infinitesimal space at the top of the column. But if we endeavor to compute by Equation 1 the concentrations in the column at later times, ambiguous results will be obtained. At a given point at a given time, the principle that the higher concentrations move faster than the lower will give multiple values—high values from high concentrations descending rapidly from the top of the column, and low values descending more slowly from lower down in the column. A mathematical study shows that wherever such an ambiguity would arise from the application of Equation 1, a discontinuity will arise. In the specific case given, a boundary or "front" will descend the column; below this front the concentration is zero, and above it is that of the feed. This discontinuity must necessarily descend at a rate determined by material balance. Figure 2 shows how the discontinuity descends at a uniform rate. The sharp boundaries observed in chromatography give a visual indication of the discontinuity.

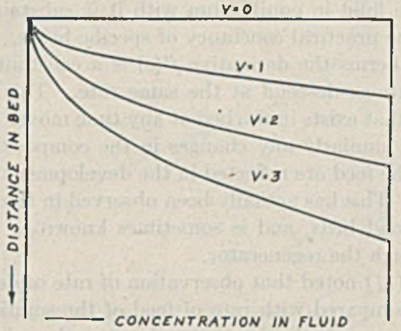

Figure 1. Initial Uniform Concentration of Adsorbate on Solid, with Pure Solvent Added at Top of Bed

Freundlich isotherm, equilibrium at all points, V = volume of solvent passed

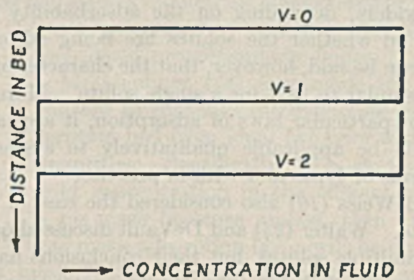

Figure 2. Solid Initially Free of Adsorbate with Solvent Containing Adsorbate Added at Top of Bed

Isotherm linear or curved in same sense as Freundlich isotherm, equilibrium at all points, V = volume of solvent passed

Of course all columns are finite, and the concentrations of solute in the fluid at the bottom layer are the concentrations in the effluent. Thus the theory accounts for the sudden appearance of solute in the effluent, which constitutes the "break" in gas masks. It will be noted that the existence of these sharp boundaries depends on the curvature which is characteristic of adsorption isotherms. Were the curvature reversed, no "break" would occur on adsorption, whereas one would appear on desorption.

It is not practicable to discuss all the different cases that may arise because of different initial distributions of the solute in the solid, changing concentrations in the feed, and different isotherms, but they may all be handled by Equation 1, subject to the qualification of the last two paragraphs.

There is one case, however, of special interest—that in which the isotherm is a straight line, at least within the limits of concentration being studied. Actually, considerable portions of certain adsorption isotherms may be considered as straight. Also, in the case of heat transfer, though the term "isotherm" is an unfortunate one, the relation between the heat content of the solid and the fluid in equilibrium with it is substantially linear because of the practical constancy of specific heats. In the case of linear isotherms the derivative $f'(c)$ is a constant, and hence all concentrations descend at the same rate. This means that any pattern that exists in the bed at any time moves bodily down the bed, and similarly any changes in the composition (or heat content) of the feed are reflected in the development of a pattern in the solid. This has actually been observed in the case of heat transfer in solid beds, and is sometimes known as blowing the pattern through the regenerator.

Le Rosen (*11*) noted that observation of rate of descent of the "break" as compared with rate of feed of the solution affords a convenient means for computing points on the adsorption isotherm. Tiselius (*22*) also discussed the material balance which gives the rate of descent.

TWO SOLUTES, EQUILIBRIUM ASSUMED

The general case for more than one solute has not been solved. However, Walter (*24*), taking as a basis the exchange reactions of zeolites, and Glückauf (*9*), starting with the Langmuir adsorption isotherm, studied the case in which the equilibrium relation between dissolved and adsorbed solute is given by equations of the form,

$$b_1 = \frac{z_3c_1}{1 + z_5c_1 + z_6c_2} \text{ and } b_2 = \frac{z_4c_2}{1 + z_5c_1 + z_6c_2}$$

where the subscripts to b and c refer to the two solutes, the z values are constants for the particular system being studied, and the concentrations in the fluid entering are assumed to be constant. Glückauf does not give a derivation or detailed results, and Walter's results cannot be conveniently summarized because they vary widely, depending on the adsorbability of the two solutes and on whether the solutes are being adsorbed or desorbed. It can be said, however, that the character of the results is generally similar to that for a single solute. Moreover, while developed for particular laws of adsorption, it appears that the results should be applicable qualitatively to systems obeying other isotherms of types met with in practice.

Offord and Weiss (*16*) also considered the case of two solutes in a brief note. Walter (*24*) and DeVault discussed qualitatively the case of multiple solutes, but their conclusions hardly go beyond what can be deduced from the two-component cases and from known experimental results.

There can be no question as to the validity of the equilibrium theory for those systems where the restrictions implied in the theory are realized. The results of chromatography are proof that the assumed conditions are realized in some cases. The question as to the limits within which this theory is valid can be answered only by a study of those cases in which the neglected factors (particularly rate of adsorption) are not negligible.

NONEQUILIBRIUM CASES, SINGLE SOLUTE

The problem for the case of equilibrium may be considered as completely solved. This is by no means true for the much more complex cases where equilibrium is not attained. However, various cases have been studied with more or less success.

HEAT TRANSFER CASE. Anzelius (*1*), Nusselt (*15*), Schumann (*20*), and Furnas (*8*) have discussed the case where the isotherm is linear, and the rate of transfer of solute between solid and fluid is proportional to the difference between the actual concentration in the fluid and the concentration corresponding to equilibrium with the solid. They were concerned with heat transfer rather than material transfer, but their results are equally applicable to the latter, provided the conditions specified are met.

Anzelius, Schumann, and Furnas confined themselves to the case where the initial concentrations in the solid and in the fluid are uniform, and where the concentration in any individual solid grain is uniform at any one time. For this case Furnas reduced the problem to a series of charts which give the relation between the three dimensionless quantities involved. Here the more general treatment of Nusselt will be summarized:

Let t = time elapsed from beginning
s = linear velocity of fluid in column above solid
a = rate of transfer of solute from fluid to solid, units of solute transferred per unit time per unit bulk volume of solid per unit difference in concentration between actual concentration in solid and equilibrium concentration in solid corresponding to actual concentration in liquid
$b = q + kc$ be the isotherm for system in region covered by formulas to be given g, k = constants
$m = a/M$
$n = ak/s$

Let the initial concentration of the solute in the solid in the column be given by $b = g(x)$, where g is any function and may be purely arbitrary; c is to be measured from the level of the concentration in the entering fluid, so that $c_0 = 0$, and b is to be measured from the concentration in equilibrium with the entering fluid. Then Nusselt's result may be expressed in the form:

$$c = \frac{n}{k} e^{-nx-mt} \int_0^x e^{n\epsilon}\, g(\epsilon) I_0[2\sqrt{mnt(x - \epsilon)}]d\epsilon$$

where ϵ is a variable used only for the integration and I_0 is the Bessel function of zero order for an imaginary argument. Similarly,

$$b = g(x)e^{-mt} - e^{-nx-mt} \int_0^x e^{n\epsilon}\, g(\epsilon) \sqrt{\frac{mnt}{x - \epsilon}}\, iI_1[2\sqrt{mnt(x - \epsilon)}]d\epsilon$$

where I_1 is the Bessel function of the first order. Nusselt does not give a derivation for the case where the initial concentration in the solid is uniform and the concentration in the entering fluid varies; however, it may be deduced from his treatment that, if concentrations are measured from this initial concentration and $c = h(t)$ represents any arbitrary change in the concentration of the entering fluid with time, then

$$b = me^{-nx-mt} \int_0^t e^{m\epsilon}\, h(\epsilon) I_0[2\sqrt{mnx(t - \epsilon)}]d\epsilon$$

$$c = \frac{h(t)e^{-nx}}{k} - \frac{e^{-mt-nx}}{k} \int_0^t e^{m\epsilon}\, h(\epsilon) \sqrt{\frac{mnx}{t - \epsilon}}\, iI_1[2\sqrt{mnx(t - \epsilon)}]d\epsilon$$

These formulas can be evaluated by graphical integration for any values of x and t, even when the functions g and h are represented by curves for which no equations are available. They may be used for the case of heat transfer, the quantities b and c being heat contents in that case. The quantity a, the heat transfer coefficient, must be expressed in terms of heat content difference rather than temperature difference, as is usual.

In his derivation, Nusselt assumes that the solute contained in the fluid in the pores is negligible. However, this restriction may be removed by placing t in the formulas by t', equal to $t - (\alpha x/s)$.

Walter (*25*) gave a similar derivation (based on constant feed composition and uniform initial distribution in the solid) and discussed some approximations which should simplify calculations.

Nusselt also considered the case where there is a gradient in concentration between the inside and the outside of the grains, and developed a stepwise method of solution, too elaborate to reproduce here and of doubtful utility. Wicke (*28*) also discussed this case, without giving any directly applicable solution.

Saunders and Ford (*18*) and Tsukhanova and Shapatina (*23*) considered the heat transfer case as discussed by Furnas; they introduced the properties of the fluid, which determine the heat transfer, into the dimensionless quantities involved. This, however, does not alter the theory substantially.

As might be expected, where the rate of transfer is high relative to the rate of flow, the results in the case discussed approach the sharp boundaries characteristic of the equilibrium case; as the transfer rate decreases, the boundary becomes progressively blurred. This may be illustrated by the curves of Figure 3, selected from those of Furnas. It may be pointed out that qualitatively the equations of subsequent sections lead to similar curves.

In addition to the treatments already discussed, there is a considerable body of work on the case of regenerators for heat transfer, where the regular alternation of hot gas and air results in a final state in which the cycles repeat themselves without change. Mathematical developments leading to exact solutions and approximations suitable for design are both available, but will not be analyzed here (*10*).

ZEOLITE CASE. Thomas (*21*) considered the case of a uniform solid base exchange material traversed by a solution (whose entering composition is constant) containing an exchangeable cation. He assumes that the rate of transfer of the cation to the solid from the solution is proportional to

$$r_1(w - b)c - r_2(c_0 - c)$$

where r_1 and r_2 are the rates of the forward and reverse exchange reactions, respectively, and w is the initial exchange capacity of the zeolite. He finds that:

$$\frac{c}{c_0} = \frac{I_0(2\sqrt{r_1r_2DE}) + e^{r_1D}\int_0^{r_1D} e^{-\epsilon}\, I_0(2\sqrt{r_2E\epsilon})d\epsilon}{I_0(2\sqrt{r_1r_2DE}) + e^{r_1D}\int_0^{r_1D} e^{-\epsilon}\, I_0(2\sqrt{r_2E\epsilon})d\epsilon + e^{r_1E}\int_0^{r_1E} e^{-\epsilon}\, I_0(2\sqrt{r_2D\epsilon})d\epsilon}$$

where $D = c_0(t - \alpha x/s)$; $E = mxw/s$

A similar formula applies to b. Thomas points out that the formulas can be evaluated by series expansions.

CASES OF IRREVERSIBLE REACTION. Several authors have discussed cases in which the reverse reaction is negligible in amount. Bohart and Adams (*2*) who were interested in the adsorption of chlorine on charcoal, and Walter (*25*), who was concerned with cases such as the zeolites where a chemical reaction occurs, assume that the rate of material transfer is proportional to $(w - b)c$. Bohart and Adams found that, assuming the usual constant input composition and uniform initial composition in the solid,

$$\frac{c}{c_0} = \frac{e^{r_1c_0t}}{e^{r_1c_0t} - 1 + e^{\frac{r_1wx}{s}}} \qquad \frac{b}{w} = \frac{1 - e^{r_1c_0t}}{e^{r_1c_0t} - 1 + e^{\frac{r_1wx}{s}}}$$

Walter gave a similar expression for b/w.

Du Domaine, Swain, and Hougen (*7*) assumed that the rate of material transfer is proportional to $(w - b)^2c$. The equation which they derived can be evaluated only by trial and error. However, they provided charts by means of which a solution can readily be found, once certain dimensionless quantities are computed.

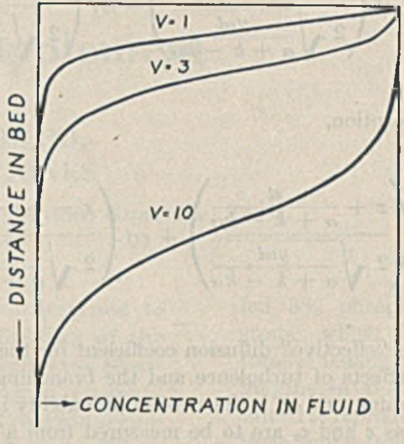

Figure 3. Solid Initially Free of Adsorbate, with Solid Containing Adsorbate Added at Top of Bed

Isotherm linear, equilibrium not attained, V = volume of solvent passed

CASE OF CONSTANT PATTERN. When a solute exhibiting the usual type of isotherm is being adsorbed from a uniform solution on a bed initially free from solute, the curvature of the isotherm tends to produce a sharp boundary, whereas the finite rate of material transfer tends to blur the boundary. Under these circumstances the boundary will, after a certain time, assume a fixed gradient pattern, which travels down the column of solid without substantial change. Wicke discussed this situation, and showed that throughout the bed the concentration on the solid is proportional to the concentration in the liquid at the same time and place. Assuming that the rate of transfer is proportional to the degree of departure from equilibrium at each point, he presents a graphical method for computing the gradient pattern, given the isotherm and the last-mentioned proportionality factor.

Mecklenburg (*13*) also made use of this concept to correlate the departure of an adsorption bed from ideal behavior with known quantities. Specifically, if c_x is the threshold concentration in the effluent at which a gas mask becomes useless, then an actual gas mask adsorption layer will be equivalent to an ideal gas mask (with perfectly sharp break) which is shorter by a quantity equal to

$$Zs\left(\ln \frac{c_0 - c'}{c - c'} - \frac{c_0}{c - c'}\right)$$

where c' is the concentration in the solvent corresponding to equilibrium with the actual concentration on the solid, and Z is a function of certain properties of the adsorbent layer, which in practice is determined empirically.

EFFECT OF LONGITUDINAL DIFFUSION

Almost all workers in the field have assumed that the effect of axial diffusion is negligible, and there is little evidence that this type of diffusion is a factor in the results obtained. However, Wicke made a careful analysis of the mechanism of axial mixing, and also reported that in one set of experiments certain results are to be attributed to this cause. He derived a formula for the case of a linear isotherm and uniform initial conditions in solution and solid. He found that for adsorption,

$$\frac{c}{c_0} = \frac{1}{2}\left[2 - erf\left(\frac{x + \dfrac{st}{\alpha + k - k\alpha}}{2\sqrt{\dfrac{y\alpha l}{\alpha + k - k\alpha}}}\right) - erf\left(\frac{x - \dfrac{st}{\alpha + k - k\alpha}}{2\sqrt{\dfrac{y\alpha l}{\alpha + k - k\alpha}}}\right)\right]$$

while for desorption,

$$\frac{c}{c_0} = \frac{1}{2}\left[erf\left(\frac{x + \dfrac{st}{\alpha + k - k\alpha}}{2\sqrt{\dfrac{y\alpha l}{\alpha + k - k\alpha}}}\right) + erf\left(\frac{x - \dfrac{st}{\alpha + k - k\alpha}}{2\sqrt{\dfrac{y\alpha l}{\alpha + k - k\alpha}}}\right)\right]$$

where y is an "effective" diffusion coefficient for the solute, embracing the effects of turbulence and the branching of streams around the grains, and *erf* is the error or probability integral. In these formulas c and c_0 are to be measured from a level in the linear region of the isotherm, so that $b = kc$.

CONCEPT OF THEORETICAL PLATES

While the concept of a theoretical plate has generally been defined with reference to countercurrent operations, Martin and Synge (*12*) applied it to percolation. They defined the height equivalent to a theoretical plate as the distance along the column of solid between the level at which c has a particular value and the point at which b has a value corresponding to equilibrium with the particular value of c. Justification for this mode of treatment must rest on proof that the height thus defined is reasonably constant for a given fluid system, solid, and rate of feed. In the heat transfer case it can be shown that this condition is realized, and that one of the dimensionless quantities employed by Furnas, axk/s, is in fact approximately equivalent to the number of theoretical plates between the top and the point x. This may be verified by examining the curves given by Furnas. Whether the plate concept is applicable in other cases will require further study.

Martin and Synge made use of the plate concept to study a special case, with linear isotherm, in which all the solute is adsorbed on the top layer of solid at the beginning and then washed down with solvent. The equations are given in the original article (*12*). Consden, Gordon, and Martin (*5*) extended the theory to a flat adsorber, as in the case of a spot of solution on filter paper.

EXPERIMENTAL WORK

While review of the experimental data is beyond the scope of this paper, the literature is so scattered that the following summary of papers which have been encountered may be useful. This summary is not to be considered exhaustive.

Data on heat transfer from gas to solid have been presented by Furnas (*8*), Saunders and Ford (*18*), and Tsukhanova and Shapatina (*23*). Myers, Eastes, and Urquhart (*14*), and Du Domaine, Swain, and Hougen (*7*) studied water softening. Bohart and Adams (*2*) and Schilow, Lepin, and Wosnessensky (*19*) adsorbed chlorine on charcoal. Wicke (*28*) adsorbed carbon dioxide on charcoal. Mecklenburg (*13*) describes experiments adsorbing chloropicrin on charcoal. Ponndorf and Knipping (*17*) adsorbed water and acetone vapor on silica and on charcoal. Weil-Malherbe (*26*) studied benzopyrene, dissolved in hydrocarbon solvents, on silica and on alumina. Cassidy (*3*) and Cassidy and Wood (*4*) adsorbed lauric and stearic acids on carbon and silica gel. Martin and Synge (*12*) adsorbed amino acids dissolved in chloroform on silica gel soaked with water.

PRESENT STATUS

At the present time theory is ahead of experimental work in this field. The equilibrium theory of the percolation of multiple solutes is not well worked out, but it would seem that usable generalizations are in sight. On the other hand, very little experimental information is available on the equilibrium relations when several solutes are present. Until such information is available, the case of many solutes in one solvent, as in the decolorization of oil or sirup, cannot be calculated.

In cases where the transfer rates affect the result, the various cases which have been worked out theoretically should provide a basis for reasonable approximations in almost any case for a single solute. But all the equations presented contain rate quantities, the values of which cannot be predicted at present. The experimental material, though considerable in the aggregate, is far too scattered to permit any useful correlations to be made.

For more than one solute, the effect of rate has hardly been studied at all, either theoretically or experimentally.

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LITERATURE CITED

(1) Anzelius, A., *Z. angew. Math. Mech.*, 6, 291–4 (1926).
(2) Bohart, G. S., and Adams, E. Q., *J. Am. Chem. Soc.*, 42, 523 (1920).
(3) Cassidy, H. G., *Ibid.*, 62, 3076 (1940).
(4) Cassidy, H. G., and Wood, S. E., *Ibid.*, 63, 2628 (1941).
(5) Consden, R., Gordon, A. H., and Martin, A. J. P., *Biochem. J.*, 38, 224 (1944).
(6) DeVault, D., *J. Am. Chem. Soc.*, 65, 532 (1943).
(7) Du Domaine, J., Swain, R. L., and Hougen, O. A., Ind. Eng. Chem., 35, 546 (1943).
(8) Furnas, C. C., Bur. Mines, *Bull.* 361 (1932).
(9) Glückauf, E., *Nature*, 156, 205, 571 (1945).
(10) Hausen, H., *Z. angew. Math. Mech.*, 9, 173–200 (1929) and 11, 105–14 (1931); Lubojatzky, E., *Metall u. Erz*, 48, 205–14 (1931); Rummel, K., *J. Inst. Fuel*, 4, 160–74 (1931); Rummel and Schack, *Arch. Eisenhüttenw.*, 2, 473–80, 481–6 (1929); Schmiedler, W., *Z. angew. Math. Mech.*, 8, 385–93 (1928).
(11) Le Rosen, A. L., *J. Am. Chem. Soc.*, 64, 1905 (1942); 67, 1683 (1945).
(12) Martin, A. J. P., and Synge, R. L. M., *Biochem. J.*, 35, 1358 (1941).
(13) Mecklenburg, W., *Z. Elektrochem.*, 31, 488 (1925).
(14) Myers, R. J., Eastes, J. W., and Urquhart, D., Ind. Eng. Chem., 33, 1270 (1941).
(15) Nusselt, W., *Z. Ver. deut. Ing.*, 71, 85 (1927).
(16) Offord, A. C., and Weiss, J., *Nature*, 155, 725; 156, 570 (1945).
(17) Ponndorf, W., and Knipping, H. W., *Beitr. Klin. Tuberk.*, 68, 751 (1928).
(18) Saunders, O. A., and Ford, H., *J. Iron Steel Inst.*, 141, 291P (1940).
(19) Schilow, N., Lepin, L., and Wosnessensky, S., *Kolloid-Z.*, 49, 288 (1929).
(20) Schumann, T. E. W., *J. Franklin Inst.*, 208, 405 (1929).
(21) Thomas, H. C., *J. Am. Chem. Soc.*, 66, 1664 (1944).
(22) Tiselius, A., *Arkiv Kemi, Mineral. Geol.*, 14B (22), 32 (1941).
(23) Tsukhanova, O. A., and Shapatina, E. A., *Bull. Acad. Sci. U.R.S.S., Class Sci. Tech.*, 1943, 62.
(24) Walter, J. E., *J. Chem. Phys.*, 13, 229 (1945).
(25) *Ibid.*, 13, 332 (1945).
(26) Weil-Malherbe, H., *J. Chem. Soc.*, 1943, 303.
(27) Weiss, J., *Ibid.*, 1943, 297.
(28) Wicke, E., *Kolloid-Z.*, 86, 307 (1939); 93, 129 (1940).
(29) Wilson, J. N., *J. Am. Chem. Soc.*, 62, 1583 (1940).

Presented before the Eleventh Annual Chemical Engineering Symposium (Adsorption and Ion Exchange) held under the auspices of the Division of Industrial and Engineering Chemistry, American Chemical Society, at Columbia University, New York, under the title "Recent Developments in the Theory of Percolation and Related Processes".

FUSED TRICALCIUM PHOSPHATE FERTILIZER

Possible Animal Feed Supplement

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Experiments described in this paper were designed to distinguish between the physiological availability of the component phosphorus in a TVA fused tricalcium phosphate and the toxicity of the unremoved fluorine. Growth, storage of phosphorus in white rats, and reproduction through several generations were the criteria. When fused tricalcium phosphate of no more than 0.3% fluorine content was fed to the animals over a 90-day period as 1% of their diet, to provide a total phosphorus level of 0.2%, they showed normal growth and phosphorus retention. Measured by reproduction through the fourth generation, the fused phosphate, fed in a diet with a total phosphorus level of 0.4%, proved 75 to 93% as effective as a standard material of established phosphorus-feeding value.

THE war period supply of bone meal and other suitable phosphate carriers has been reported as less than the estimated requirements for domestic livestock feeding (*5*). Stimulated by the need for new sources of phosphorus in livestock feeding, workers at The University of Tennessee have been studying the nutritional utility of fused tricalcium phosphate, the Tennessee Valley Authority product intended for soil fertilization. This material, which carries not more than 0.4% fluorine, is the result of a thermal process by which the fluorapatite of the raw rock is decomposed and 85% or more of the component fluorine is expelled. The molten draw is quenched and sized to specification. Complete expulsion of fluorine is deemed unnecessary, and possibly not desirable, when the fused tricalcium phosphate is to be used as a fertilizer (*7*). If the phosphorus of this product proves effective as a nutritional supplement, the question arises as to how much fluorine can be allowed in the product without attendant menace to normal growth and reproduction. The new product has been designated and defined as "fused tricalcium phosphate, a product composed chiefly of the alpha form of the compound represented by the formula $Ca_3(PO_4)_2$" (*6*).

In the fourth report of the Committee on Animal Nutrition of the National Research Council, Mitchell (*8*) recommended that the admissible levels of fluorine in a mineral mixture for cattle should be considered tentatively as 0.13%, and in the total dry feed as 0.003% (30 parts per million). He considered 0.01% fluorine (100 p.p.m.), dry basis, to be approximately the borderline content for phosphates fed to swine, sheep, and cattle. This recommendation was made on the basis of experimental work done chiefly with raw rock phosphate which contains about 3.5% fluorine. The committee states that these levels are tentative and that additional studies are needed.

Phillips, Hart, and Bohstedt (*11*) reported typical fluorine toxicosis in dairy cows when raw rock phosphate was fed as 0.625% of the grain mixture. Phillips *et al.* (*10*) state that no injurious effects appeared for the first three years of the experiment in which rock phosphate was fed as 0.625% of the grain mixture, but that during the next two years there was loss in weight, appetite, and milk production.

Tolle and Maynard (*12*) found that a phosphatic limestone containing 0.92% fluorine was utilized as effectively as bone meal in bone formation. They also found that a group of animals fed 3% phosphatic limestone, which furnished a total of 0.03% (300 p.p.m.) fluorine in the diet, continued to reproduce and rear their young from five matings as satisfactorily as did a group receiving ground limestone.

Fraser *et al.* (*3*) found that a high proportion of the phosphorus and calcium of several fused phosphates, containing 0.05 and 0.22% fluorine, was available for the nutrition of the rat; but their experiments were not designed to test the toxicity of the material.

Barrentine, Maynard, and Loosli (*1*) found that a thermally defluorinated phosphate was slightly less efficacious than their calcium phosphate control, at very low levels. When this defluorinated product was used to raise the phosphorus content of the diet to 0.50% or more, the phosphate was as effective as the calcium phosphate in the formation of bone.

Ellis *et al.* (*2*) rate a sample of fused tricalcium phosphate "very good", or 80% as effective as bone meal in animal feeding tests carried out by four collaborating laboratories.

The present experiments were designed to test the suitability of fused tricalcium phosphate fertilizer as a mineral feed supplement for animals. Such suitability involves (*a*) the physiological availability of the phosphorus and (*b*) the toxicity of the component fluorine.

COMPOSITION OF DIETS

For the study of effects of fused tricalcium phosphate during the growing period, rats were given four diets that differed, chiefly in the nature of the carriers of phosphorus and fluorine. The diets were designed to be otherwise identical and adequate in all respects for normal growth and development, except that phosphorus and calcium were brought to levels near the minimum for rapidly growing animals. At this minimal level any lack of availability of the phosphorus in the test product is evident. Phosphorus contents ranged from 0.20–0.24% and calcium contents from 0.30–0.35%, giving Ca/P ratios from 1.4 to 1.7. The diets were modifications of control diet 1, which consisted of the following parts per hundred: lactalbumin 18, starch plus yeast extract 68, Snowdrift vegetable fat 8, Osborne and Mendel (*9*) salt mixture 4, and cod liver oil 2. Diet 2 was the same as the control except that phosphorus and calcium were omitted from the salt mixture; the fused tricalcium phosphate was the chief source of these elements and constituted about 1% of the total diet. The fused tricalcium phosphate products used contained

Table I. Calculated Fluorine Content of Diets

Diet	F Content, P.P.M.
Osborne and Mendel salt mixt.	11
Dicalcium phosphate	13
Fused phosphate, 0.04% F	15
Fused phosphate, 0.2% F	32
Fused phosphate, 0.3% F	43
Fused phosphate, 0.55% F	67

0.04, 0.2, 0.3, or 0.55% fluorine, and all were 80-mesh screenings. In diet 3, where dicalcium phosphate was the chief source of phosphorus, the salt mixture was modified so that its phosphorus and calcium contents were approximately the same as those of the other diets. Diet 4 was the same as the control except that sufficient sodium fluoride was added to make the fluorine content identical with the percentages of fluorine furnished by the tricalcium phosphate in the variations of diet 2.

Diets 1 and 2 were compared in the breeding experiments. Two variants of fused tricalcium phosphate were used in diet 2 to determine whether products carrying 0.2 and 0.3% fluorine can be fed to an animal throughout life, and to succeeding generations, without vitiation of normal reproduction. To distinguish between the effects of fluorine toxicity and phosphorus deficiency, the comparisons were made at two phosphorus levels. At one level the phosphorus content was made 0.2% of the total diet, approximately the minimum for normal growth to maturity if the phosphorus supplied is readily available; the second level of 0.4% of the total diet was intended to assure a supply of phosphorus adequate for growth, reproduction, and lactation.

The fluorine content of every diet was calculated from the amounts present in the salt mixture and in the mineral supplements, as shown in Table I. Fluorine analyses of four of the total diets were made by G. A. Shuey of this station, with the following results: 15 p.p.m. for the control diet containing Osborne and Mendel salt mixture, 13 p.p.m. for that containing dicalcium phosphate, 37 p.p.m. for that containing fused tricalcium phosphate of 0.3% fluorine content, and 43 p.p.m. for the one designed to contain a like amount of fluorine in the form of sodium fluoride. The analytical and the calculated values indicate that fluorine of the diets was derived solely from the salt mixture and mineral supplements.

The level of the fused tricalcium phosphate for the experimental diets was chosen so that the mineral supplement would supply the phosphorus necessary to bring the total up to approximately 0.2%, which is the minimal level for normal growth and bone development during the rapid growth of white rats. This meant that about two thirds of the total phosphorus was supplied by the fused tricalcium phosphate, the remainder being present in the lactalbumin and yeast extract of the basal diet. Since all of the phosphates used contained about 13% phosphorus, it was necessary to have them constitute about 1% of the diet in order to furnish the desired total of that element. Incidentally, this is in accordance with the amount of bone meal usually recommended in the feeding of farm animals. Ordinarily about 1% bone meal is added to the grain mixture; this would be about 0.8% of the total dry feed, assuming that the grain mixture constitutes 75% of the ration.

Previous experiments showed that the phosphorus in the control diet supplied by the Osborne and Mendel salt mixture was in a form readily available for normal growth and development. The group of rats fed this diet, therefore, served as a criterion by which to compare availability of the phosphorus supplied as fused tricalcium phosphate and as dicalcium phosphate. The diet with dicalcium phosphate was included so that the fused tertiary phosphate could be compared with the binary phosphate that had proved effective in the feeding of farm animals.

EXPERIMENTAL ANIMALS

In the growth experiments, five rats of the same sex, age, and weight, and of identical nutritional and hereditary history, were placed on each of the four comparable diets. The animals were started on experiment at 30 to 31 days of age. Feeding was continued for 30 days, the period of most rapid growth, but was extended to 60 and 90 days in which case additional series of five rats each were fed 0.2 and 0.3% fluorine phosphates. A quadruplicate feeding technique was used for equalization of food consumption to minimize the variable due to individual differences in appetite. Body weights were recorded and the carcasses analyzed for phosphorus.

Three breeding experiments were set up at the following levels of phosphorus and fluorine: (*a*) 0.2% fluorine phosphate and controls at the 0.2% phosphorus level, (*b*) 0.2% fluorine phosphate and controls at the 0.4% phosphorus level, and (*c*) 0.3% fluorine phosphate and controls at the 0.4% phosphorus level. At each given phosphorus and fluorine level (for example, 0.2% P and 0.2% F), four parent breeding lots were started, each lot consisting of two males and three females. Two lots were fed the control diet and two received the phosphate diet, the rats on each control diet being matched with respect to litter and weight with those of the corresponding phosphate diet. From the young of each of the four parent lots, two breeding lots were made up; and from the young of each of these second generation lots, one breeding lot was set up. The young of the third generation (that is, fourth generation rats) were weighed and killed at weaning. In the case of all breeding lots, the females were mated repeatedly over

Table II. Physiological Availability of Phosphorus Fed as Fused Tricalcium Phosphate and as Osborne and Mendel Salt Mixture

		Indications from Growth				Indications from Phosphorus Storage			
		Growth, grams				P stored, grams			
F in phosphate, %	Duration of expt., days	Control	Fused phosphate	Probability	Significance of difference	Control	Fused phosphate	Probability	Significance of difference
0.04	30	103	103	..	No difference	0.479	0.421	0.1	Not significant
0.2	30	100	97	0.5	Not significant	0.470	0.366	0.01	Significant
0.2	60	156	150	0.5	Not significant	0.780	0.683	>0.05	Not significant
0.2	90	196	197	0.5	Not significant	1.059	1.042	0.5	Not significant
0.3	30	110	95	0.01	Significant	0.488	0.382	0.01	Significant
0.3	60	154	152	0.5	Not significant	0.916	0.814	0.01	Significant
0.3	90	185	181	0.5	Not significant	1.184	1.143	0.1	Not significant
0.55	30	112	98	0.01	Significant	0.464	0.332	0.01	Significant

Table III. Physiological Availability of Phosphorus Fed as Fused Tricalcium Phosphate and as Dicalcium Phosphate[a]

		Indications from Growth				Indications from Phosphorus Storage			
		Growth, grams				P stored, grams			
F in phosphate, %	Duration of expt., days	Fused phosphate	Dicalcium phosphate	Probability	Significance of difference	Fused phosphate	Dicalcium phosphate	Probability	Significance of difference
0.04	30	103	105	0.5	Not significant	0.421	0.435	0.5	Not significant
0.2	30	97	90	0.1	Not significant	0.366	0.407	>0.05	Not significant
0.2	60	150	145	0.5	Not significant	0.683	0.695	0.5	Not significant
0.2	90	197	197	...	No difference	1.042	1.057	0.5	Not significant
0.3	30	95	98	0.1	Not significant	0.382	0.411	0.1	Not significant
0.3	60	152	143	0.05	Significant	0.814	0.831	0.5	Not significant
0.3	90	181	180	0.5	Not significant	1.143	1.100	0.01	Significant

[a] Contained 0.04% fluorine.

TABLE IV. PHYSIOLOGICAL AVAILABILITY OF THE PHOSPHORUS FED IN THE CONTROL DIET ALONE AND WITH ADDED FLUORINE

		Indications from Growth				Indications from Phosphorus Storage			
		Growth, grams				P stored, grams			
F equivalent[a], %	Duration of expt., days	Control	Control + F	Probability	Significance of difference	Control	Control + F	Probability	Significance of difference
0.2	30	100	97	0.5	Not significant	0.470	0.447	0.1	Not significant
0.2	60	156	155	0.5	Not significant	0.780	0.803	0.5	Not significant
0.2	90	196	200	0.5	Not significant	1.059	1.109	0.1	Not significant
0.3	30	110	109	0.5	Not significant	0.488	0.492	0.5	Not significant
0.3	60	154	157	0.5	Not significant	0.916	0.928	0.5	Not significant
0.3	90	185	183	0.5	Not significant	1.184	1.186	0.5	Not significant
0.55	30	112	108	0.5	Not significant	0.464	0.467	0.5	Not significant

[a] Equivalent to that in the corresponding phosphate.

TABLE V. EFFECT OF TOTAL PHOSPHORUS OF THE DIET ON REPRODUCTION

	Control		Fused Tricalcium Phosphate	
	No. born	No. raised	No. born	No. raised
Control *vs.* 0.2% F fused tricalcium phosphate				
Minimal P, 0.2% in diet	891	473	450	290
Adequate P, 0.4% in diet	978	691	761	445
Increase	87	218	311	155
% increase	10	46	69	53
Control *vs.* 0.3% F fused tricalcium phosphate				
Minimal P, 0.2% in diet	416	205	334	230
Adequate P, 0.4% in diet	549	308	592	414
Increase	133	103	258	184
% increase	32	50	77	80

a period of one year and three months (unless death by accident intervened); this is nearly the entire reproductive period in the white rat. All young were given serial numbers and weighed at birth and at weaning, at which time those not used for breeding were killed. This procedure involved sixty breeding lots, with repeated matings throughout the reproductive period. In a digest of the breeding results, differences caused by accidental deaths of mothers were eliminated in an effort to afford a clear and fair picture of those effects which might be attributed to the use of fused tricalcium phosphate. For example, when a female in the control group died before the end of the breeding period, her length of life was noted and a female in the corresponding breeding lot receiving fused phosphate was given credit only for the young born during a like period.

Student's *t*-test was used in statistical analysis of the data to establish the significance of differences in results obtained from the various diets. The formula used was that given by Goulden (*4*) for paired variates. The term "probability" used in Tables II, III, and IV represents the frequency with which the difference between two mean values may be due to chance alone and not to any real difference resulting from the diets. When the probability is 0.05 or less, the difference between the means may be considered significant.

PHYSIOLOGICAL AVAILABILITY OF PHOSPHORUS

To compare the physiological availability of the phosphorus supplied as fused tricalcium phosphates with that of the Osborne and Mendel salt mixture, the results were subjected to statistical analysis, Table II. The data indicate: (*a*) The phosphorus of the fused tricalcium phosphate of 0.04% fluorine content is as effective for growth and phosphorus storage as that of the Osborne and Mendel salt mixture. (*b*) The phosphorus of the materials of higher fluorine content is not quite so effective as that of the Osborne and Mendel salt mixture. (*c*) Over the 60- and 90-day periods the slower growth rate and concomitant decrease in need for phosphorus gradually offset the differences in effectiveness. Hence the animals fed the 0.3% fluorine phosphate diet over a 90-day period show no significant differences in comparison with control animals.

Dicalcium phosphate of low fluorine content is admittedly a safe and effective mineral supplement for animal feeding, and therefore was used as a standard of comparison for the fused products of different fluorine content. The results (Table III) indicate that the specimens of fused tricalcium phosphate tested were as effective as the dicalcium phosphate of 0.04% fluorine content. Moreover, any significant differences in the experimental results were in favor of fused tricalcium phosphate.

DISTINCTION BETWEEN FLUORINE EFFECT AND INADEQUACY OF PHOSPHORUS. The data of Table IV indicate that sodium fluoride exerted no adverse effect upon growth or upon phosphorus storage when it was fed in amounts corresponding to those introduced through fused tricalcium phosphate with a fluorine content as great as 0.55%. Hence, the differences noted in Table II may have been caused by a part of the phosphorus of the fused tricalcium phosphate being present in a form not readily assimilable, rather than by a toxic effect of fluorine.

REPRODUCTION

EFFECT OF TOTAL DIETARY PHOSPHORUS. Table V compares the numbers of young born from and those raised by animals fed phosphorus at two levels, designated as minimal and adequate. Obviously, the increase in phosphorus level from 0.2 to 0.4% resulted in an increase in numbers born and numbers raised to weaning, whether the animals had been fed the control diet or one that contained fused tricalcium phosphate of either 0.2 or 0.3% fluorine content. The mean increase in numbers born for the control diets was 21%; for the phosphate diets, 73%. The mean increases in numbers of rats raised were 48% for the control diets and 67% for the phosphate diets. This demonstrates that an adequate level of total phosphorus is necessary before poor reproductive performance can be ascribed to fluorine toxicity.

EFFECT OF FUSED TRICALCIUM PHOSPHATE. The data of Table VI set forth the reproductive performances induced by the two samples of fused tricalcium phosphate of different fluorine content and by the Osborne and Mendel salt mixture. Since the animals represented by the results in part *A* had been on experiment longer than those in parts *B* and *C*, the comparison between the groups is made on the basis of percentages rather than total numbers.

At the phosphorus level deemed the minimum for growth, the animals on the 0.2% fluorine phosphate diet produced 67% as

TABLE VI. FUSED TRICALCIUM PHOSPHATE COMPARED WITH OSBORNE AND MENDEL SALT MIXTURE AS A SOURCE OF PHOSPHORUS FOR REPRODUCTION

	No. Born	No. Raised
A. Minimal phosphorus		
Control (O. & M. salt mixture)	844	490
0.2% F fused tricalcium phosphate	568	391
$\left(\frac{\text{Phosphate}}{\text{Control}}\right) 100$	67%	80%
B. Adequate phosphorus		
Control (O. & M. salt mixture)	909	641
0.2% F fused tricalcium phosphate	770	479
$\left(\frac{\text{Phosphate}}{\text{Control}}\right) 100$	85%	75%
C. Adequate phosphorus		
Control (O. & M. salt mixture)	623	377
0.3% F fused tricalcium phosphate	488	350
$\left(\frac{\text{Phosphate}}{\text{Control}}\right) 100$	78%	93%

many young and raised 80% as many as those on the control diet. This performance tends to support the growth data in that the phosphorus of the tricalcium phosphate was less available than that in the Osborne and Mendel salt mixture. At the higher phosphorus level the animals on the 0.2% fluorine phosphate produced 85% as many young as those on the control diet and raised 75% as many. The 85% value would give this phosphate material a rating of "very good" in relation to the Osborne and Mendel salt mixture when appraised according to the method of Ellis *et al.* (*2*), who rated as very good a phosphate that was 80% as effective as bone meal, when growth and bone ash were the criteria. At the adequate phosphorus level, the animals on the 0.3% fluorine phosphate diet produced 78% as many young as those on the control diet and raised 93% as many. Apparently when reproduction is the basis of comparison, the 0.3% fluorine fused phosphate is a satisfactory source of phosphorus to rats.

SUMMARY AND CONCLUSIONS

1. Eighty-mesh fused tricalcium phosphate, containing 0.2 to 0.55% fluorine, was fed at a minimal dietary phosphorus level to white rats during the 30-day period of their most rapid growth. This was found to be less assimilable than inorganic phosphate of the standard Osborne and Mendel salt mixture. The difference in degree of assimilability was not manifest when the phosphorus demand of the growing animal was less—that is, during the 60- and 90-day periods. The difference was less apparent also when the level of total phosphorus was raised from 0.2 to 0.4% in the breeding experiments. With such increases in phosphorus content, there were increases of 53 to 80% in numbers born and raised on the phosphate diets.
2. When sodium fluoride was introduced into the diet to provide a fluorine content equal to that fed as fused tricalcium phosphate, there was no detrimental effect upon growth of the rats to maturity or upon their bodily retention of phosphorus.
3. The 80-mesh fused tricalcium phosphate containing as much as 0.3% fluorine proved as efficacious as the precipitated dicalcium phosphate in the promotion of rat growth to maturity and in phosphorus storage.
4. Eighty-mesh fused tricalcium phosphate of 0.2 or 0.3% fluorine content was fed at a 1% level, and the phosphorus content of the diet was brought to 0.4%. The fused material proved to be 78–85% as effective as the phosphate of an Osborne and Mendel salt mixture when effectiveness was measured by reproduction, and 75–93% when effectiveness was measured by lactation.
5. The data obtained indicate that fused tricalcium phosphate of 80-mesh, containing not more than 0.3% fluorine, was virtually as effective as the control phosphate of the Osborne and Mendel salt mixture, when evaluated by rat growth and body storage of phosphorus during a 90-day period. When judged by reproduction and lactation, the fused phosphate proved from 75 to 93% as good as the salt mixture. The results also indicate that nutritional ineffectiveness of a phosphatic product should not be attributed to its fluorine content until the factor of low phosphate availability has been taken into account.

LITERATURE CITED

(1) Barrentine, B. F., Maynard, L. A., and Loosli, J. K., *J. Nutrition*, 27, 35–42 (1944).
(2) Ellis, N. R., Cabell, C. A., Elmslie, W. P., Fraps, G. S., Phillips, P. H., and Williams, D. E., *J. Assoc. Official Agr. Chem.*, 28, 129–42 (1945).
(3) Fraser, H. F., Hoppe, T. C., Sullivan, J. H., and Smith, E. R., IND. ENG. CHEM., 35, 1087–90 (1943).
(4) Goulden, C. H., "Methods of Statistical Analysis", pp. 42, 267, New York, John Wiley & Sons, 1939.
(5) Jacob, K. D., *Feedstuffs*, 16, 18–32 (1944).
(6) *J. Assoc. Official Agr. Chem.*, 28, 38 (1945).
(7) MacIntire, W. H., Winterberg, S. H., Hatcher, B. W., and Palmer, George, *Soil Sci.*, 57, 425–42 (1944).
(8) Mitchell, H. H., Natl. Research Council, *Reprint Circ. Series* 113 (1942).
(9) Osborne, T. B., and Mendel, L. B., *J. Biol. Chem.*, 37, 557–601 (1919).
(10) Phillips, P. H., Bohstedt, G., Fargo, J. M., Hart, E. B., and Halpin, J. G., Wis. Agr. Expt. Sta., *Bull.* 428, 9–12 (1934).
(11) Phillips, P. H., Hart, E. B., and Bohstedt, G., *Ibid.*, *Research Bull.* 123 (1934).
(12) Tolle, Chester, and Maynard, L. A., Cornell Univ. Agr. Expt. Sta., *Bull.* 530 (1931).

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VITAMIN CONTENT OF PEAS

Effect of Freezing, Canning, and Dehydration

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THE objective of this investigation was to determine, at the time of serving, some of the nutritive levels of peas. Direct comparisons were made on identical lots at the same stage of maturity, preserved by canning, freezing, and dehydration. Eight varieties of sweet peas were grown at the Maryland station during 1944. The plots were large enough so that they could be harvested with commercial equipment and threshed in a standard viner. The shelled peas were thoroughly mixed at the viner and then separated into the various sieve sizes. In all cases the prevailing sieve size typical for the variety was used for processing and for vitamin determinations. The peas were thoroughly washed, cooled, and processed within 2 hours. The variety Dark Podded Thomas Laxton was used in comparative studies of the three methods of preservation. Large samples of No. 4 sieve peas of this variety were taken from the same lot for freezing, canning, and dehydrating.

Blanching studies conducted several years ago at this station indicated that a better quality of frozen peas was obtained by blanching at 190° F. than in boiling water, and this temperature was selected for the 1944 studies. Twenty-five to thirty pounds of peas were blanched in a wire basket in 30 gallons of water in a steam-jacketed kettle where the temperature could be accurately controlled. The peas were agitated during blanching and were then cooled immediately in cold running water.

Some lots of peas were blanched with steam. A special steam blanching box with a water seal made it possible to obtain a temperature of 214° F. in the center of 30 pounds of peas in a wire basket within 30 seconds. All steam blanching treatments were made at 214° F.

Samples for freezing were separated into floaters and sinkers in a 13% brine after blanching in water at 190° F. for various times. The peas were washed and packed in one-pound, mois-

Comparable lots of eight varieties of peas were canned, frozen, and dehydrated, and ascorbic acid was determined on the product after 6-month storage, before and after cooking. There was considerable variation in ascorbic acid levels among varieties, and an interaction between blanching time and variety. Canned peas (considering both peas and liquor) had a higher ascorbic acid content than frozen or dehydrated peas after 6- or 9-month storage. Dehydrated peas contained about one third as much ascorbic acid as frozen or canned peas; when stored under carbon dioxide, they had a higher level than those stored under air or in vacuum. Ascorbic acid retention (dry weight basis) of the stored products (after cooking), compared with the original content, was 58% for the canned material, 53% for the frozen, and 19% for the dehydrated. The carotene content of the frozen peas was higher than that of the canned or dehydrated lots. The frozen and canned peas retained about two thirds and the dehydrated peas about one half of the original thiamine content. Prolongation of the storage period from 6 to 9 months resulted in further appreciable loss of ascorbic acid from the frozen and canned peas.

ture- and vaporproof containers and were frozen at −25° F. with an air blast of 1000 feet of air per minute. The samples were stored at this temperature for one month and at 0° F. for the balance of the storage period.

Peas for canning were blanched for 3 minutes in hot water (190° F.), separated in 13% brine, cooled, and filled into No. 1 cans. The peas in the can were covered with boiling sugar-salt solution (25 pounds of sugar and 15 pounds of salt in 100 gallons of water); the cans were promptly sealed on a semiautomatic closing machine and processed for 25 minutes at 245° F.

Table I. Effect of Blanching on Ascorbic Acid Content of Dark Podded Thomas Laxton Peas, before Freezing and after 6 Months of Frozen Storage

Min. of Blanching at 190° F. in Water	Ascorbic Acid						
				Cooked frozen			
	After blanching[a], mg./100 g.	Frozen 6 mo.[a], mg./100 g.	Retention[b], %	Drained peas[a], mg./100 g.	Liquor[c], mg./100 g.	Total, mg./100 g.	Retention[b], %
0	23.5 (81.0)	...	...	...	...	...	...
1	15.4 (80.6)	4.8 (79.9)	19.1	3.2 (82.3)	1.1	4.3	19.6
1.5	18.8 (81.4)	5.2 (80.0)	21.0	4.5 (83.5)	1.7	6.2	30.7
2.0	18.8 (81.9)	12.5 (83.0)	59.3	7.2 (83.6)	3.5	10.7	32.6
2.5		9.4 (82.6)	43.5	5.5 (83.8)	3.0	8.5	42.7
3.0	16.7 (81.2)	8.5 (82.5)	39.5	5.2 (83.5)	2.4	7.6	37.2
3 .0 (steam)	18.3 (82.0)	9.4 (82.0)	42.1	6.7 (83.5)	3.3	10.0	51.9
Av.	17.6 (81.4)	8.3 (81.7)	37.4	5.4 (83.5)	2.5	7.9	39.1

[a] Figures in parentheses indicate per cent moisture.
[b] Calculated on moisture-free basis.
[c] Calculated on basis of drained weight represented by liquor.

Peas for dehydration were likewise separated in brine, after blanching in hot water (190° F.) for 3 minutes, and were then placed on the drying trays at the rate of 1.5 pounds per square foot. Dehydration was accomplished in a two-stage central exhaust tunnel with a temperature in the primary end of 180° F. and 1200 linear feet of air per minute, and were finished at 160° F. in the secondary tunnel.

METHODS OF ANALYSIS

The concensus of the station workers in the northeastern region is that vitamin values should be expressed on the wet basis, and losses in terms of the fresh weight of the original fresh sample. If the purpose is to discover when and where vitamin losses occur, this method has definite advantages, as emphasized by the work of Clifcorn and Heberlein (*2*). However, the purpose of the present study was to determine the actual vitamin content of frozen, canned, and dehydrated peas when a given amount of each was prepared for serving. Since every precaution had been taken to secure typical samples for all three methods of preservation from the same lot of peas, it was believed that the actual content of vitamins in 100 grams of peas prepared for serving would give the fairest evaluation of the effect of the preservation method on the nutritive level.

The data in the tables are presented on both the wet and dry basis, and the moisture content is included for those interested in the loss of soluble solids during processing. The reason for presenting the apparent vitamin retention on a dry weight basis is to facilitate comparison among various processing and storage treatments.

Excess moisture was removed from both the freshly washed and the thawed frozen peas with paper towels before weighing for both moisture and vitamin determinations. Moisture content of all samples was determined in a vacuum oven at 28 inches of vacuum and 70° C. The samples were left in the vacuum oven for 14 hours.

Ascorbic acid was determined by the titration method of Bessey and King (*1*). Moore's method of carotene analysis was used as modified by Moore and Ely (*5*). Thiamine was determined by the method outlined by Conner and Straub (*3*).

One-pound packages of frozen peas were placed in 100 ml. of boiling distilled water and cooked for 8 minutes after boiling was resumed; the cooked peas were drained through a Büchner funnel for 2 minutes, and the liquid portion was saved for analysis. The canned peas were brought to a boil and boiled for 2 minutes; the proportion of liquor to drained peas had been previously determined in order to calculate the quantity of vitamins in the peas and liquor. The dehydrated peas were soaked in distilled water for 20 minutes and then slowly simmered for 35 minutes.

ASCORBIC ACID

Effect of Blanching Time. The retention of ascorbic acid in frozen Dark Podded Thomas Laxton peas, stored 6 months, was determined before and after cooking for various blanching times at 190° F. At this blanching temperature after storage there was a higher level of ascorbic acid in peas at the 2-minute blanch than at either 1 or 1.5 minutes (Table I). In fact there was a much higher ascorbic acid level after 6-month storage in the peas blanched for 3 minutes than in those blanched 1 or 1.5 minutes. This was probably due either to failure of inactivation of enzymes or possibly to regeneration. There was a decline in

Table II. Effect of Blanching Time on Ascorbic Acid Content of Eight Varieties of Frozen Peas in Storage 6 Months

Variety	Ascorbic Acid (Mg./100 G. Wet Wt.) after Water Blanch (190° F.) for:				
	1 min.	1.5 min.	2 min.	2.5 min.	3 min
Thomas Laxton	...	...	10.51	...	11.98
Glacier	...	...	13.94	...	12.94
Teton	4.11	...	11.60	...	8.71
Canner King	13.94	12.92	10.86	...	9.80
Shasta	14.30	13.67	13.72	...	13.22
No. 312	13.93	...	12.09	...	13.10
Dark Podded Thomas Laxton	4.75	5.20	12.47	9.35	8.54
Early Harvest					
Sinkers	...	...	11.57	...	13.20
Floaters	...	...	8.07	...	10.59

TABLE III. ASCORBIC ACID IN EIGHT VARIETIES OF PEAS AFTER 6-MONTH STORAGE

	Fresh at Harvest		Frozen, Not Cooked			Canned, Not Cooked		
Variety	Moisture, %	Ascorbic acid[a]	Moisture, %	Ascorbic acid[a]	Retention, %[b]	Moisture, %[c]	Ascorbic acid[a,d]	Retention, %[b,d]
Glacier	80.4	21.9	81.9	13.9	69.1	82.8	15.7	82.0
Teton	78.3	10.6	78.5	11.6	71.4	81.8	11.0	79.5
Shasta	80.3	22.5	80.4	13.7	61.1	82.9	15.1	77.3
Thomas Laxton	81.3	18.6	81.0	10.5	55.8	83.7	12.7	78.1
Canner King	79.7	20.7	78.2	10.9	49.0	82.7	13.4	76.2
Pride	82.7	26.8	81.3	13.4	46.1	84.3	17.6	72.3
Early Harvest	78.5	17.5	74.2	11.6	55.2	78.8	15.9	91.7
Dark Podded Thomas Laxton	81.0	23.5	83.0	12.5	59.3	84.7	14.1	75.1
			Mean retention, %		58.4			79.0

[a] Milligrams per 100 grams wet weight.
[b] Calculated on moisture-free basis.
[c] Drained peas.
[d] Peas and liquor.

TABLE IV. VITAMIN LEVELS IN DARK PODDED THOMAS LAXTON PEAS AFTER STORAGE AND AFTER COOKING

		Ascorbic Acid Mg./100 G.		Carotene Mg./100 G.		Thiamine, Mg./100 G.	
Treatment	Moisture, %	Wet wt.	Dry wt.	Wet wt.	Dry wt.	Wet wt.	Dry wt.
Fresh, unblanched	81.0	23.5	123.4	...	...	0.317	1.668
Frozen, 6 mo.	83.0	12.5	73.2	0.378	1.98	0.184	1.082
Frozen, cooked (peas and liquor)	73.6	10.7	64.9	...	...	...	...
Canned, 6 mo. (peas and liquor)	84.7	14.1	92.8	0.333	1.80	0.168	1.098
Canned, cooked (peas and liquor)	83.6	11.9	72.0	...	...	...	...
Dehydrated, 6 mo.							
Air pack	5.7	20.8	22.0	1.582	1.68	0.720	0.764
CO_2 pack	5.6	25.3	26.8	...	...	0.825	0.874
Vacuum pack	5.6	23.8	25.2	...	...	0.658	0.697
Dehydrated, cooked							
Air pack (total)	68.2	7.0	21.1	...	...	...	...
CO_2 pack (total)	65.9	7.1	20.5	...	...	...	...
Vacuum pack (total)	69.1	7.6	23.7	...	...	...	...

TABLE V. INFLUENCE OF LENGTH OF STORAGE ON ASCORBIC ACID CONTENT OF FROZEN AND CANNED DARK PODDED THOMAS LAXTON PEAS

	Ascorbic Acid, Mg. per 100 Grams			
	6-month storage		9-month storage	
	Wet wt.	Dry wt.	Wet wt.	Dry wt.
Frozen, uncooked[a]	12.5	73.2	9.89	53.78
Frozen, cooked[b]	10.7	64.9	7.09	35.34
Canned, uncooked[b]	14.1	92.8	11.27	67.80
Canned, cooked[b,c]	11.9	72.0	9.19	61.76

[a] The ascorbic acid content of the original fresh peas was 23.5 wet and 123.4 dry basis.
[b] Drained peas and liquor.
[c] Boiled for 2 minutes.

retention when the blanching time was extended beyond 2 minutes. The 3-minute steam blanch was approximately equal to the 2.5-minute water blanch.

Ascorbic acid determinations on the frozen product after 6-month storage have shown that the effect of blanching time varies with pea variety (Table II). Thus, the 2-minute blanch was optimum for Dark Podded Thomas Laxton and Teton; the 1-minute blanch was optimum for Canner King, Shasta, and No. 312. The 3-minute blanch appeared to be optimum for Thomas Laxton and Early Harvest, although the significance of these differences in ascorbic acid may be unimportant. The fact that the sinkers in a 13% brine showed more retention of ascorbic acid after the 3-minute blanch substantiates the general belief that more mature peas require longer blanch.

There is a tendency among commercial packers to shorten blanching times in an effort to improve quality of frozen vegetables. In some cases overblanching has resulted in products of poorer quality, but these data illustrate the fallacy of using the minimum blanch for products which are to be stored for any length of time. The data on varieties also show that there are certain inherent biological differences among varieties which necessitate studies to determine the optimum blanch for each variety. For this reason the data on minimum blanching times are presented. However, where retention comparisons are made (Table III), only those ascorbic acid values from the 2-minute blanch are used to determine averages.

EFFECT OF VARIETY. Table III shows varietal differences in ascorbic acid in frozen and in canned samples after 6-month storage. The data are presented on both wet and moisture-free bases, and the total solids may be determined from the moisture percentages. The retention was determined on the moisture-free basis of the original ascorbic acid content of the raw product.

The retention of ascorbic acid after 6-month frozen storage varied from 46.1% for Pride to 71.4% for Teton, with an average for the eight varieties of 58.4%. The retention in the drained canned peas after the same storage period varied from 41.0% for Pride to 53.4% for Teton, with an average of 47.4. The total retention of the canned peas (drained peas plus liquor) varied from 72.3% for Pride to 91.7% for Early Harvest, with an average of 79.0. Glacier, containing a high level of ascorbic acid, and Teton, a medium level variety, had high retention in the frozen state. With one exception those varieties which had a high level in the frozen peas likewise had a high level in the canned product.

EFFECT OF PROCESSING METHOD. Ascorbic acid was determined in frozen, canned, and dehydrated samples of Dark Podded Thomas Laxton after 6 months. Analyses were made on the processed products before and after cooking, with the liquor and drained peas analyzed separately in each instance. The dehydrated material included samples packed in air, in carbon dioxide, and under vacuum (Table IV).

The canned peas before additional heating had a higher ascorbic content (14.1 mg. per 100 grams) when both drained peas and liquor were included than the uncooked frozen peas (12.5 mg. per 100 grams). The canned peas and liquor contained about 75% of the original ascorbic acid content after 6-month storage, expressed on a moisture-free basis. The frozen peas contained about 60% of the original content. Part of the difference, on the dry weight basis, can be ascribed to loss of soluble solids in the canned peas.

The authors wish to point out that the ascorbic acid figures presented should not be used by biochemists or nutritionists as measures of biologically active vitamin C, as dehydroascorbic acid was not determined. However, previous work indicated the value of using ascorbic acid to measure the influence of certain handling and storage methods on the deterioration of quality.

The dehydrated peas stored under carbon dioxide had a slightly higher retention than those stored under vacuum and a significantly higher retention than those stored in air in tin cans. Ascorbic acid levels in the dehydrated lots amounted to about 20% of the original content.

The frozen, canned, and dehydrated samples were cooked to serve by recommended methods in order to compare the final nutrient levels in lots of peas processed by the several procedures. Retention was determined on the dry basis, using the dry weight of the cooked drained product in each case. If the weights of the uncooked product had been used, the results in case of the frozen peas would have been approximately 15% lower because of differences in moisture content. Direct comparison of the cooked frozen and cooked canned peas shows a slightly higher ascorbic acid content in the canned product on both fresh and moisture-free bases. The cooked dehydrated samples contained approximately one third as much ascorbic acid as the cooked frozen or canned products. These results are somewhat at variance with those of Farrell and Fellers (*4*) on snap beans. However, they did not compare samples prepared from the same lot of beans grown under the same conditions and harvested at the same time.

Effect of Storage Period. Although most of the data reported here are for a 6-month storage period, a few samples of frozen and canned peas were analyzed for ascorbic acid at the end of 9 months. Table V shows a continued loss of ascorbic acid during the additional 3 months of storage in both frozen and canned samples.

CAROTENE AND THIAMINE

Table IV shows the carotene and thiamine contents of certain of the samples. Unfortunately the original carotene content of the fresh peas was not obtained. Analyses after 6-month storage of the frozen, canned, and dehydrated products gave carotene contents of 1.98, 1.80, and 1.68 mg. per 100 grams, respectively, on a moisture-free basis. The thiamine content of the frozen and canned samples was about the same or slightly above 1.0 mg. per 100 grams (moisture-free basis) The thiamine level of the dehydrated samples was 0.87 mg. for the carbon dioxide pack, 0.76 mg. for the air pack, and 0.70 mg. for the vacuum pack. The original thiamine content of the fresh peas was 1.67 mg. per 100 grams.

LITERATURE CITED

(1) Bessey, O. A., and King, C. G., *J. Biol. Chem.*, 103, 687–98 (1933).
(2) Clifcorn, L. E., and Heberlein, D. G., Ind. Eng. Chem., 36, 168 (1944).
(3) Conner, R. T., and Straub, G. J., Ind. Eng. Chem., Anal. Ed., 13, 380–4 (1941).
(4) Farrell, K. T., and Fellers, C. R., *Food Research*, 7, 171–7 (1942).
(5) Moore, L. A., and Ely, Ray, Ind. Eng. Chem., Anal. Ed., 13, 600–1 (1941).

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Temperature Efficiency in Distillation

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IN THE fractional distillation of binary systems in plate columns, the temperature on a plate may be used as a measure of the plate efficiency. The equation for the transfer of heat across the liquid-vapor interface is:

$$q = HS(T - T_L) = -V'Mc\frac{dT}{dt} \tag{1}$$

This equation follows immediately from the definitions of H, the over-all coefficient of heat transfer, and of c, the specific heat. Integration between the limits $T = T_1$ (temperature of vapor entering the plate) when $t = 0$, and $T = T_2$ when $t = \tau$ (vapor leaving the plate) gives

$$\frac{T_2 - T_1}{T_L - T_1} = E_T = 1 - e^{\frac{-HS\tau}{McV'}} \tag{2}$$

where E_T is called the temperature efficiency. This quantity was first defined by Carey (*1*).

The derivation for the equation for diffusion efficiency (with vapor-film resistance controlling) follows. The equation for diffusion of a binary system (*3*) is:

$$\frac{-dp_A}{dx} = \frac{\alpha\rho_A\rho_B}{M_AM_B}(u_A - u_B) \tag{3}$$

Defining the molal rate of diffusion per unit area as

$$N_A = \rho_A u_A/M_A \tag{4}$$

and the diffusivity as

$$D = R^2T^2/\alpha P \tag{5}$$

and applying the perfect gas law,

$$\rho_A/M_A = p_A/RT \tag{6}$$

Then:
$$\frac{-dp_A}{dx} = \frac{RT}{DP}(p_BN_A - p_AN_B) \tag{7}$$

Now:
$$P = p_A + p_B \tag{8}$$

and for equal-molal counterdiffusion

$$N_B = -N_A \tag{9}$$

Therefore:
$$-dp_A/dx = RTN_A/D \tag{10}$$

or integrating from p_g to p_i,

$$N_A = \frac{D}{RTL}(p_g - p_i) \tag{11}$$

$$N_A = \frac{DP}{RTL}(y_g - y_i) \tag{12}$$

The diffusion rate can also be expressed as

$$N_A = -d(V'y)/Sdt \tag{13}$$

Combining Equations 12 and 13, integrating from $y_g = y_1$ at $t = 0$ to $y_g = y_2$ at $t = \tau$, and dropping subscripts,

$$\frac{y_2 - y_1}{y_i - y_1} = E_D = 1 - e^{-DPS\tau/RTLV'} \tag{14}$$

This equation defines the local diffusion efficiency, E_D, first used by Murphree (*4*).

The similarity between the equations for temperature efficiency and diffusion efficiency is apparent. Perry (*5*) has presented experimental data to indicate that these two quantities are nearly equal. We shall now derive the analytical relation between these two quantities.

Combining Equations 2 and 14,

$$\frac{\log(1 - E_T)}{\log(1 - E_D)} = \frac{H/Mc}{DP/RTL} = m \tag{15}$$

Now, by definition,

$$k_g = N_A/(p_g - p_i) \tag{16}$$

for equal-molal counterdiffusion of a binary system,

$$k_g = D/RTL \tag{17}$$

from Equation 11. Thus, Equation 15 may be written as

$$m = \frac{H/Mc}{k_gP} \tag{18}$$

From the Chilton-Colburn equation (*2*),

$$k_g = \frac{H}{McP}\left(\frac{c\rho D}{k_H}\right)^{2/3} \tag{19}$$

we obtain

$$m = \left(\frac{c\rho D}{k_H}\right)^{-2/3} \tag{20}$$

According to Sherwood (*6*) $(c\mu/k_H)$ for all gases is approximately 0.74; therefore,

$$m = \frac{(\mu/\rho D)^{2/3}}{0.74} \tag{21}$$

The quantity $(\mu/\rho D)$ is approximately constant for all temperatures and pressures and is usually between 0.67 and 0.75 for most gases. These two limits give

$$1.01 > m > 0.94 \tag{22}$$

Substituting these values of m in Equation 15, we find that E_D and E_T are usually within 0–5% of each other.

Thus, the near-equality of the point temperature efficiency and the point diffusion efficiency in binary systems is primarily a consequence of the Chilton-Colburn equation. This conclusion does not apply to multicomponent systems; in fact, the diffusion efficiency of each component is, in general, different from that of the others.

NOMENCLATURE

c = specific heat of vapor
D = diffusivity
E_D = local diffusion efficiency
E_T = temperature efficiency
g = subscript referring to vapor phase
H = over-all coefficient of heat transfer from vapor to liquid
i = subscript referring to liquid-vapor interface
k_g = film coefficient of diffusion
k_H = thermal conductivity
L = diffusion film thickness
$m = \dfrac{H/Mc}{DP/RTL}$
M = molecular weight
N_A = molal rate of diffusion of component A per unit area
P = total pressure
p_A = partial pressure of component A in vapor
q = rate of heat transfer
R = gas constant
S = interfacial area of bubble
t = time
T = vapor temperature
T_L = temperature of liquid on plate
u_A = velocity of diffusion of component A
V' = moles of vapor in bubble
x = diffusion path length
y = mole fraction in vapor
α = coefficient of resistance to diffusion
μ = gas viscosity
ρ_A = partial density of component A in vapor phase
τ = total time of contact on plate

LITERATURE CITED

(1) Carey, Sc.D. thesis, Mass. Inst. of Tech., 1930.
(2) Chilton and Colburn, Ind. Eng. Chem., 26, 1183 (1934).
(3) Lewis and Chang, *Trans. Am. Inst. Chem. Engrs.*, 21, 127 (1928).
(4) Murphree, Ind. Eng. Chem., 17, 747 (1925).
(5) Perry, Chemical Engineer's Handbook, 1st ed., p. 1192 (1934).
(6) Sherwood, "Absorption and Extraction", p. 37 (1937).

Peptization of Peanut and Cottonseed Proteins

EFFECT OF DIALYSIS AND VARIOUS ACIDS

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PEANUTS and cottonseed are potential sources of vegetable proteins for industrial utilization. Previous publications (*2, 3, 5, 8*) have emphasized the most suitable conditions for extracting the proteins from solvent-extracted seed meals with sodium hydroxide and inorganic salt solutions. Investigations on the extraction of peanut and cottonseed meal proteins by acids have not been extensive. Some data are available on the peptization of peanut meal proteins by hydrochloric acid (*3*) and of cottonseed meal proteins by sulfuric acid (*8*), but no greater acid concentration was used in either instance than was necessary to reach a pH value of 1.5. With increased emphasis on fiber production from various proteins where relatively high concentrations of acids are commonly employed in the precipitating bath, it has become desirable to ascertain the solubility characteristics of peanut and cottonseed proteins in relatively concentrated solutions of different acids.

Approximately 90% of the protein of peanut meal is extracted by water (pH 6.8). It has been inferred that this high aqueous extractability can be explained by the presence in peanut meal of naturally occurring salts (*10*) and lecithin (*7*) which are reported to be responsible for the high water solubility of soybean meal proteins. However, this explanation is inadequate for all seed meal proteins since cottonseed meal proteins, for example, are only sparingly soluble in water under the same conditions (*8*).

The purpose of the present investigation is to demonstrate the effect of the dialyzable meal constituents upon the extractability of peanut and cottonseed meal proteins, and to present data concerning the solubility characteristics of the proteins in these meals and of the isolated proteins in different acid solutions. While the protein solubility data presented may be found useful in selecting satisfactory conditions for the industrial processing of peanut and cottonseed proteins, it is appreciated that the kind of acid and its concentration may not be the only, or even the most important, factors to be considered in such instances. In the production of protein fibers, for example, the precipitating bath usually consists of a combination of acids together with inorganic salts and organic compounds which exert pronounced effects upon protein solubility.

MEALS AND PROTEINS

Peanut Meal. A composite sample (*2*) of a Pearl variety of peanuts (white skins) grown in 1943 was used in this work. The peanuts were mechanically shelled, cracked, and flaked in the early summer of 1944, and the flakes were batch-extracted by a continuous flow of cold Skellysolve F (a naphtha solvent boiling at 30–60° C.). Residual solvent was removed by aeration at room temperature, and the extracted flakes were ground to produce a fine meal of the following composition: moisture 10.6%, nitrogen 9.08%, ash 5.14%.

Cottonseed Meal. Fresh cottonseed meats received from a Mississippi mill in 1943, were cracked, flaked, and extracted in a

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Data are presented to compare the peptization behavior of the proteins of peanut and cottonseed meals, proteins of the corresponding dialyzed meals, and isolated proteins. While the shapes of the pH–peptization curves for cottonseed and peanut meals differ, the response of the proteins to the removal of dialyzable meal constituents is the same in both cases. This shows that the presence of naturally occurring substances in both meals decreases markedly the peptizability of the meal nitrogen at certain acid pH values but exerts no effect at alkaline pH values. Data concerning the peptization behavior of the proteins of peanut and cottonseed preparations in relatively concentrated solutions of various acids are presented. Hydrochloric and sulfuric acids exhibit the broadest working range of concentration for protein precipitation (1.0 to 5.0 *N*); the amount of protein precipitated by either acid is practically constant within this range. In general, acetic and phosphoric acids are poor protein precipitating agents while monochloroacetic acid compares favorably at 1.0 to 3.0 *N* acid concentration with hydrochloric and sulfuric acids. Trichloroacetic acid is a slightly better protein precipitant than hydrochloric or sulfuric acid, but is effective over a narrower range of acid concentration (0.5 to 2.0 *N*). At concentrations of trichloroacetic acid above 2.0 *N*, as much as 95% of the proteins of peanut or cottonseed meal may be soluble. This is an essential consideration in instances where trichloroacetic acid is used as a quantitative protein precipitant.

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large Soxhlet-type extractor with ethyl ether[2]. Residual solvent was removed by aeration at room temperature, and hull particles were removed from the oil-free meats by means of a Raymond separator mill. The meal had the following composition: moisture 11.5%, nitrogen 8.21%, ash 8.70%.

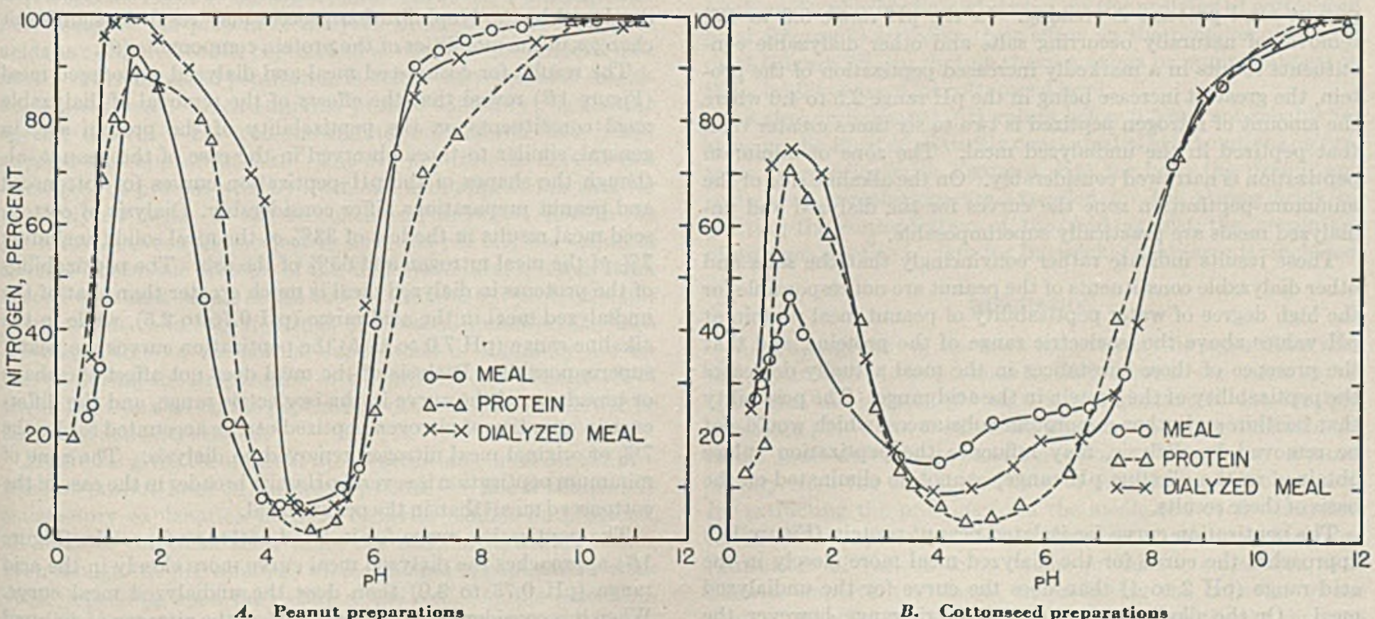
Peanut Protein. Peanut meal was extracted with a dilute sodium hydroxide solution, and the extract (pH 8.0) was removed by centrifugation. The protein was precipitated at pH 4.5 by the addition of hydrochloric acid, and the protein was recovered by centrifugation. The moist protein was suspended in water (thymol added), transferred to cellophane (Visking) membranes, and dialyzed against running distilled water at 4° C. for 3 days. The protein suspension was then removed from the membranes, and the protein was dried by lyophilization (*9*). The dried protein had the following composition: moisture 10.4%, nitrogen 15.43%, ash 0.31%, total phosphorus 0.645%, and inorganic phosphorus 0.014%.

Cottonseed Protein. Ethyl ether–extracted cottonseed meal was extracted by occasional stirring with sodium hydroxide solution for 30 minutes, and the extract (pH 11.0) was removed by centrifugation. The protein was precipitated at pH 4.0 by the addition of hydrochloric acid, and the protein was then treated by the method described for peanut protein. The dried protein had the following composition: moisture 10.64%, nitrogen 14.0%, ash 0.22%, total phosphorus 1.164%, and inorganic phosphorus 0.013%.

PROCEDURES FOR DETERMINING NITROGEN

A. The procedure for determining the percentage of total meal nitrogen peptized has been given in detail (*3*) but may be described briefly as follows: 2.5-gram portions of the meal, contained in separate 200-ml. screw-cap centrifuge bottles, were treated with 100 ml. of water containing sufficient sodium hydroxide solution or acid solution to give the final pH value desired. The suspensions were allowed to stand for 3 hours at room temperature with occasional shaking and were then clarified by centrifuging. The pH values of the centrifuged solutions were determined by a glass electrode, and total nitrogen was determined on duplicate aliquots by either the semimicro- or micro-Kjeldahl method. All of the nitrogen values reported in this paper were calculated on the basis of the total volume of solvent added in each case.

B. The procedure for determining the percentage of total nitrogen peptized for dialyzed meal samples follows: 2.5-gram portions of the meals were transferred to cellophane membranes with 50 ml. of water and dialyzed at 4° C. against running distilled water for 48 hours. The contents of the membranes were transferred to 100-ml. glass-stoppered graduated cylinders, and the volumes were adjusted to 100 ml. by adding water and sufficient sodium hydroxide solution or acid solution to give the final pH values desired. The remainder of the procedure was exactly as described under *A* except that, in calculating the percentage of total nitrogen peptized, the total nitrogen of the dialyzed meal was considered to be equal to the total nitrogen of the original



A. Peanut preparations *B.* Cottonseed preparations

Figure 1. Hydrochloric Acid–Sodium Hydroxide pH–Peptization Curves Showing Percentage of Total Nitrogen Peptized

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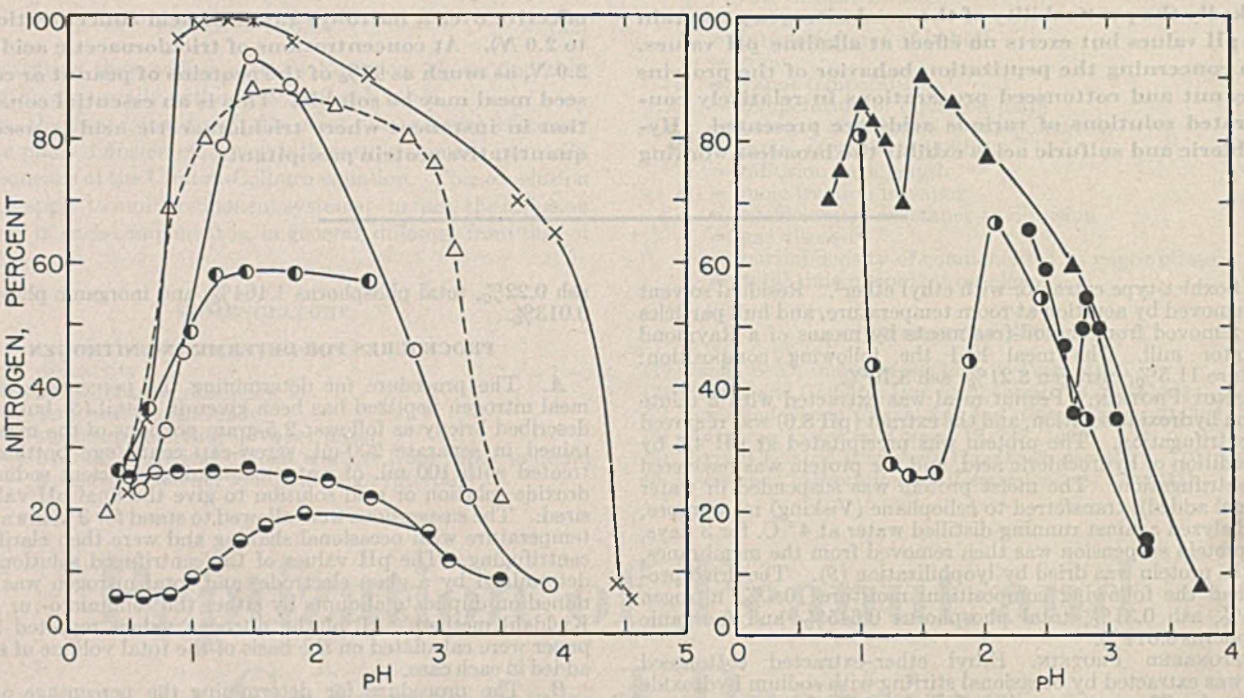
[2] Subsequent batches of the same flaked meats were extracted with Skellysolve F, Skellysolve F followed by ethyl ether, and ethyl ether followed by chloroform. The pH–peptization curve shown in Figure 1*B* for ether-extracted meal is representative of all the cottonseed meals, regardless of solvent or combination of solvents used for removing the oil.

meal minus that lost during dialysis. The nitrogen lost during dialysis was calculated as the difference between the total nitrogen contained in the original meal and the average value obtained by analyzing several samples of meal after dialysis.

C. The procedure employed for determining the percentage of total nitrogen peptized in experiments where the isolated protein was used was exactly as given under *A* except that only 1.25 grams of protein were treated with 100 ml. of solvent.



A. Peanut meal: HCl ○, H_2SO_4 ◓, CCl_3COOH ⊖; dialyzed peanut meal: HCl ×, H_2SO_4 ◐; isolated peanut protein: HCl △

B. Peanut meal: H_3PO_4 ▲, CH_3COOH ●, $CH_2ClCOOH$ ◑

Figure 2. Acid pH–Peptization Curves, Showing Percentage of Total Nitrogen Peptized for Peanut Preparations

PEPTIZATION OF MEALS AND PROTEINS

The hydrochloric acid–sodium hydroxide pH–peptization curves for peanut meal, dialyzed peanut meal, and isolated peanut protein are shown in Figure 1*A*. The effect of the removal of dialyzable solids, amounting to 23% of the meal and including 5% of the nitrogen and 71% of the ash, on the peptization of the peanut meal proteins is striking. In the pH range 0.9 to 4.5, removal of naturally occurring salts and other dialyzable constituents results in a markedly increased peptization of the protein, the greatest increase being in the pH range 2.5 to 4.0 where the amount of nitrogen peptized is two to six times greater than that peptized in the undialyzed meal. The zone of minimum peptization is narrowed considerably. On the alkaline side of the minimum peptization zone the curves for the dialyzed and undialyzed meals are practically superimposable.

These results indicate rather convincingly that the salts and other dialyzable constituents of the peanut are not responsible for the high degree of water peptizability of peanut meal protein at pH values above the isoelectric range of the proteins, and that the presence of these substances in the meal actually decreases the peptizability of the protein in the acid range. The possibility that lecithin and other nonprotein substances, which would not be removed by dialysis, may influence the peptization values obtained in the alkaline pH range, cannot be eliminated on the basis of these results.

The peptization curve for isolated peanut protein (Figure 1*A*) approaches the curve for the dialyzed meal more closely in the acid range (pH 2 to 4) than does the curve for the undialyzed meal. On the alkaline side of the isoelectric range, however, the curve for the protein departs considerably from the curves for both the dialyzed and undialyzed meals. These results might be taken to indicate that a substance (or substances) is removed by precipitation and dialysis of the protein which is not removed by dialysis of the meal itself, and that this hypothetical substance exerts a slight peptizing effect on the protein over the entire pH range. While this possibility cannot be ignored, it appears more likely that the low peptizability of the isolated protein compared to that in the dialyzed meal is due to partial denaturation of the protein during the lyophilization process, with concomitant lowering of its solubility. That denaturation during lyophilization may occur is borne out by electrophoretic data obtained on whole protein, which demonstrate that even the mild conditions employed in the lyophilization process may result in significant changes in the mobilities of the protein components (*6*).

The results for cottonseed meal and dialyzed cottonseed meal (Figure 1*B*) reveal that the effects of the removal of dialyzable meal constituents on the peptizability of the protein are, in general, similar to those observed in the case of the peanut, although the shapes of the pH–peptization curves for cottonseed and peanut preparations differ considerably. Dialysis of cottonseed meal results in the loss of 33% of the meal solids, including 7% of the meal nitrogen and 65% of the ash. The peptizability of the proteins in dialyzed meal is much greater than that of the undialyzed meal in the acid range (pH 0.75 to 2.5), while in the alkaline range (pH 7.0 to 11.5) the peptization curves are nearly superimposable. Dialysis of the meal does not affect the shape or broadness of the curve in the isoelectric range, and the difference in quantity of nitrogen peptized can be accounted for by the 7% of original meal nitrogen removed on dialysis. The zone of minimum peptization is several pH units broader in the case of the cottonseed meal[2] than in the peanut meal.

The peptization curve for isolated cottonseed protein (Figure 1*B*) approaches the dialyzed meal curve more closely in the acid range (pH 0.75 to 3.0) than does the undialyzed meal curve. When it is considered that at least 15% of the nitrogen of dialyzed cottonseed meal remains in the mother liquor when the protein is precipitated at pH 4.0 for the purposes of isolation, it is possible that this soluble fraction is, in part, responsible for the rather broad and unusually shaped isoelectric zone for the undialyzed meal.

From these results it is evident that salts and other dialyzable constituents of cottonseed meal decrease the peptizability of the proteins in the acid range (pH 0.75 to 3.0) but exert little or no effect at other pH values. It would also appear that, if lecithin is responsible for the high water peptizability of peanut and soybean proteins, a similar peptization effect might be expected in the case of cottonseed proteins. This is obviously not true.

EFFECT OF VARIOUS ACIDS

Owing to the current emphasis upon the production of fibers and other industrially useful materials from proteins, it would be expected that an understanding of the peptization behavior of peanut and cottonseed meal proteins in the presence of relatively high concentrations of different acids would be one of the prerequisites for developing satisfactory processing conditions. It is obvious that the solubility data presented for proteins in solutions of a single acid cannot be used directly to predict the solubility behavior of these proteins under conditions which involve the use of acid mixtures or acids together with inorganic salts and/or various organic compounds.

A number of strong acids were investigated, such as hydrochloric, sulfuric, and trichloroacetic, and weaker acids, such as acetic, phosphoric, and monochloroacetic, which might be used for extraction and precipitation of proteins and in protein fiber-precipitating baths. In the case of mixtures of protein with strong acids, values approximating pH 0.5 are attained at relatively low acid concentrations, and consequently the pH values of mixtures which contain higher concentrations of strong acids have little significance. The pH values are more significant, however, in the case of the weaker acids where concentrations approaching 5 *N* are required to attain a pH value of approximately 1.0. Acetic acid, the weakest of the acids employed, yields a pH of only 2.3, even in 5 *N* concentration. For these reasons the peptization data are presented graphically, using both the pH and acid concentration scales (Figures 2, 3, and 4).

Figure 2*A* shows the pH-peptization curves for peanut meal dialyzed peanut meal, and isolated peanut protein with strong acids. Of first consideration is the difference between the actions of hydrochloric acid and sulfuric acid which must, in part, represent a specific effect of the sulfate ion. However, a much greater percentage of the protein of dialyzed meal is peptized by both acids as compared to the peptization of the proteins of undialyzed meal. This increased peptization is due to the removal of dialyzable constituents which suppress protein solubility; hence the specific difference between the sulfate and chloride ions is not so great as it appears at first. The pH-peptization curve for isolated peanut protein with hydrochloric acid approaches that for the dialyzed meal. It can be concluded, therefore, that in the pH range between the isoelectric zone and pH 0.5, the action of strong acids on the proteins of the undialyzed meal is not in strict accord with that found in the case of the isolated proteins; this conclusion is valid only if enough of the meal constituents which are responsible for the normal suppression of solubility are removed during the preparation of the protein (*4*). The effect of trichloroacetic acid on the peptization of the meal proteins will be discussed in a later section.

Figure 2*B* gives the unusual pH-peptization curves for the proteins of peanut meal in the weaker acids. While a completely satisfactory explanation of their behavior cannot be provided, all three of the weak acids cause the same sequence of events, even though the pH values at which changes in peptization occur vary, depending upon the nature of the acid. As the concentration of each weak acid is increased, a peak in the peptization curve is first obtained, followed by an abrupt decrease in peptization as the acid concentration is further increased and, finally, by an increase in peptization at the highest acid concentration. This behavior appears to be characteristic of peanut meal proteins with the weaker acids. It indicates also that the weaker acids in high concentrations should not be reliable precipitating agents for peanut protein when they are used alone.

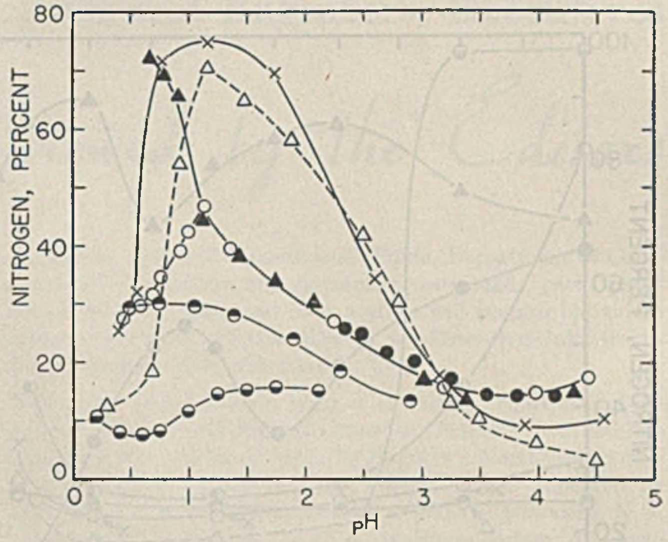


Figure 3. Acid pH–Peptization Curves Showing Percentage of Total Nitrogen Peptized for Cottonseed Preparations

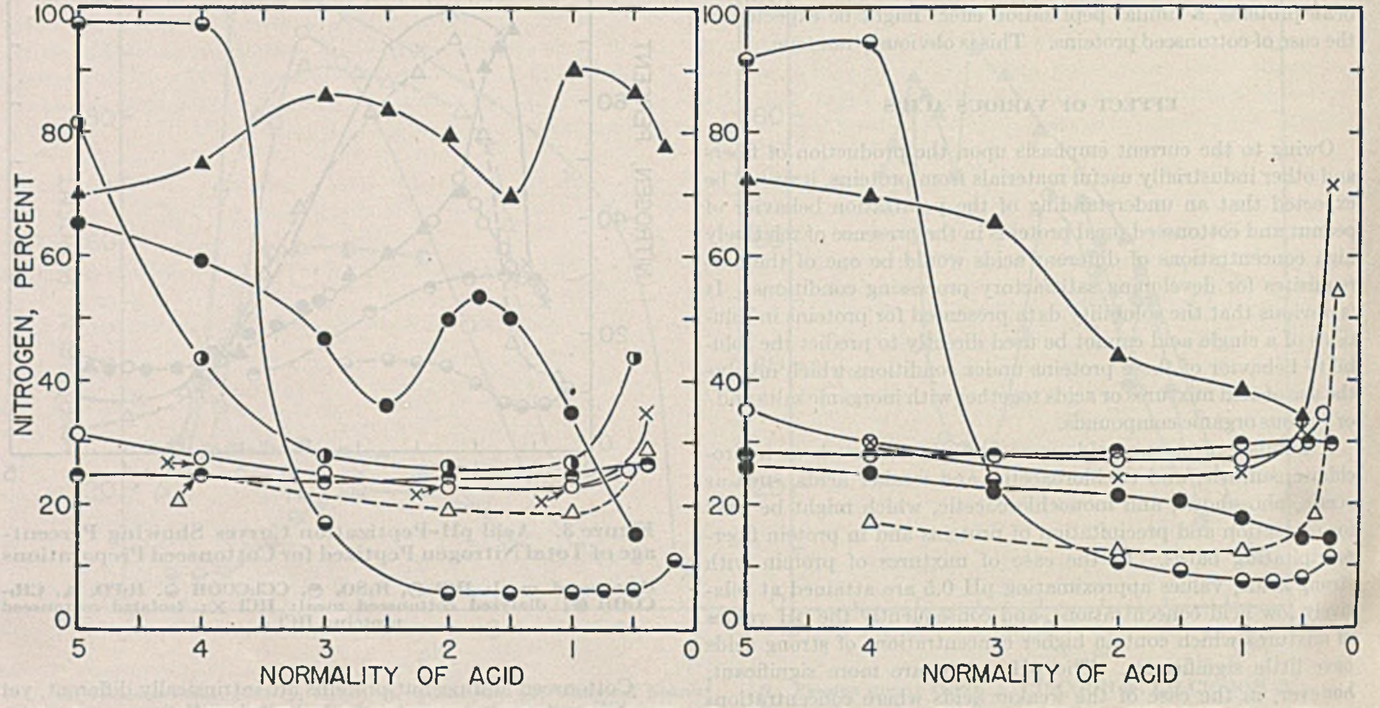
Cottonseed meal: HCl ○, H_2SO_4 ◓, CCl_3COOH ◒, H_3PO_4 ▲, CH_3-COOH ●; dialyzed cottonseed meal: HCl ×; isolated cottonseed protein: HCl △

Cottonseed and peanut proteins are intrinsically different, yet their over-all peptization characteristics in solutions of strong acids are similar in many respects, as the data of Figure 3 show. Hydrochloric acid peptizes a greater percentage of the nitrogen of undialyzed cottonseed meal than does sulfuric acid, but the difference is not so great as in the case of peanut meal. The proportionately greater peptization at pH 1.1 of the nitrogen of dialyzed cottonseed meal and isolated protein, as compared with that of the undialyzed meal, demonstrates that the presence of a naturally occurring, dialyzable meal constituent(s) decreases the acid peptizability of the meal proteins. The effect of the weak acids, phosphoric and acetic, on the proteins of cottonseed meal (Figure 3) is unlike their effect on the proteins of peanut meal (Figure 2*B*), in that no sharp maxima or minima appear in the solubility curves for cottonseed meal.

As already indicated, pH values below 0.5 are not reliable for showing the effect of relatively concentrated acid solutions on proteins. Accordingly, in Figure 4 data for both the peanut and cottonseed preparations are extended for the strong acids by plotting the concentration of the acid against the percentage of nitrogen peptized; data for the weaker acids are also included.

DISCUSSION

Since a large part of the work reported in this paper deals with the peptization of the proteins as they occur in the meals rather than with the isolated proteins, it is important to observe that at certain pH values the isolated proteins and the proteins in the meals yield different peptization values. This factor is noteworthy from the standpoint both of selecting suitable methods for extracting the proteins from the meals and of devising uses for the isolated proteins. When the effect of relatively high concentrations of various acids on the proteins is considered, it is likewise important to know, in predicting the behavior of the protein, whether the proteins in the meals and in the dialyzed meals yield essentially the same peptization values as do the



A. **Peanut meal: HCl ○, H_2SO_4 ◓, CCl_3COOH ◒, H_3PO_4 ▲, CH_3COOH ●, $CH_2ClCOOH$ ◐; dialyzed peanut meal: HCl ×; isolated peanut protein: HCl △**

B. **Cottonseed meal: HCl ×, H_2SO_4 ◓, CCl_3COOH ◒, H_3PO_4 ▲, CH_3COOH ●; dialyzed cottonseed meal: HCl ×; isolated cottonseed protein: HCl △**

Figure 4. Curves Showing Percentage of Total Nitrogen Peptized

isolated proteins. In this connection it is significant that there are no differences in the shapes of the strong acid peptization curves (Figure 4) for the proteins of peanut meal, dialyzed peanut meal, and isolated peanut protein. The same is true for the corresponding cottonseed preparations. Furthermore, since there is no appreciable difference between the actions of sulfuric and hydrochloric acids at concentrations greater than 1.0 *N*, both are equally good precipitating agents for the proteins of peanut and cottonseed at acid concentrations of 1.0 *N* or above.

The action of trichloroacetic acid on proteins is of theoretical importance since this acid is generally thought to be nearly specific for the quantitative precipitation of proteins. From the data in Figures 2*A*, 3, and 4 it is apparent that trichloroacetic acid is a good precipitant for the proteins of peanut and cottonseed only under certain limited conditions. Thus, in the case of peanut meal which has been treated with trichloroacetic acid, a constant minimum protein solubility occurs in the range 0.5 to 2.0 *N* trichloroacetic acid. This is the critical range since an increase in acid concentration to 4.0 *N* results in the peptization of more than 95% of the meal nitrogen. A similar trichloroacetic acid solubility phenomenon has been reported in the case of soybean meal (*1*). The range of minimum solubility for the proteins of cottonseed meal in this acid is even narrower than for peanut meal—namely, 0.5 to 1.0 *N* trichloroacetic acid. As was found to be true with peanut meal, higher trichloroacetic acid concentrations result in the peptization of increased amounts of nitrogen, as much as 95% of the nitrogen of cottonseed meal being soluble in 4.0 *N* trichloroacetic acid.

Monochloroacetic acid, a weak acid which was investigated at high concentrations for peanut meal only (Figure 4*A*), yields results which parallel those for hydrochloric and sulfuric acids over the concentration range 1.0 to 3.0 *N*, and then deviate to approach the results obtained for trichloroacetic acid.

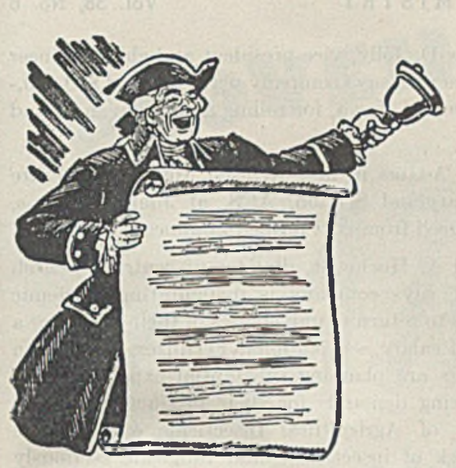
The proteins of peanut and soybean meals show, in general, the same alkaline peptization behavior. Sufficient peptization data for the proteins of soybean meal in relatively highly concentrated acid solutions are not available in the literature to make possible a detailed comparison with the proteins of peanut meal, but such data as are available can be considered comparatively. The proteins of peanut meal are peptized to approximately the same extent in dilute hydrochloric and phosphoric acid solutions as are the proteins of soybean meal (*11*), but not nearly to the extent of the latter in dilute sulfuric or trichloroacetic acid solution (*11*). The peptization of the proteins of soybean meal does not appear to decrease at higher concentrations of hydrochloric and sulfuric acids (*11*) so rapidly as that of the proteins of peanut meal.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the Analytical, Physical Chemical and Physical Division of this laboratory for making a considerable number of the nitrogen determinations reported in this paper.

LITERATURE CITED

(1) Becker, H. C., Milner, R. T., and Nagel, R. H., *Cereal Chem.*, 17, 447 (1940).
(2) Burnett, R. S., and Fontaine, T. D., Ind. Eng. Chem., 36, 284 (1944).
(3) Fontaine, T. D., and Burnett, R. S., *Ibid.*, 36, 164 (1944).
(4) Fontaine, T. D., Pons, W. A., Jr., and Irving, G. W., Jr., unpublished results.
(5) Fontaine, T. D., Samuels, C. S., and Irving, G. W., Jr., Ind. Eng. Chem., 36, 625 (1944).
(6) Irving, G. W., Jr., Fontaine, T. D., and Warner, R. C., unpublished results.
(7) Nagel, R. H., Becker, H. C., and Milner, R. T., *Cereal Chem.*, 15, 766 (1938).
(8) Olcott, H. S., and Fontaine, T. D., *J. Am. Chem. Soc.*, 61, 2037 (1939); 62, 1334 (1940).
(9) Pomes, A. F., and Irving, G. W., Jr., *Science*, 101, 22 (1945).
(10) Ryndin, T., *Colloid J.* (U.S.S.R.), 2, 811 (1936).
(11) Smith, A. K., and Circle, S. J., Ind. Eng. Chem., 30, 1414 (1938).



MAY'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ May 2. Civilian Production Administration discloses penicillin shipped out of country in April is five and one-half times as much as monthly exports of all drugs and medicines from this country in 1938, but must continue under allocation.∼∼University of Chicago places order with GE for 100,000,000-volt betatron designed for x-ray and atomic research.∼∼British Labor Government proposes to vest absolute control of atomic research development and use in Ministry of Supply.∼∼Owens Corning Fiberglas announces extremely lightweight Fiberglas vehicle insulation which was developed for use in military aircraft.∼∼Wm. B. Stout, aircraft and automobile designer, displays "car of the future" with Fiberglas body.

¶ May 3. W. E. Cake, director of plantations U. S. Rubber Co., predicts Malayan rubber crop will reach 50 per cent of potential capacity by end of year.∼∼CPA freezes government stockpile of cadmium as result of 45 per cent cut in output owing to strikes. ∼∼Imperial Chemical Industries of London plans £9 million expansion in its dyestuffs.∼∼Secretary of Commerce Wallace appearing before a Senate Commerce subcommittee asks government aid to industry to promote industrialization of undeveloped areas, particularly in South and West.∼∼Reserve Officers Association of N. Y. adopts resolution urging U. S. to withhold all information on atom bomb from other nations.

¶ May 4. Farrington Daniels, director University of Chicago Metallurgical Laboratory, says scientists there have completed plans for producing power from atomic reactions.

¶ May 5. Evans Clark, executive director Twentieth Century Fund, says it plans broad study of cartels under supervision of business men, economists, and leaders in labor and agriculture.

¶ May 6. Wm. L. Laurence, of the *New York Times*, receives Pulitzer Prize of $500 for his eye-witness account of atom bombing of Nagasaki and for 10 articles published in *New York Times* on development, production, and significance of atomic bomb.∼∼Secretary Krug announces program for centralizing government's petroleum policy and for continuing informally wartime relationship with petroleum industry.∼∼R. J. Dearborn, chairman Patents and Research Committee NAM, urges Senate passage of Lanham Trade-Mark Bill which would modernize American trade-mark laws and protect consumer and manufacturer.

¶ May 7. House Appropriations Committee recommends $150,000 for anthracite research laboratory authorized by Congress in 1942 but never built because of war.∼∼Howard E. Fritz, vice president in charge of Goodrich's research, says as result of 10 years' research and discovery of carbon white, bright-hued synthetic rubber tires are now possible.∼∼President Truman authorizes State Department to send invitations to 11 foreign nations, including the Soviet Union, which are members of United Nations' Atomic Energy Commission, to send observers to atomic bomb tests at Bikini.

¶ May 8. Office of International Trade, Department of Commerce, says potassium and ammonium compounds, paste, paint colors, lead arsenate, and lead acetate will require individual licenses for export effective May 14.∼∼Executive Order terminates Petroleum Administration for War.

¶ May 9. Roger Adams, head of chemistry department, University of Illinois and chairman Board of Directors ACS, receives Theodore Wm. Richards Medal of Society's Northeastern Section at MIT.∼∼Celanese Corp. says CPA has approved its application to build addition to plastics plant at Belvidere, N. J. ∼∼Senator Millard E. Tydings, speaking before American Society of Mechanical Engineers, urges destruction of all atomic bomb plants.

¶ May 10. A 14-ton German V-2 rocket, the second ever to be fired in this country, roars into the ionosphere from White Sands Proving Ground, Las Cruces, N. Mex., and climbs almost 75 miles as a large party of military and naval men and scientists witness the shape of things to come.∼∼Glenn H. Haskell, president U. S. Industrial Chemicals, Inc., says new commercial method for synthetic production of methionine has been perfected by company and will reduce costs by about 97 per cent.∼∼Ralph E. Pettit, development engineer of Alcoa, says company's metallurgists have developed process so that aluminum can be produced in lasting colors of red, green, blue, yellow, gold, and all intermediate shades and may also be chromium plated or polished to a high reflective finish.

¶ May 11. President Truman, accepting honorary degree at Fordham University, urges education for use of atom bomb in peace.

¶ May 12. War Assets Administration offers Magnesium Reduction Co.'s plant in Luckey, Ohio, for sale for production of magnesium metal and magnesium alloys by the ferrosilicon process.

¶ May 13. Joint Army-Navy Task Force reveals 77 vessels to be attacked with atomic bomb at Bikini Atoll will be in formation resembling a huge pinwheel with the *Nevada* at the bull's-eye.∼∼J. P. Staples, general manager Pittsburgh Corning Corp., says company plans to build two plants at Sedalia, Mo., for production of glass block and Foamglas.∼∼R. S. Wilson, vice president Goodrich Tire & Rubber, urges adoption of generic term to replace "synthetic rubber".∼∼W. S. S. Rodgers, chairman Texas Co., says company has acquired site on Delaware River for construction of its first major East Coast refinery.∼∼D. Harold Copp, instructor in physiology University of California, says medical benefits of a single atomic fission product, radioactive carbon 14, will be great enough to justify atomic energy project cost.∼∼Commercial Solvents closes its main plant at Peoria, Ill., because of coal and corn shortages.

¶ May 14. Maryland Section ACS announces establishment of Remsen Memorial Lectureship in honor of Ira Remsen.∼∼Linus

Pauling, California Institute of Technology, is selected by National Willard Gibbs Jury to receive 35th award of Willard Gibbs Medal.

¶ May 15. Sherwin Williams announces resin coatings for DDT crystals which make this pest killer more efficient and longer lasting.∼∼Enrico Fermi tells George Westinghouse Centennial Forum an atomic oven can run as hot as man wishes.

¶ May 16. J. Robert Oppenheimer, University of California, tells Westinghouse Centennial Forum that establishment of an atomic development authority would be proper place to start world government.∼∼Department of Justice files antitrust suit against International Nickel Co. of Canada and its American subsidiary, International Nickel Co., Inc., asking complete separation of American subsidiary from parent Canadian company.∼∼Office of War Mobilization and Reconversion imposes severe restrictions on consumption of industrial alcohol and places source products under allocation.

¶ May 17. Bernard M. Baruch begins active preparations for first meeting of Atomic Energy Commission of UN.∼∼Arnold E. Pitcher, general manager of Du Pont's plastics department, says company will begin construction of new plastics factories near Parkersburg, W. Va., within the month.∼∼Willard H. Dow, president, says Dow Chemical will immediately resume production of magnesium at its seawater plant, Freeport, Tex.∼∼Isador Lubin, U. S. delegate to Economic and Employment Commission, proposes full investigation by UN of peace use of atom.∼∼Bill to set up atomic energy control in Canada is introduced in Canadian Parliament.

¶ May 18. Counsel for Libbey-Owens-Ford and other flat glass companies, defendants in a suit brought by Attorney General May 23, 1945, denies all charges of restraint of trade and antitrust law violations.∼∼President Truman, in message to moderator of General Assembly of Presbyterian Church in U. S., says atomic age has ended one age and begun another—"the new and unpredictable age of the soul".∼∼ACS awards 60 ACS predoctoral fellowships aggregating nearly $100,000 to students of chemistry and chemical engineering whose training was interrupted by the war.

¶ May 19. Joseph W. Barker, president Research Corp., announces grants amounting to $175,000 to 28 universities and colleges, in honor of Frederick G. Cottrell, for a year's research in chemistry and physics.∼∼National Committee on Atomic Information says its Washington headquarters will serve as base of operations for national organizations, including educational, business, church, labor, and women's groups, to join in countrywide campaign to inform average citizen about atomic energy.

¶ May 20. Supreme Court agrees to review antitrust suit brought by Government against National Lead, Titan Co., and Du Pont.∼∼George W. Merck, receives Medal for Merit from Secretary of War Patterson for his direction of the War Research Service.∼∼Dow Chemical sets up new laboratory to continue and greatly expand metals and cathodic protection research program begun 6 years ago.

¶ May 21. Chemists' Club N. Y. awards honorary memberships to Wm. Cullen, a director of Imperial Chemicals, Ltd., Sir Robert Robison, Oxford University, Maximilian Toch, president Toch Bros., Willis R. Whitney, formerly vice president and director of research GE.∼∼U. S. Department of Agriculture places 3-day limit a month on distillers' use of grain during June and July.

¶ May 22. Royal Dutch airliner takes 20,000,000 units of penicillin to Netherlands on its opening New York-to-Amsterdam service.∼∼Eastman Kodak reveals that radioactive by-products of a single bomb explosion spread in a few days over an area about the size of Australia.∼∼Gen. Carl A. Spaatz says the new B-36 bomber will fly 10,000 miles with an atomic bomb.

¶ May 23. Thomas D. Jolly, vice president and chief engineer Aluminum Co. of America, says company plans to build $30,000,000 plant near Davenport, Iowa, for rolling aluminum sheet and plate.

¶ May 24. Roger Adams in first Remsen Memorial Lecture delivered before Maryland Section, ACS, at Johns Hopkins, predicts power produced from coal burned in mines.

¶ May 26. Carroll A. Hochwalt, director of central research Monsanto Chemical, says company is inaugurating academic leave for its scientists to return to universities of their choice for a year of study at full salary.∼∼National Fertilizer Association reveals manufacturers are planning substantial expansion programs to meet growing demands for their products.∼∼L. S. Hitchner, executive of Agricultural Insecticide & Fungicide Association, says lack of insecticides and fungicides seriously threatens farm crops.

¶ May 27. National Fertilizer Association says its members are planning to increase production facilities from 10 to 65 per cent.∼∼H. V. Lauer, field supervisor of raw materials Carnegie-Illinois Steel Corp., at National Association of Purchasing Agents annual meeting in Chicago predicts that development of coal chemicals is still far from its peak.∼∼Diamond Alkali reveals plans for establishing central research and development department near Cleveland and a central engineering department.∼∼W. A. Higinbotham, chairman Federation of Atomic Scientists, in speech before organization meeting of National Committee on Atomic Information, says at least two major secret weapons are in existence which scientists believe are potentially as dangerous to mankind as atomic bomb.∼∼Julian Huxley, executive secretary preparatory commission United Nations Educational, Scientific, and Cultural Organization, on visit to U. S., proposes that Atomic Energy Control Commission deal with practical applications of atomic energy, civilian and military, while UNESCO occupies itself with atomic developments in pure science.∼∼R. P. Dinsmore, vice president Goodyear Tire & Rubber, tells newsmen at dinner in Detroit preceding automobile industry's golden jubilee celebration that automobile tire lasting 100,000 miles will be developed from improved synthetic rubber.∼∼John I. Collyer, president B. F. Goodrich, says supply shortages may cut tire production.

¶ May 28. War and Navy Departments and leading scientists and research institutions endorse revised draft of National Science Foundation legislation when hearings begin before House subcommittee on Interstate and Foreign Commerce. Secretary of War Patterson tells committee Office of Scientific Research and Development "more than any one agency contributed to victory in World War II".∼∼One hour broadcast by two dozen men and women, officials and scientists, urges sovereignty pool by UN for atomic energy control.∼∼War Assets Administration offers Front Royal, Va., sulfuric acid plant, leased and operated during the war by General Chemical, for sale.∼∼Secretary of Commerce Wallace welcomes technical mission from Belgium, here to discuss technical information blacked out from that country since 1940.

¶ May 30. George E. Folk, special advisor to the National Association of Manufacturer's committee on patents and research, says NAM favors Representative Mills' bill for creation of a National Science Foundation.∼∼J. M. Tucker, director Du Pont's Jackson Laboratory, says construction of addition to laboratory at Deepwater Point, N. J., will begin soon.∼∼International Telephone and Telegraph Corp. is building a new research laboratory, constructed largely of aluminum and other pressed or extruded metals, Carl Brandt, vice president George A. Fuller Co., contractors, announces.

¶ May 31. British Atomic Scientists Association recommends international control of atomic energy by a UN agency in memorandum for submission to Atomic Energy Commission of UN.

PROVEN CATALYSTS NOW AVAILABLE FOR NEW USES!

● During the past fifteen years, the research staff of Universal Oil Products Company has developed and brought into commercial production many catalysts for the Petroleum Industry. Cracking, dehydrogenation, polymerization, hydrogenation, aromatization, isomerization, and many other petroleum processes utilize catalysts which have been developed during this era of intensive catalyst research.

It has been our experience that many of these catalysts, developed specifically for a petroleum process, can be used directly or with slight modification, in other processes. We are therefore offering UOP catalysts, in commercial and pilot plant stages of development, to industrial and academic investigators.

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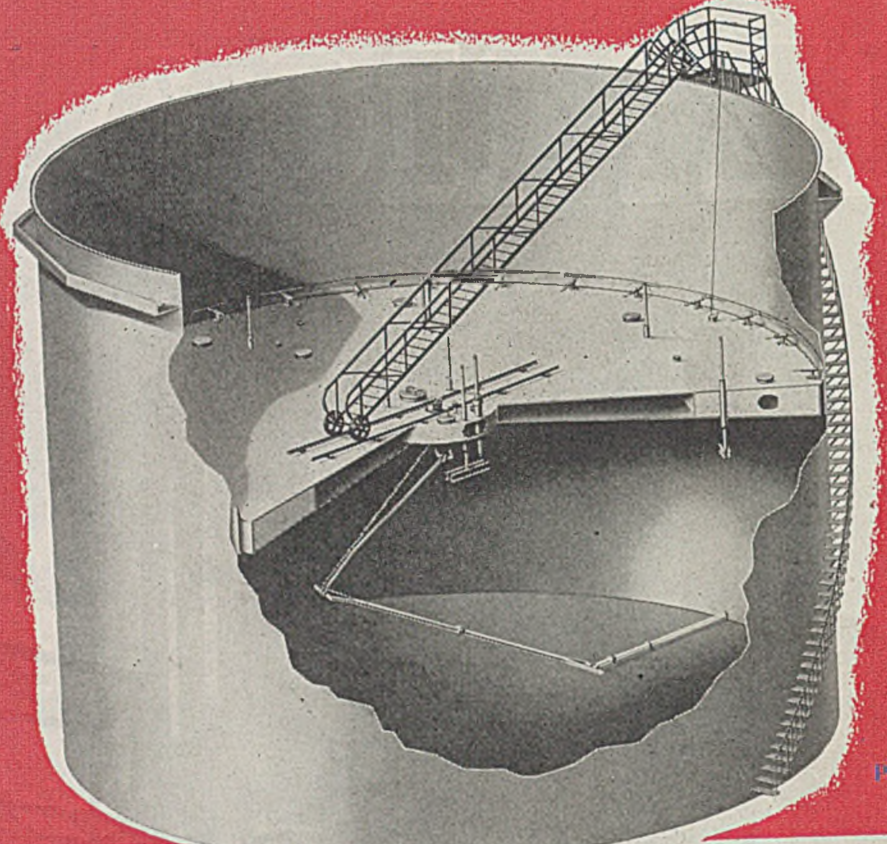

Patents applied for

. . for use on tanks that are filled and emptied several times a year

the HORTON FLOATING ROOF

The Horton Floating Roof is only one of several types of tank roofs and tanks built by the Chicago Bridge & Iron Company to reduce evaporation losses. Others include Horton Lifter Roofs, Hortonspheres, Hortonspheroids and Hemispheroids.

Flat-bottom storage tanks with the *improved* Horton Floating Roof provide chemical and process plants and the petroleum industry with an efficient means of preventing evaporation and reducing fire hazard during the handling of volatile liquids.

The Horton Floating roof has a double deck which insulates the liquid and eliminates practically all "boiling." This means that it can be used to stop practically all evaporation loss from liquids of relatively high volatility.

The Horton Floating Roof rides on the liquid at all times—traveling up and down as the tank is filled and emptied. This "blanketing" of the liquid in the tank at all levels prevents evaporation losses due to daily breathing and also reduces corrosion on the underside of the roof.

A close-fitting seal effectively closes the space between the deck and tank shell and prevents evaporation loss from occurring at that point.

These features and many more are found only in the *improved* Horton Floating Roof. Write our nearest office for a copy of Bulletin B which contains complete details or quotations on installations.

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Current Developments in EQUIPMENT AND DESIGN

The use of capacity ratings should prevent high costs and breakdowns.

Discussed by Charles Owen Brown

MANY years ago a book was published covering the advances made in several scientific fields during the preceding year. In the chapter on Electrochemistry a noted authority reported on storage batteries. At that particular time there was a wave of proposals by the chronic corner-store inventors to pep up or revitalize all sorts of devices by adding a patented or secret restorer. A wide variety of useful equipment was listed for improvement by these miraculous additive agents, and the lead storage battery was not overlooked. Several of the secret but highly publicized revitalizers were bottles of 98% sulfuric acid. By increasing the acid concentration, a small increase in energy would be taken from the battery until additional sulfate deposits offset the advantage. Now and then some of these quick restorers were based upon good theory and chemistry. One of the more popular remedies contained 5 ounces of salt cake (at a dollar a package); it was to be added to the battery several hours before charging to make sure it was completely in solution. This treatment brings about real improvement in the energy output of a badly sulfated lead accumulator. Relatively large doses of phenol and other chemicals, more or less effective, were offered in order to reap a tremendous profit from the thrifty or uninformed.

These popular specialties received due comment by the author-scientist. He was against all such practices. They were, one and all, to be condemned. Thus far we have no quarrel with this advice; .but the authority went on to explain his point, if memory serves us accurately, with the following touching comparison: After a horse has given his best willingly throughout a life of long days filled with heavy tasks and has come to his feeble end, it is neither humane, fair, nor effective to attempt to improve his strength by beating or by injecting stimulants. We cannot believe this advice is applicable or useful in any study of storage batteries, lead or otherwise. No trace of a soul or other human emotion is to be found in any combination of metals and electrolytes—at least not in modern ones. If one accepts this as true, the author's advice seems erroneous. If one can pep up a battery, originally costing five dollars, and obtain a 10% life increase by adding ten cents' worth of strong acid, it seems worth while even if the battery is eventually discarded. Our only objection would be against charging excessive prices for the treatment.

There is no intention in this discussion of being disrespectful toward any author's teachings; we use this example only to clarify a policy often used in operating and replacing plant equipment. Some engineers are overcautious in the use of equipment, and some, of course, err the other way. The proper policy is somewhat dependent on the equipment involved. During the processing of any piece of standard equipment, such as electric motors, centrifugal pumps, and agitators, it is logical to fix the load at no less than the limit, or full rating, of that equipment. If some error has been made and a breakdown occurs, a new unit can be secured at once; but with all special or built-to-order equipment, one must be more careful. A wise course would be to load such equipment to 95, 90, or even 85% of rating to make certain breakdowns are avoided. Not only would replacement of one piece of equipment cause a serious delay, but might stop production in the plant. Furthermore, one can accept the rated capacity of standard equipment with considerable confidence, for ratings are set by a large group of research and design experts who have a background of actual experience gained from thousands of field tests.

Equipment classified today as special will become standard as soon as sufficient knowledge is gained from experience with many field tests. One can hasten the accumulation of exact data on the fine points of equipment performance by continually using the products of one manufacturer rather than by trying all types available. Standardization within the purchaser's engineering department has many advantages and will permit intelligent loading of equipment to the maximum. As one becomes acquainted with relatively new equipment, one may discover that the real capacity is greater than the rated capacity; the manufacturer has been conservative. After reliable data have been accumulated to substantiate these findings, the higher capacity should be used by the plant engineer. It is not necessary that the manufacturer of the equipment be convinced of the wisdom of using the new rating. His viewpoint is understandably different; he is expected to formulate a rating for average conditions and not for the most efficient applications possible.

A skillful plant engineer is able to assemble equipment for a process with all units loaded to a real capacity; he thereby reduces appreciably the capital cost of the plant. He will be safe in

(*Continued on page 70*)

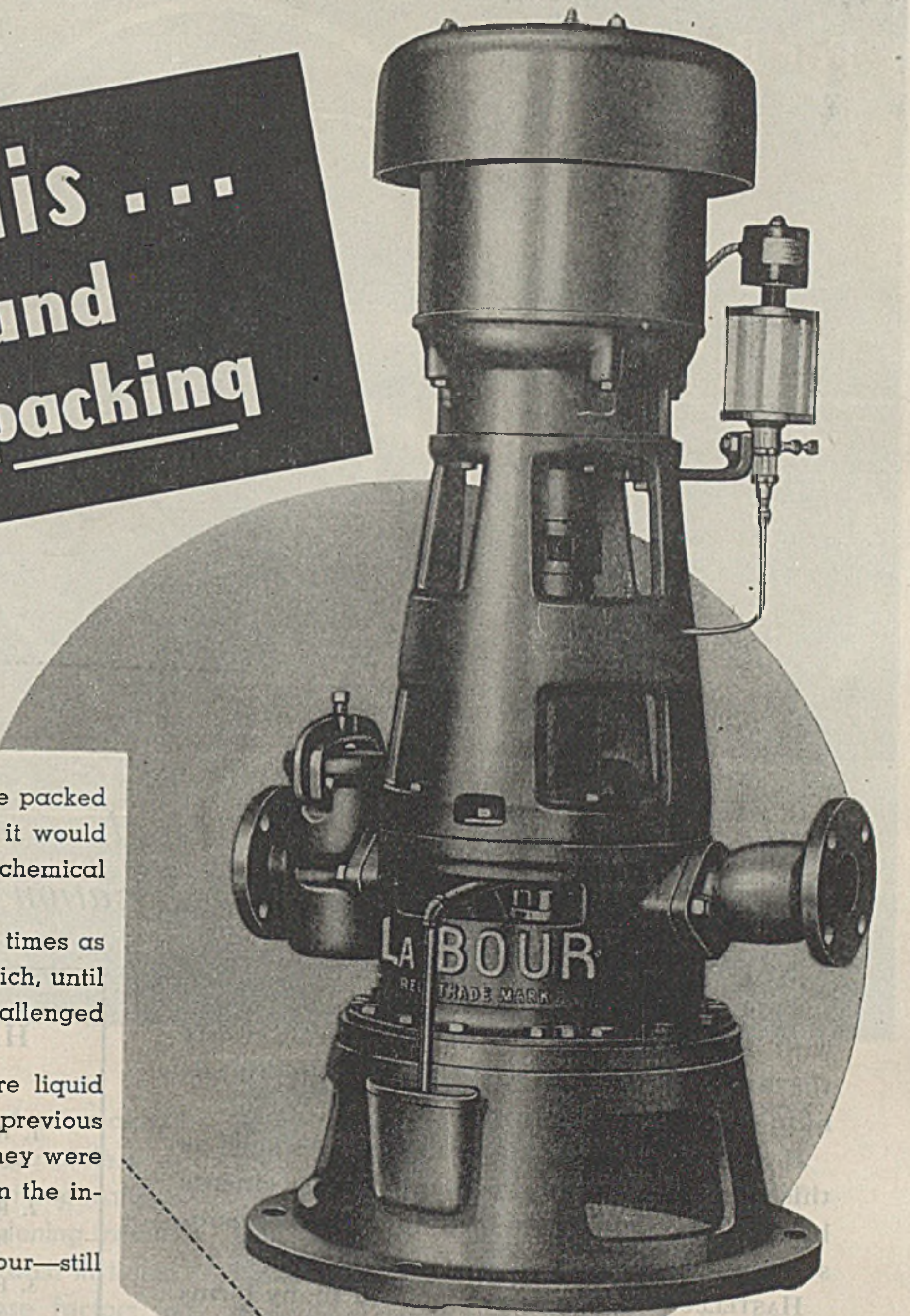
Equipment and Design

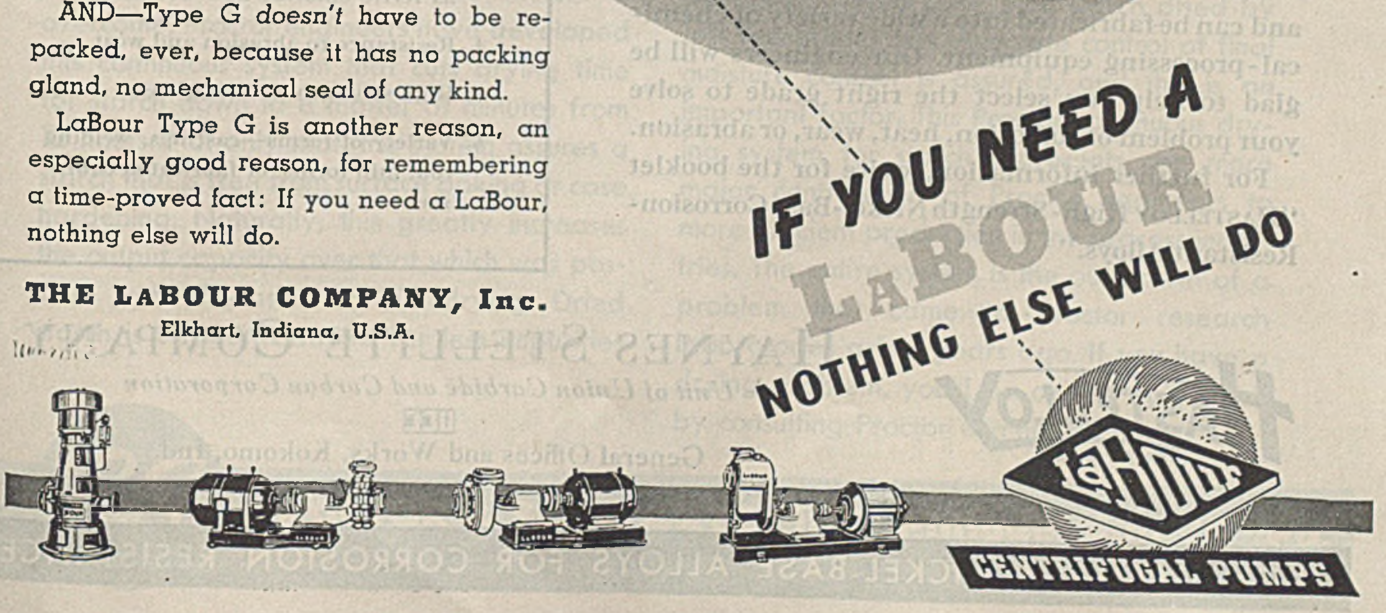
doing this under three conditions: first, when the equipment is all standard and easily replaced; second, when special equipment is protected by spare capacity or units; third, when the equipment is such that a breakdown merely stops production or use of the unit without endangering life or property. For example, a small hoist, lifting a 2-ton basket of yarn spools out of a dye vat, could create quite a mess and might scald a workman if the hoist failed.

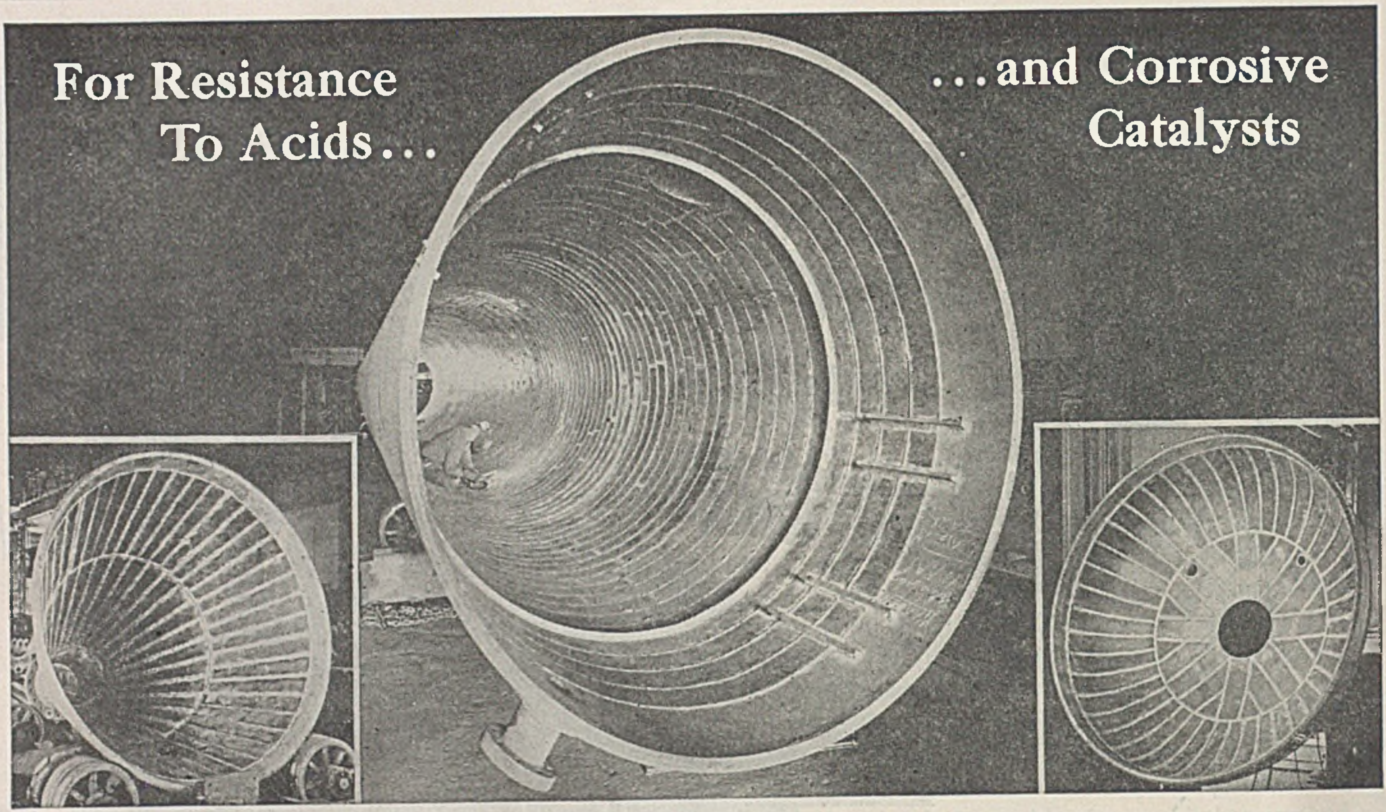
A more serious example also comes to mind. Several years ago the managers of a foundry decided to manufacture equipment for the chemical industry. They supplied a ball mill to a clever purchasing agent for $2900, to meet the same grinding capacity the plant engineer expected from a Marcy mill costing $6500. It is interesting to compare the two mills briefly. The first was a $^3/_8$-inch-thick sheet-steel shell riveted to the flange on two cast iron ends, which carried the cast iron shafts all in one piece. The mill turned in two simple bearings which required two 6-foot cement piers as foundations. The mill was driven by a large cast iron gear, keyed to the shaft outside of one main bearing and a pinion gear on a jack shaft, with a belt pulley. This shaft also required two cement supporting piers. The drive from the motor was through an 8-inch belt. It was apparent to any chemical engineer that the $2900 mill was a batch mill, whereas the Marcy mill was a continuous mill. It was likewise clear that the cheaper mill would not do one-half rated capacity, at best; consequently a second similar mill had to be purchased. The two mills required a new main drive shaft and a larger motor. The equipment finally cost about $8500, including shaft and motors. The Marcy mill was equipped with a common base and motor, and a pinion gear engaging a fully machined steel gear mounted directly on the steel body of the mill. The mill was also equipped with an alloy steel, replaceable liner, and special alloy steel ball load.

The history of operations of the two mills is worth noting. The batch mills were built by joining the steel shell to the ends with taper head rivets inserted from the inside. The first row of balls at the end of the mill wore a round groove in the steel shell which removed the entire tapered head and allowed the rivets to fall out. About forty days after the mill was started, it broke in two at the driven end seam, tore loose from the cement piers, and rolled along the floor to the building wall. An operator barely escaped being crushed. Later the Marcy mill was installed and gave excellent performance at rated capacity. Nothing could have prevented the crackup of the batch mill because of its fundamental design faults. However, when equipment appears to be too light or runs at high speed, it must not be loaded to capacity. This invites a breakdown, interrupts production, and perhaps causes serious injury. Fortunately, the equipment of experienced manufacturers is usually reliable, efficient, and accurately rated.


all this . . .
and
no packing


LA BOUR
REG. TRADE MARK


IF YOU NEED A
LABOUR
NOTHING ELSE WILL DO
LaBour
CENTRIFUGAL PUMPS


For Resistance To Acids...
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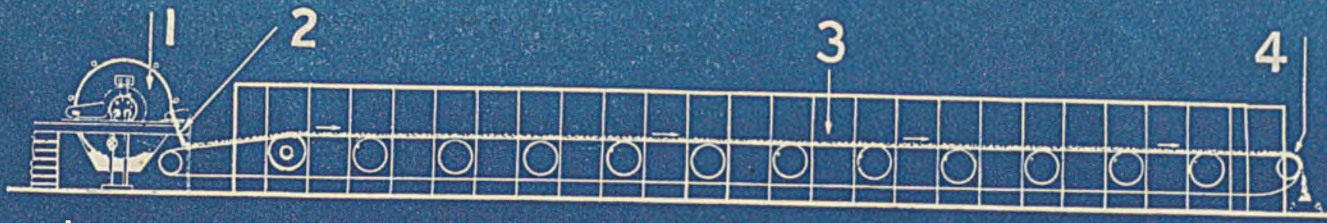
PROCTOR CONTINUOUS CONVEYOR SYSTEM

SPEEDS OUTPUT . . . IMPROVES QUALITY OF STARCH



1. Starch is mechanically dewatered by means of a rotary vacuum filter.
2. Having been scored on the filter, starch is delivered to conveyor of dryer in the form of ½" cubes, with a moisture content of 78.5% (B.D.W.B.).*
3. Due to the pre-forming of the starch on the filter and breaking the filter cake into ½" cubes, it is possible to dry starch rapidly—thus preventing case hardening and assuring thorough drying. Having been broken up into small pieces, it is possible for air to circulate through the bed of material on the conveyor. Temperatures average 180°F. at beginning of the cycle and 215°F. at the end.
4. Starch leaves dryer with a moisture content of 13.6% (B.D.W.B.). Capacity of dryer shown is about 4600 pounds (C.D.W.†) per hour.

Bone Dry Weight Basis.

†Commercial Dry Weight.

The physical characteristics of starch make it a difficult product to dry in large scale production. Dried too fast—or with temperatures that are too high—case hardening results and the dispersibility of the starch in liquid is ruined. Yet, with all of these factors to overcome, Proctor engineers have developed this continuous system that cuts drying time for starch down to a matter of minutes from 12 hours. Not only that, the system assures a starch that is free from surface baking or case hardening. Naturally, this greatly increases the output capacity over that which was possible with old-fashioned kiln drying. Dried starch is cleaner, contains far less impurities and has a better color than starch dried by less recent methods. Accurate control of final moisture content is assured, and this is an important factor. This Proctor continuous drying system for starch represents one more major contribution of Proctor engineers to more efficient production in the process industries. The entire system is the outgrowth of a problem that came to Proctor research laboratories a few years ago. If you have a drying problem, you'll be on the right track by consulting Proctor engineers now!

Close-up shows ½" cubes of starch . . . the form in which it enters the dryer, after having been scored on the filter. Circulation of heated air through the bed of these cubes promotes rapid, uniform drying.

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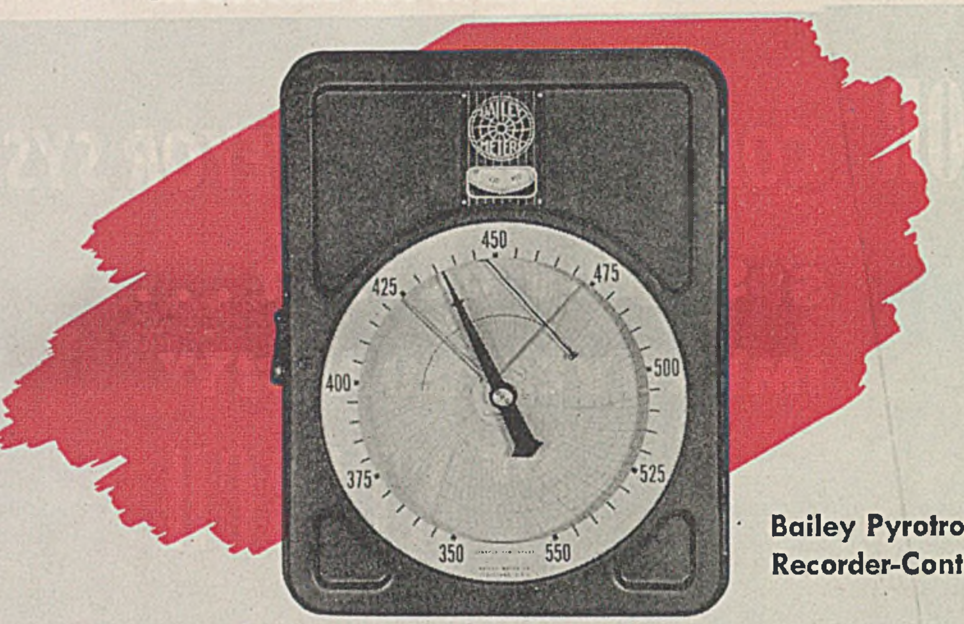

Bailey Pyrotron Recorder-Controller

Looking for Better Temperature Instruments?

...Then check these features of Pyrotron Electronic Resistance Thermometers...

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Bailey Pyrotron Resistance Elements are made of highest purity platinum—the material used by the Bureau of Standards in establishing basic standards for temperatures from —190°C to +660°C.

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Pyrotron Controllers may operate: on-off electrical systems by either electronic relays or electric contacts, modulated electronic systems, or air-operated systems. Two temperatures may be recorded on the same chart and controlled by a single instrument.

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Bailey Pyrotrons may be arranged to put temperature facts into convenient usable forms. If two or more temperatures are related, they may be recorded as continuous records on the same chart for easy comparison. The average of several temperatures or the difference between two temperatures may be recorded as a single continuous record which may be retransmitted to a distant point or used to actuate a control system.

EASY INSTALLATION

Bailey Pyrotrons do not require careful leveling or protection against vibration. Three ordinary copper wires are all that is needed to connect each temperature sensitive element with the recorder. Power may be taken from any 115 volt 60 cycle circuit.

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The absence of galvanometers, batteries and standardizing equipment, together with the use of interchangeable unit assemblies, reduces Pyrotron maintenance to the vanishing point.

ABUNDANT POWER

A separate motor drive for each temperature furnishes abundant power to operate a recording pen, a controller and an alarm switch.

For the full story on this unusual electronic resistance thermometer which is suitable for ranges between —100°F and 1200°F, ask for Bulletin No. 230-A. P-9

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Current Developments in INSTRUMENTATION

Flow measurement and a new temperature time cycle controller are discussed.

Discussed by Ralph H. Munch

Flow is one of the commonest and most important quantities which the instrument engineer is called upon to measure and control. Chemical plants, petroleum refineries, and power plants make extensive use of many types of equipment to measure and control flow. The present discussion will be limited to the oldest and most widely used class of flow sensitive devices, the differential pressure type.

Sextus Julius Frontinus, who was inspector of the public fountains in Rome about 106 B.C., noted that the amount of water discharged through an orifice in a given interval of time depends not only on the size of the orifice but also on the hydrostatic head. Benedetto Castelli (1577–1644) concluded that the rate of flow was proportional to the hydrostatic head. However, Torricelli, whom we more often associate with the barometer, deduced in 1643 that the rate of fluid flow was proportional to the square root of the head. His reasoning was based on Galileo's experiments with falling bodies. The square root relation was confirmed experimentally by various workers shortly thereafter.

Daniel Bernoulli (1700–1782) showed that for a fluid in motion, the sum of the kinetic energy, the potential energy, and the pressure energy was constant along a given streamline. This relation is expressed by Bernoulli's fundamental equation of hydrodynamics:

$$\frac{P_1}{\rho} + \frac{1}{2}\frac{V_1^2}{g} + h_1 = \frac{P_2}{\rho} + \frac{1}{2}\frac{V_2^2}{g} + h_2$$

where P_1, P_2, = pressure, lb./sq. ft.
ρ = density, lb./cu. ft.
V_1, V_2 = velocity, ft./sec.
g = acceleration due to gravity, ft./sec./sec.
h_1, h_2 = height, ft.

Torricelli's theorem states the relation between velocity of discharge from an orifice in the bottom of a reservoir and the hydrostatic head. For this case V_1, the velocity in the reservoir, may be considered zero, P_1 equals P_2 since both are equal to atmospheric pressure, and h_2, the reference level, is zero. Under these conditions, Bernoulli's equation reduces directly to

$$V = \sqrt{2gh}$$

which is Torricelli's theorem. Its derivation from Bernoulli's equation established its correctness, so that it displaced the incorrect linear relation of Castelli. It is interesting to note that about seventeen hundred years were required to develop the correct relation between flow and head after the initial observation that they were related.

Although the basic theory upon which flow measurement depends has long been known, many factors are involved which cannot readily be calculated. The Brown Flowmeter Engineering Handbook by Louis Gess and R. D. Irwin, published by Brown Instrument Company, is an excellent treatment of the practical use of flowmeters. The opening chapter gives a simple account of the principles of orifice flowmeter measurement. It discusses the effect of flow disturbances produced by elbows, valves, and other fittings. Charts give the minimum lengths of straight pipe above and below the orifice as a function of the ratio of orifice to pipe diameter for various arrangements of fittings. Chapter 2 discusses the thin-plate orifice and the various types of pressure taps used with it. Brown flowmeters of various types are described in the next chapter. Details of meter body design and interchangeable-range tubes are covered. Mechanical, pneumatic, and electrical types for a wide range of conditions are described. Chapter 4 contains useful data, mostly in tabular form, for approximating an orifice ratio and differential pressure. The methods described are rapid and sufficiently accurate for preliminary purposes. Starting with Bernoulli's equation, the fifth chapter derives the universal formula for flow measurement; these relations are further developed in the next chapter to give working equations suitable for calculation of practical problems. Some of the complexities involved in measuring gas flows are covered in chapter 7. Reynolds number and its relation to coefficients of discharge are next discussed. Because of the need for viscosity data in Reynolds number calculations, the following chapter gives definitions of absolute and kinematic viscosity, and tables and formulas for converting readings of common types of viscometers into absolute units. A.P.I. and Baumé specific gravity conversion charts and formulas are also included. Then come four chapters on orifice calculations for steam, water, oil, and gas flow; detailed accounts are given of the methods of making orifice calculations, including all necessary formulas and tables. Chapter 14 summarizes the equations developed in earlier sections of the book and defines all symbols used. Chapter 15 discusses the calculation of correction factors needed when operating conditions such as temperature and pressure change. The book closes with a discussion of integration methods to obtain volume from flow rate.

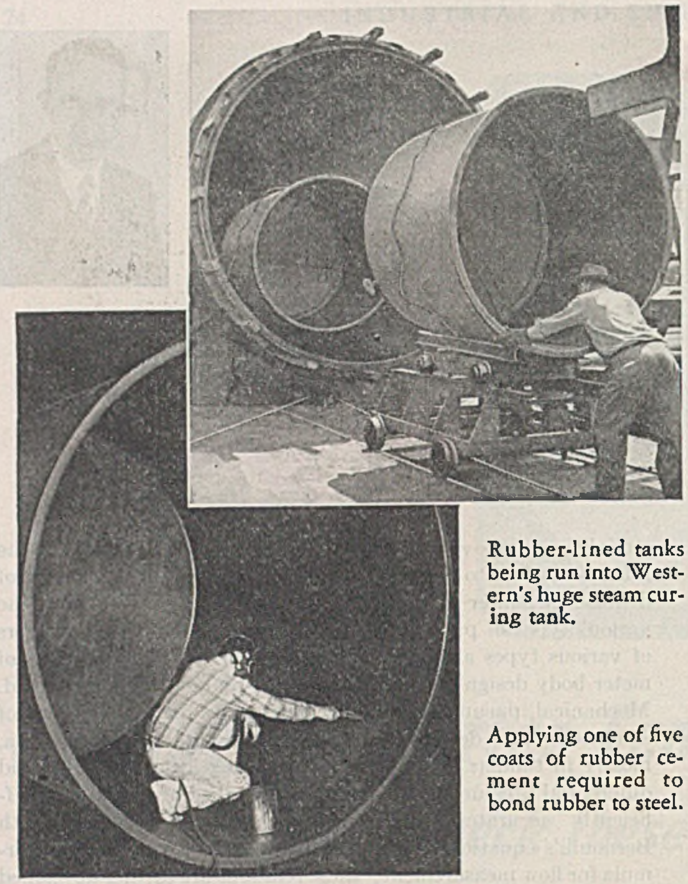
This handbook is a complete account of methods of computation involved in the selection and use of flowmeters. It contains comparatively little information on methods of installation and maintenance of the equipment once it is chosen. No one working in the field can afford to be without a copy.

Cycle Log Controller

The Foxboro Company, Foxboro, Mass., recently put on the market a unique time cycle-temperature controller. This instrument (Figure 1) will bring the process temperature up to a desired value at a predetermined rate of rise, control it at this value for a given length of time, and then shut off the heating medium. As the illustration shows, the instrument is flush-mounted with all its accessories, such as gage, control setting knobs, electrical switches, and signal lights, in a moistureproof steel cabinet.

The desired rate of rise is secured with a constant speed motor linked to the lower index pointer to drive it upscale at a uniform rate. The maximum rate is approximately 24 minutes to cross a standard 12-inch chart scale.

(Continued on page 76)



Instrumentation

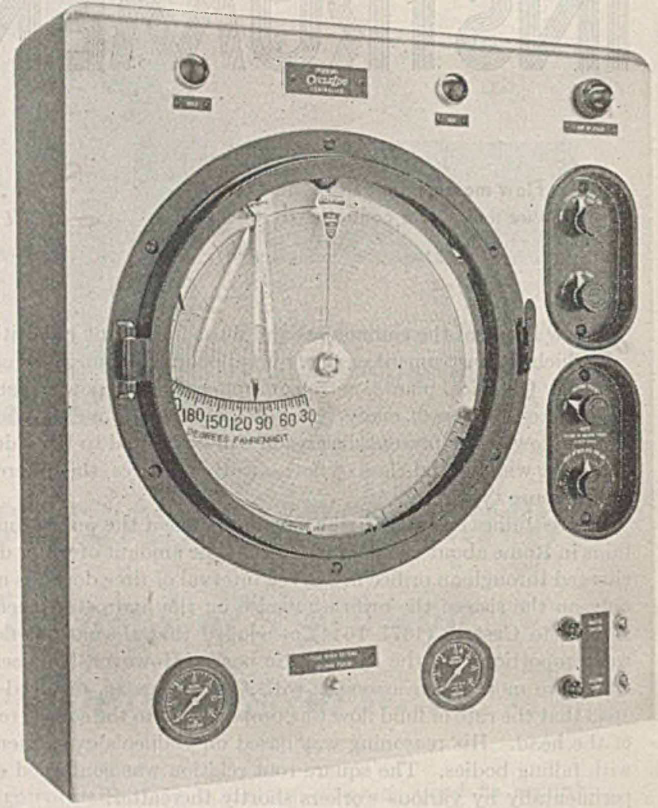


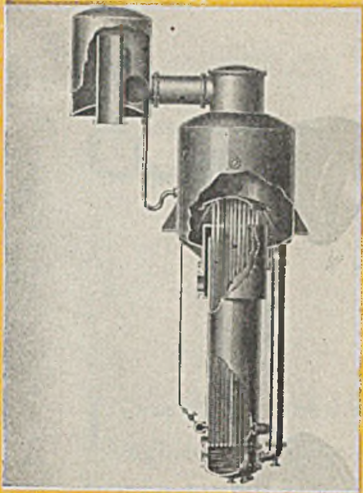
Figure 1. Foxboro Cycle Log Controller

To obtain slower rates, the current to this motor is interrupted for a given fraction of each half-minute period. Thus the actual movement is a series of very small steps rather than an absolutely smooth curve. However, the steps are so small that the curve is, for all practical purposes, continuous.

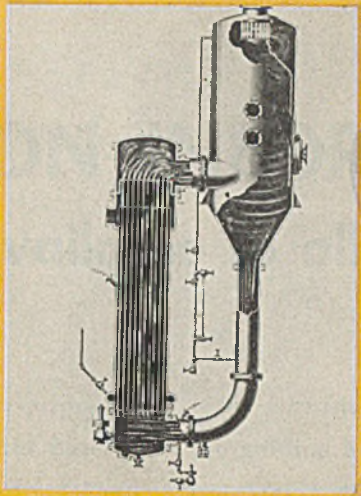
The interrupter consists of a microswitch in the circuit of the constant speed motor operated by a circular off-center cam mounted on a standard 2 r.p.m. motor. The microswitch is turned on and off once each half minute by a cam follower riding on this cam. The ratio of *off* to *on* time is varied by positioning the microswitch with the setting knob on the front panel.

The holding-period lever arm is friction-driven by the chart drive mechanism. When the arm is at zero, an auxiliary nozzle is uncovered to bleed all air from the control circuit, and a mercury switch is rotated to turn on the red signal light indicating the end of a complete cycle. The four knobs at the right of the instrument control the temperature at which the rate of rise function is to start, the rate of rise, the holding temperature, and the length of the holding period.

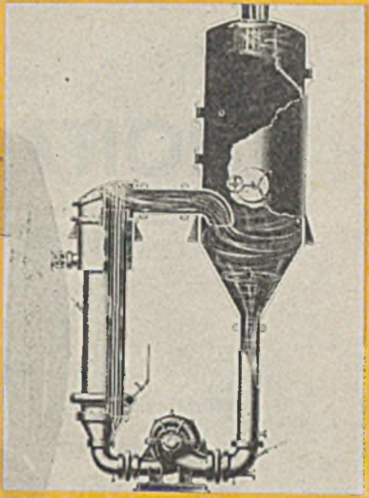
Adjustment of the holding period automatically starts the control action. If the pen is below the point at which the rate of rise function is to start, the control valve will open wide until the temperature reaches the point. During this period none of the indicating lamps will be on. Then the temperature will rise at the desired rate until the hold temperature is reached. This period is indicated by a yellow light. When the hold temperature is reached, the yellow signal light is turned off and a green one is turned on. At the completion of the hold period, the steam is turned off. The yellow light is turned off and a red one is turned on to indicate completion of the cycle. This system eliminates the use of program cams and results in a very flexible instrument.



Long Tube Film Type Evaporator

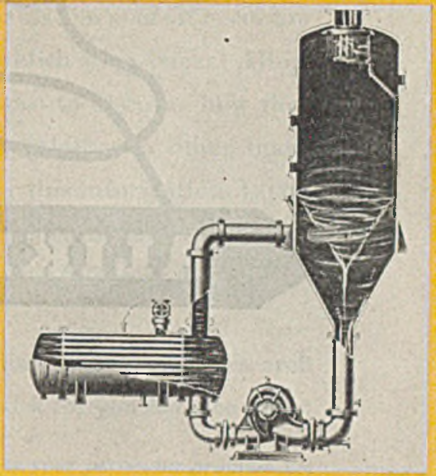


Long Tube Vertical Recirculation Evaporator



Vertical Tube Forced Circulation Evaporator

General American Conkey Evaporators



Submerged Tube Forced Circulation Evaporator

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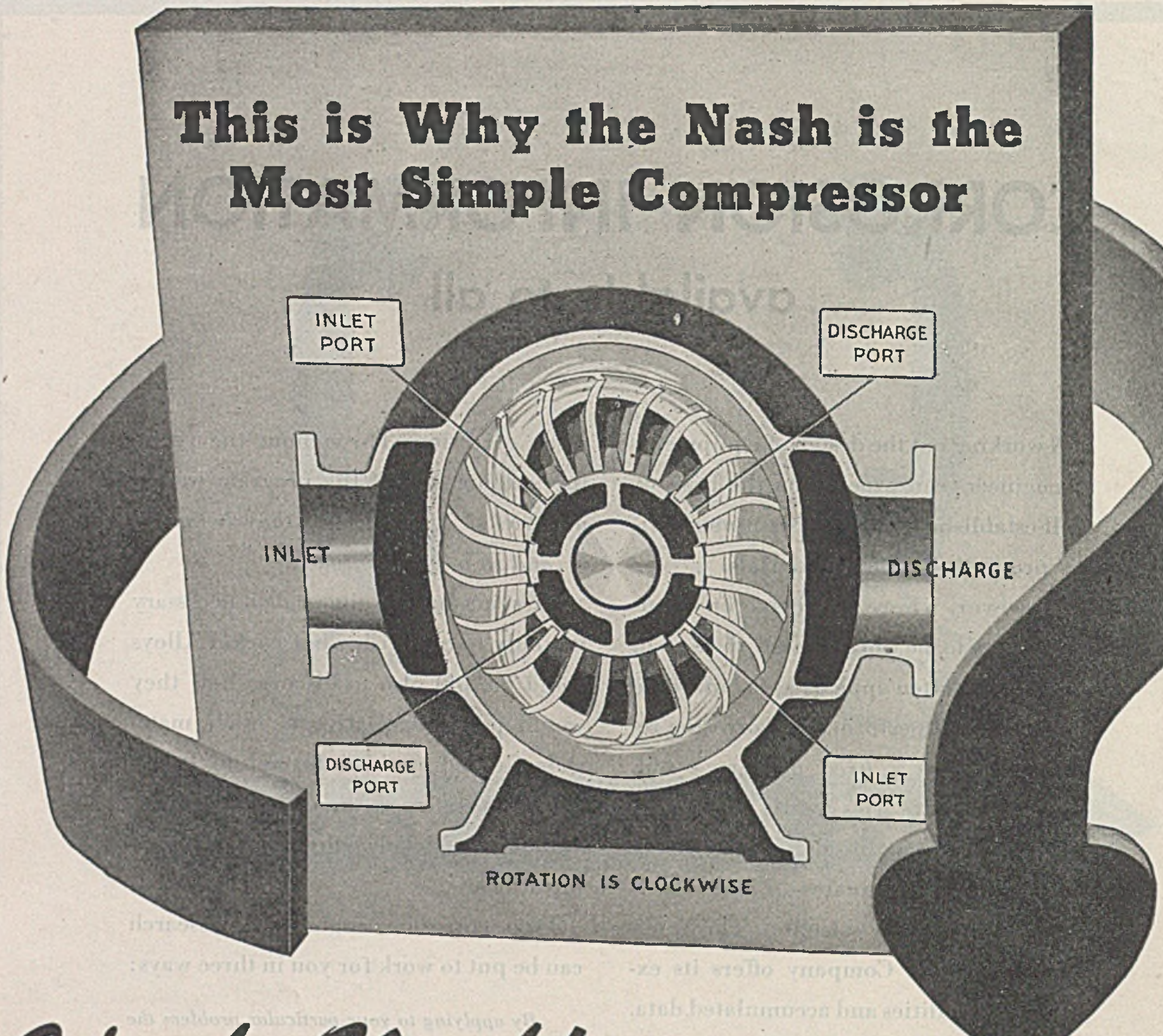
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Current Developments in
WASTE UTILIZATION

The rental of municipal sewage systems can become a convenient means for industry to dispose of its liquid wastes.

Discussed by Harold R. Murdock

When equipment becomes more readily available so that municipalities can expand and modernize their sewage disposal systems, we will hear considerable discussion on the subject of taxing those industries which purge their wastes into city sewage systems. Industry often places a serious burden upon sewage works. Its increased water volume may necessitate a larger processing plant. The toxic substances introduced by industry into the public sewers are of even greater importance. These materials interfere seriously with the bacterial processes utilized in modern disposal plants. The increasing complexity and magnitude of industrial waste problems, on one hand, and the refinement and sensitivity of the sewage treatment processes, on the other, create problems which must be solved before new sewage installations can be properly designed. Past experience clearly indicates the importance of regulating the discharge of industrial wastes into public sewer systems to keep the treatment of these residues under positive control.

In large communities which have a diversified group of relatively small industries, the volume of trade waste is not an appreciable percentage of the total sewage load. It is not, therefore, necessary to consider pretreatment of the industrial waste before it is added to the public sewer. In smaller cities, however, where the trade waste volume is proportionally substantial, real difficulties are encountered. This is particularly true if the wastes are toxic substances and the industrial activity comes from only a few types of industry.

Equity to all concerned in disposition of waste products is essential. A control board should be established to determine the effect of trade waste upon the sewage treatment plant. Furthermore, a municipality should not encourage a new industry to settle within its boundaries until a careful appraisal has been made of the compatibility of the waste from the new industry with the method of operating the public sewage plant. Cities should also consider the effect of expansion in existing industries.

Cooperation with rather than persecution of industry should be the basis for abatement of trade and sewage wastes. A good example of what not to do is reported from a small North Dakota city. The spent waters from a potato dehydrating plant had become extremely detrimental to the operation of the local sewage plant. Lack of previous knowledge, according to reports, had led to this difficulty. Cooperative study of the problem was lacking. The municipality adopted a ruling prohibiting the dumping of the waste into the sewer system until the company had indemnified the city against damage claims. The company closed the plant and moved to another city.

On the other hand, there are numerous examples of cooperative study which benefited all concerned. In a town of 3000 the excessive flow and screenings at the sewage disposal plant were due to a large leather processing plant. The company received hides in carload lots from slaughterhouses. Removal of the hair and fleshings from these hides required a considerable volume of wash water. For many years a portion of the fleshings was removed from a hand-raked bar screen, but smaller pieces and hair went through to the tanks and formed tremendous layers of scum. The number of operators required far exceeded the normal needs of such a small community. After a friendly discussion the manufacturer was persuaded to install a fine screen in his plant to remove hair and fleshings. The plant found a market for this material which paid for the screen and continues to be profitable. The city installed a comminutor at the sewage plant to macerate the remaining fleshings. Now this disposal plant is operating with a normal labor force. In many cases municipalities have found it expedient to accept the untreated waste of an industry into the sewage system in regulated amounts throughout the 24-hour day.

In 1929 Frank A. Marston stated:

> Where the sewage is treated, the cost of operation and maintenance of the sewage treatment plant is influenced by the character of the sewage, including industrial wastes, ground water, and other leakage. Certain industrial wastes may add a considerable burden of expense because of their character, whereas relatively clean rinse waters, although of similar volume, would not involve a corresponding cost. To meet this condition, it is possible to set up the following: a schedule of charges based not only upon the volume of domestic sewage or industrial wastes, but also on the degree of pollution as measured by relative amount of suspended matter, the biological oxygen demand, or some other factor.

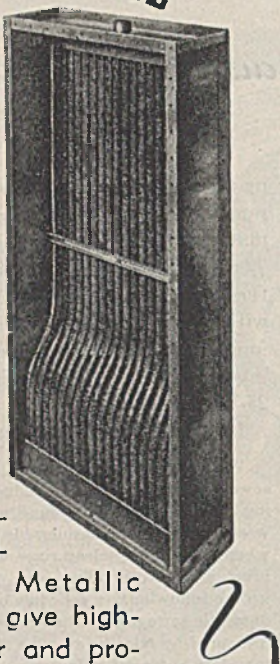
Some years ago F. H. Waring reported as follows on sewage rentals in Ohio:

> In making up a sewer rental schedule, special allowances . . . . should be made for certain unusual premises served—for example, industrial establishments where liquid wastes are admitted to the sewers. For the latter premises variations in charges in accordance with the volume may be supplemented by further variations in accordance with the strength of the industrial sewage as compared with the domestic sewage.

Hammond, Ind., has a sanitary district of about 27 square miles. Within its boundary are some seventy-five principal industrial establishments. Since 1942 all sanitary sewage originating within the district has received complete treatment, and a comprehensive program has been in progress for the satisfactory handling and disposal of all local trade wastes. With the possible exception of the wastes from a corn products plant, all industrial wastes within the district are being received for complete treatment at the sewage treatment plant or are being handled in some other manner satisfactory to the district. The volume of sewage received averages about 24 million gallons per day from an estimated population of 70,000. The population equivalent for the domestic sewage and industrial waste averages around 160,000. Because some of the industries have been active on war projects, the character of the industrial residues is expected to change; but the city does not anticipate difficulties in handling the normal industrial activity of the sanitary district.

At Cedar Rapids, Iowa, a packing plant paid the cost of construction of the public disposal plant and gives a yearly sum toward its operating cost. Similar agreements on the basis of yearly charges to industry have been worked out with creameries and laundries in Boulder, Colo., with grain elevators, creameries, and food industries in Traverse City, Mich., and in Sioux Falls, S. Dak., Phoenix, Ariz., and Orville, Ohio. Freehold, N. J., has established special rates for industrial wastes delivered by a separate sewerage system to the treatment plant. In Los Angeles, H. F. Gray reports that industries must apply for a permit to discharge liquid waste into the sewers. This permit may be refused if the waste is found

(*Continued on page 82*)



objectionable. When the treatment requirements of the waste are found to be above that of normal human sewage, a charge is made to the producer of the waste, based, according to a proposal of Gray, upon the assessed valuation of the industrial plant.

Most of the agreements mentioned have been based on yearly or some other negotiated charge. In the past three years two municipalities have assessed sewer service charges on the basis of the volume of waste and the strength and character of its constituents. Buffalo, N. Y., is reported to be the first city to apply such regulations. The service was started in February, 1943. As reported by Symons and Crane in the March, 1944, issue of *Water Works and Sewerage*, the following formula is used for calculating the charge applied:

$$R = FP_c(C - N_c) + FP_s(S - N_s)$$

where R = rate of special charge, cents/1000 cu. ft. of waste volume
F = factor for converting p.p.m. to lb./1000 cu. ft.
P_c = contract price of chlorine, cents/lb.
C = concentration of chlorine demand of waste, p.p.m.
N_c = normal dry weather chlorine demand of raw sewage, p.p.m. of sewage received at treatment works
P_s = cost in cents of chemicals for sludge conditioning, and of power for solids disposal resulting from 1 lb. of suspended solids received in raw sewage at treatment works
S = concentration of suspended solids in waste, p.p.m.
N_s = normal grit-free suspended solids of raw sewage as received at treatment works, p.p.m.

The factor P_c may vary from year to year according to the contract price for chlorine, and the factor P_s may vary according to the price of chemicals and power involved in the disposal of solids, as determined from operations for the previous year or previous two years. The factors C and S may be established by analysis (periodic or otherwise) to obtain average concentrations to be applied for any agreed length of time.

Average sewage results at Buffalo are 5.6 p.p.m. chlorine demand and 157 p.p.m. suspended solids. The special charge for 1000 cubic feet of waste amounts to 0.136 cent for each p.p.m. chlorine demand and 0.00305 cent for each p.p.m. suspended solids determined by the sewage analysis. It has not appeared economically feasible to apply a special charge when the rate is less than 1 cent per 1000 cubic feet of waste volume. The application of these charges has been successful so far in Buffalo. When questions arise, cooperative and friendly negotiations have solved the problem.

In February, 1944, New Brunswick, N. J., passed an ordinance based on the premise that all wastes should be treated at the municipal plant without pretreatment by industry. The ordinance stated: "The charges for factory effluents or industrial wastes discharged into the city sewers or tributaries thereof shall be fixed and determined according to flow, suspended solids, and chlorine demand, according to the following schedule of rates: $22.00 per million gallons, $5.00 per ton of sludge, and $5.00 per 100-pound chlorine demand." Chester Paulus, mayor of New Brunswick, reported in July, 1944, that "if industrialists are willing and do cooperate, most industrial wastes can be handled in adequately designed sewage treatment plants constructed for the treatment of domestic sewage; but in this cooperation the industrialists must be prepared to pay their full share of the cost of the plant enlargement and plant operation."

In England the responsibility for sewage disposal was transferred from the local authorities to a national board in 1936. Since that time all new discharges of factory effluent to sewers have been assessed on the basis of the actual cost of purification.

There appears to be ample justification for combining the disposal of industrial residues with municipal sewage in a common processing plant. The total cost should be lower in such a unified operation. When industries have to pay service charges, they will be more inclined to use every means available to reduce the over-all load on processing plants. This will tend to increase efforts to find uses for wastes. The entire program appears logical.

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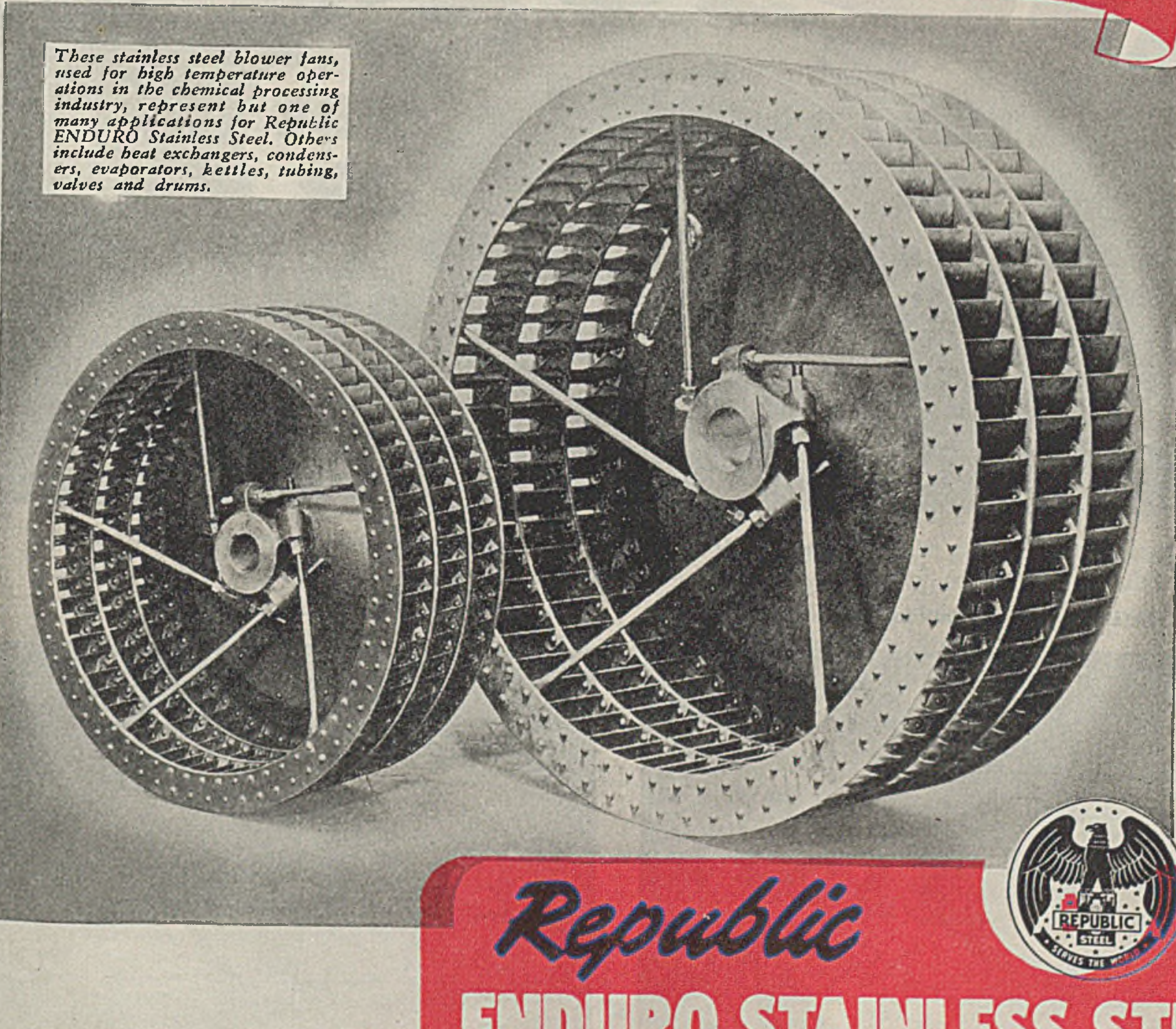

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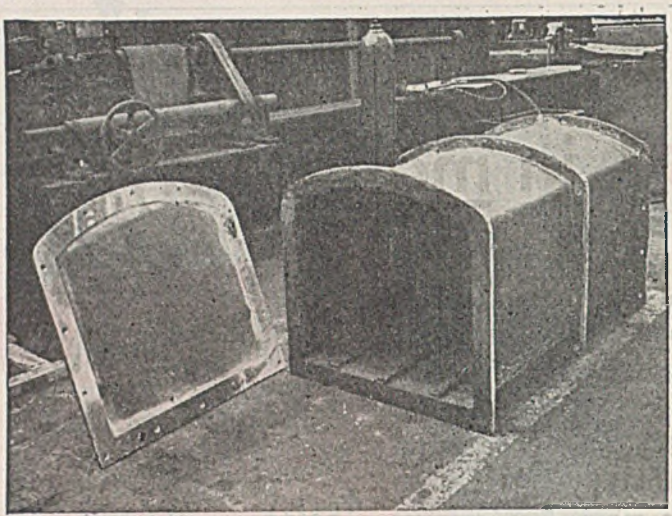
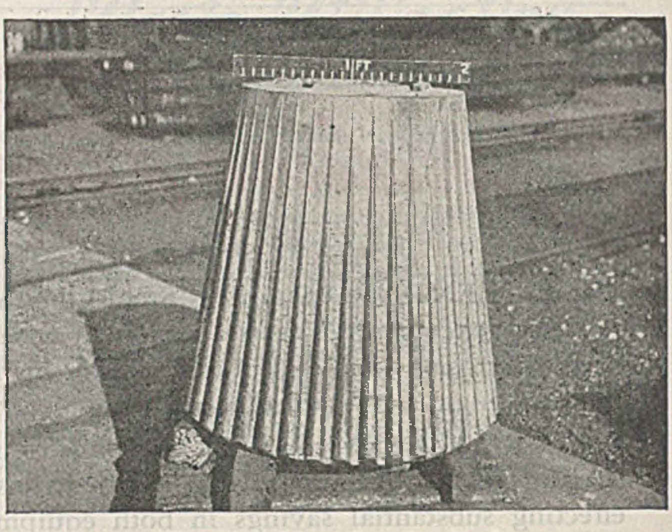
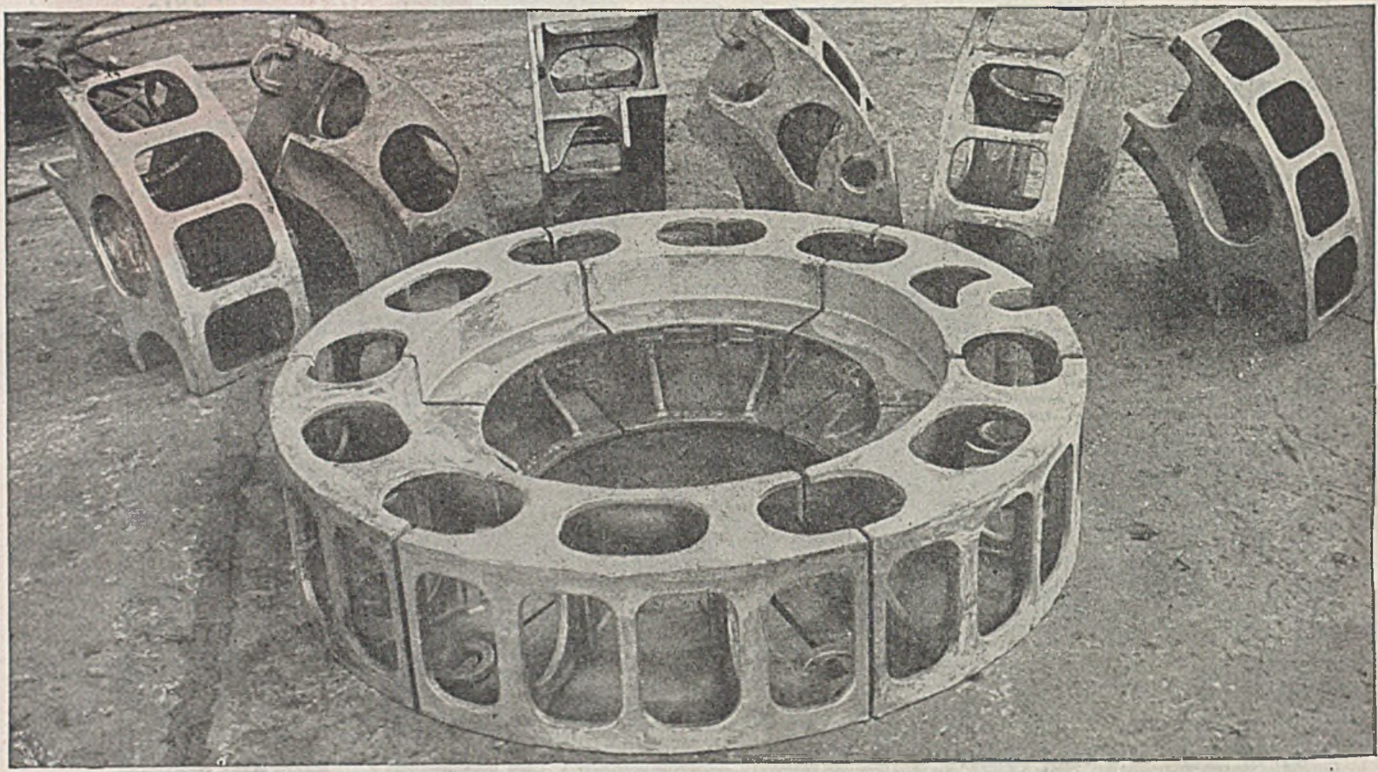


Batch Type Carborizing Retort



Alloy Chilled-Iron Cone for Crusher



Hearths for High Temperature Rotary Furnace

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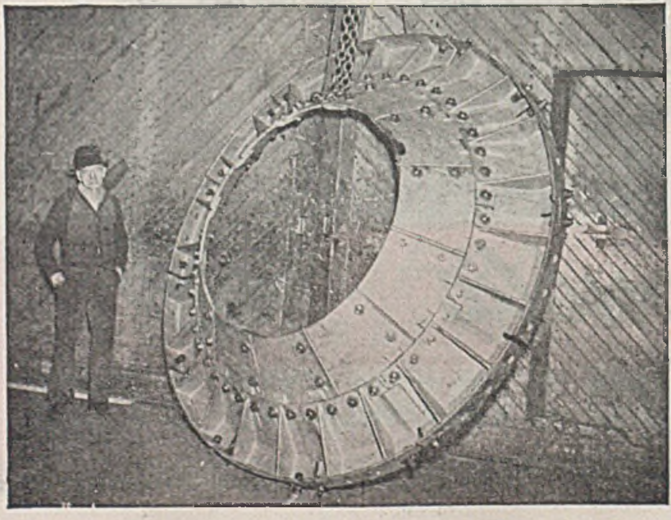
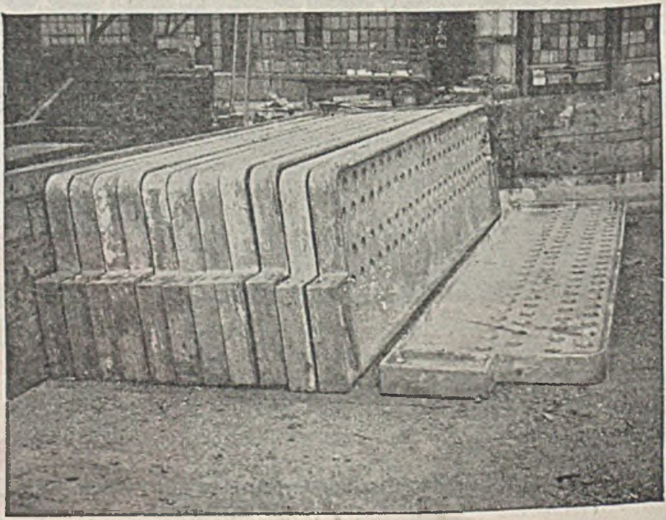
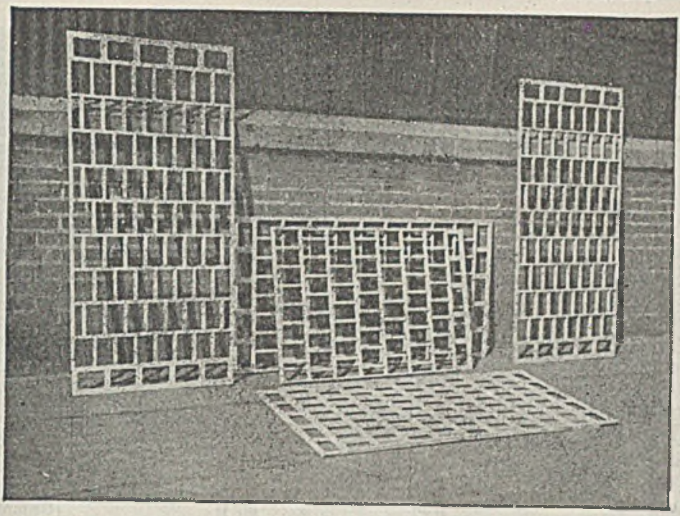
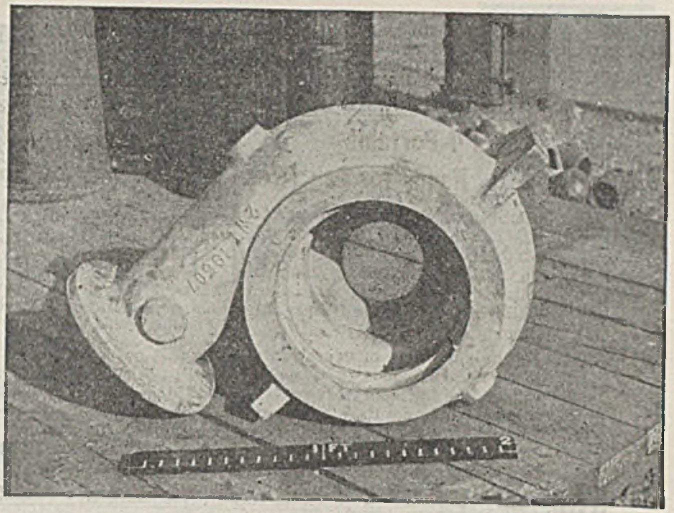


Alloy Tube Support Castings





Hearth Plates for Enameling Furnace



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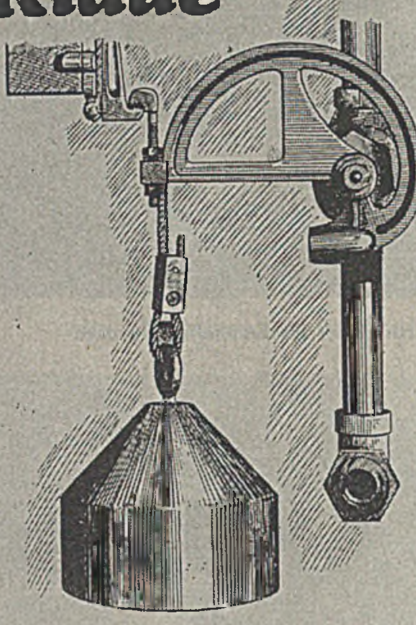

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General output at factories and mines decreased 4 per cent in October, while in the first half of

Meat May Become

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Current Developments in PLANT MANAGEMENT

Standard methods of presenting facts aid chemical plant management and also improve employer-employee relations.

Discussed by Walter von Pechmann

LARGE sums are spent yearly by the chemical industry for collecting data, with the expectation that figures speak for themselves and, therefore, will bring about improvements or will correct undesirable conditions. However, unsound theories which cannot be supported by statistical information are often given preference over carefully thought out plans. This is due to the fact that poorly presented statistical data, valuable though they may be, are not accepted by management as proof that conditions need to be changed. The manner of presentation is usually more important than the facts presented. If this were generally realized by management and employees, more emphasis would be put upon the proper presentation of facts, and more thought would be given to standardizing the method of presenting a problem. It is sometimes contended that this type of standardization restricts individualism. This is not true unless the standardization is carried to the extreme. Standardizing the method of presenting facts gives an employee the assurance that his work will be judged on the basis of accomplishments and not on the basis of the form in which his report is presented. Management, on the other hand, can more easily weigh the merit of various suggestions submitted because standardized reports can be compared directly. Another advantage of unifying methods of fact presentation lies in the exclusion of trick methods used to forward one point of view.

At the start of a project management must decide on the extent to which standardization is to be carried. Consideration must be given to the element of time. It is considered good practice to plan a standardization program completely but to put it into effect gradually. Possible resentment is thus reduced and employees can become gradually acquainted with the new plan.

The idea of standardizing the presentation of facts is not new. Every plant or every department within a plant follows a certain practice when verbal or written reports are made. A plantwide standardization program takes into consideration these established practices, selects those found most suitable, classifies them, and describes in detail when and how they should be used.

Methods of Standardizing

Management can either assign this task to a person or to a committee representing management and employees. The writer recommends the committee because employees are more inclined to cooperate in a new plan if they had a part in establishing it. Management should not draw up forms and issue instructions without first consulting those who will have to carry out the new plan. No one would think of standardizing job performance which describes in detail the functions of a job, without first obtaining the opinion of an experienced worker. When it comes to standardizing fact presentation, however, management often takes the point of view that it should decide how reports are to be made and that personnel need not be consulted. Although employees should have no voice in deciding on the extent to which standardization should be carried out, they can contribute to the success of the new plan by offering suggestions regarding the technique to be followed.

It is important to know why certain facts are presented and what relation they have to the issue. Therefore, the purpose of presenting each fact should be clearly stated, the advantages to be gained by accepting it should be clearly outlined, and it should be presented in such a way as to support the claims made. Regardless of whether facts are presented verbally or in writing, the following points must be given consideration in order: purpose, idea, claim, facts in support of claim. As an example a certain project (No. 1985) will be described:

PURPOSE. To reduce waste caused by washing products A, B, C, and D.

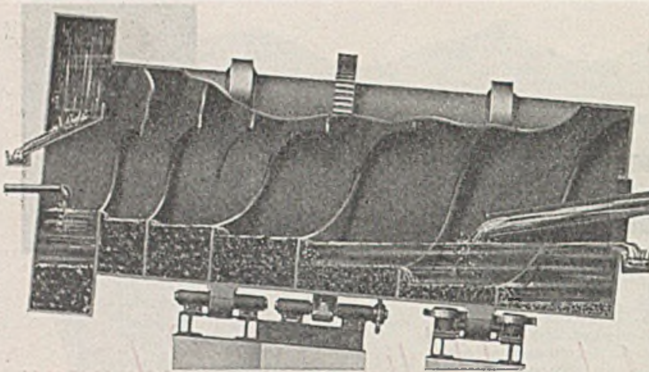
IDEA. To install a new type of screening device. At present the washing loss on products A, B, C, and D amounts to approximately 8%. This loss is caused by scraping of the product against the perforated screens during the washing process. Previous attempts to reduce this loss by cutting down the speed of mixers and thus lowering the centrifugal action have not been successful. Project 1985 suggests installing a new type of screen in the center of the tank and connecting it with the outlet by means of a pipe (a drawing may be presented here).

CLAIMS. It has been found that the new type of screen reduces waste from 8 to 1.5%. Yearly savings are estimated at approximately $8500. Washing time is not affected by the new type of screen. Cost of installation will not exceed $500 per tank. The quality of products is not affected by the new process.

FACTS IN SUPPORT OF CLAIMS. Statistics show the saving of material which results when products are washed with the new type of screen. A detailed breakdown of figures used to arrive at a yearly saving of $8500 is given. Statistics show conductivity of the products during various stages of washing with present and proposed screens. Installation costs are broken down. Statistics or samples are shown to prove that quality of product is not affected by the new type of screen.

It is important that only one idea be presented at a time and that the claims made be directly connected with this idea. If the idea, for instance, proposes the installation of one screen, yearly savings cannot be estimated on the assumption that all screens in use at the present time will be changed. Although this is common sense, the number of violations found in reports submitted daily to managements is surprising.

Employees may fail to mention factors which are disadvantageous. Little is gained by proposing one improvement at the expense of another. Provisions should therefore be made to give management the assurance that the new proposal does not contain undesirable features. Common practice is to demand that employees answer the question, "Does the proposed idea have any disadvantages?" The writer has found this method rather unsatisfactory because the question is not specific enough. It is recommended that management insist upon a comparison of all factors which are common to the present method and the proposed one. Where no present method exists, all factors of the proposed method should be evaluated. The presentation of tables, graphs, and charts should be controlled. The source from which the tabulation is taken, for example, should be given to eliminate misleading conclusions. Anyone who works with statistics is familiar with manufacturers' statements which are technically correct but are presented in such a manner as to be misleading.



Plant Management

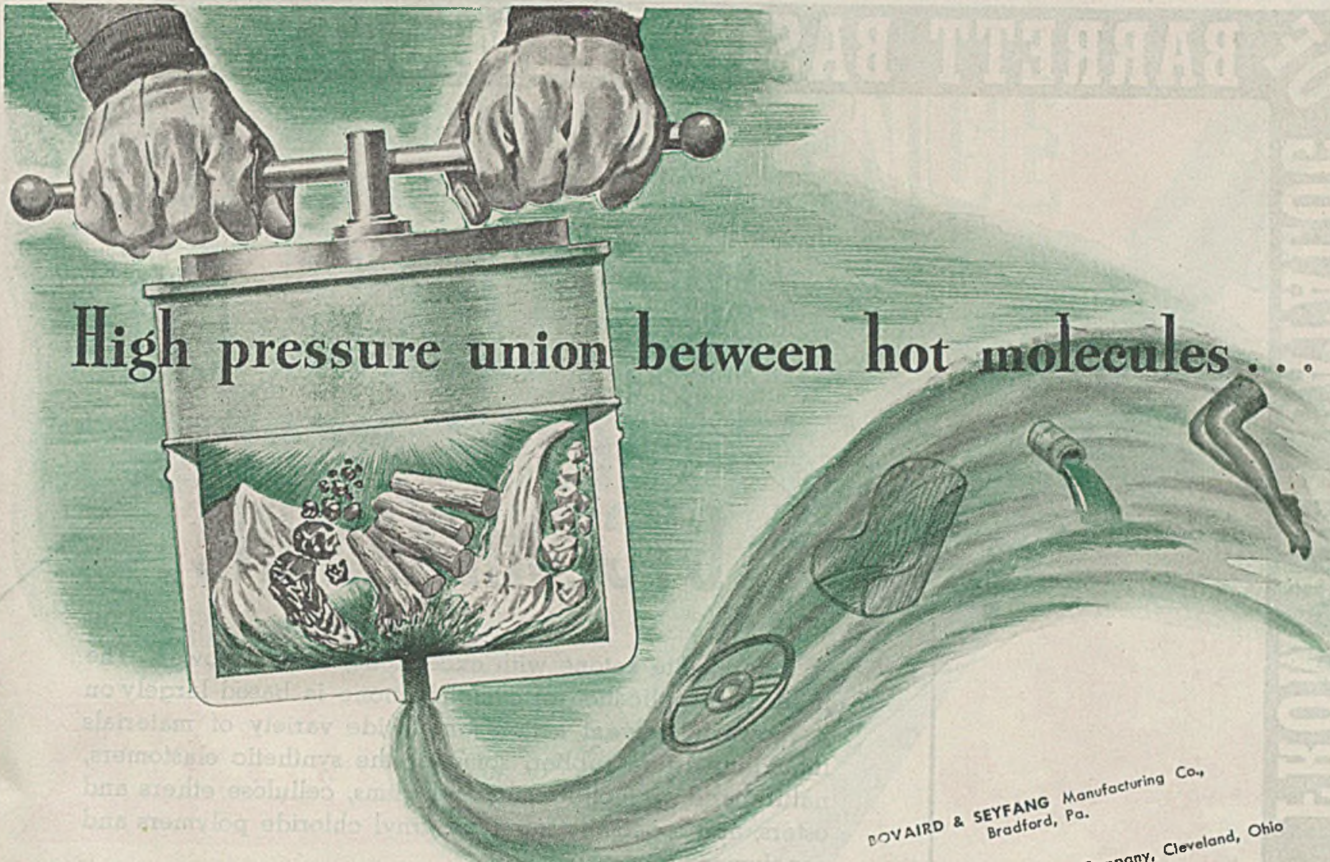
Misrepresentation is usually accomplished by purposely eliminating an important factor. The statement, for example, "investigation revealed that *X* product outsells others", is technically correct if a canvass taken in a certain territory revealed that fact. However, failure to mention that the count was taken in only one territory is misleading; the public assumes that the claim applies to all territories where the product was sold. In scrutinizing technical reports, one frequently finds that claims are based on similar techniques. Therefore, management should stipulate that working papers be submitted together with final tabulations.

Charts

Graphs are intended either to show a tendency or to enable the reader to visualize the idea quickly without having to go through voluminous tabulations. If graphs and charts do neither, they should not be used. Occasionally optical illusions are used to make a value appear greater than it actually is. Vertical lines, for example, make space appear wider and horizontal lines smaller. A white square appears larger than a black one. When standards are being developed for the presentation of facts, optical tricks should be taken into consideration. Since graphic representation is frequently used in the chemical industry, a brief list of suggested rules follows:

1. Avoid using areas or volumes when representing quantities.
2. A chart should be arranged to read from left to right.
3. Figures for the horizontal scale should be placed at the bottom and those for the vertical scale at the left of a chart. If necessary a scale may be placed at top and right also.
4. Whenever possible the numerical data from which the chart was made should be included, either on the chart or in tabular form accompanying it.
5. A column of figures relating to dates should be arranged with the earliest date at the top; separate columns, each relating to a different date, should be arranged so that the column for the earliest date is at the left.
6. When charts are colored, green should be used to indicate desirable features and red for undesirable.
7. For curves drawn on arithmetic coordinates the vertical scale should be selected so that the zero line will show on the chart. If this is impossible, the bottom line should be slightly wavy to indicate that the field is broken and does not reach zero.
8. When curves are drawn on logarithmic coordinates, the bottom and the top lines of the chart should be some power of ten on the vertical scale.
9. Curves should be drawn heavier than coordinate lines so that the curves may be clearly distinguished from the background.
10. Whenever possible a vertical coordinate line should appear for each point plotted on a curve so that the vertical lines will show the frequency of the data observations.
11. If there are not too many curves, it is desirable to show at the top of the chart the figure for each point plotted in a curve; if these figures are added (to show yearly or other totals), they may be useful to the reader.
12. The title of a chart should be complete and clear so that misinterpretation will be impossible.

Only a few concerns have attempted to standardize the verbal presentation of facts. Detailed descriptions of how verbal reports should be made probably restrict freedom of expression. However, it is advantageous to management and employees if a list of do's and dont's is developed which includes hints on how to present a problem convincingly. The importance of using correct English, presenting the problem in logical sequence, not being repetitious, avoiding arguments, and drawing conclusions pertaining only to the subject at hand, are a few of the many factors which should be mentioned. Management may also provide lectures to train employees in the proper presentation of verbal reports.



High pressure union between hot molecules . . .

CUTS THE COST OF STUFF AND THINGS

Chemists have learned to mix the unmixables. It wasn't so only a generation ago. Solids and liquids and gases which formerly remained strictly aloof from each other, today can be united under high pressure and heat.

They produce a myriad of low-cost miracles. The lustrous yet washable gowns; the beautifully stockinged leg; brilliant plastics; weed killers; quick drying paints; fireproof lumber—all are facts of life grandma didn't know about. All are results of high pressuring molecules.

Members of Dresser Industries engineer high-pressure equipment for this large scale chemistry. Pumps that push these hot mixtures around under hundreds of pounds pressure per square inch. Compressors that squeeze chemical activity into the more reluctant substances at 5000 pounds pressure. Storage tanks that hold half a million cubic feet of temperamental gas ready and waiting under a tight lid at 100 pounds to the square inch.

But the compressors and pumps and vessels are themselves made of elements which tend to unite chemically with the contents under heat and pressure. Licking corrosion in high-pressure equipment has been one of Dresser Industries' contributions to lower-cost luxury. As chemistry thinks up new problems, Dresser Industries, Inc., creates the equipment that is *First to Be New—Last to Wear Out.*

BOVAIRD & SEYFANG Manufacturing Co., Bradford, Pa.

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INTERNATIONAL Derrick & Equipment Co., Columbus, Marietta & Delaware, Ohio; Beaumont, Texas; Torrance, Calif.

PAYNE Furnace Co., Beverly Hills, Calif.

SECURITY Engineering Co., Inc., Whittier, Calif.

KOBE, Inc., Huntington Park, Calif.

ROOTS-CONNERSVILLE Blower Corporation, Connersville, Ind.

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Creative Engineering
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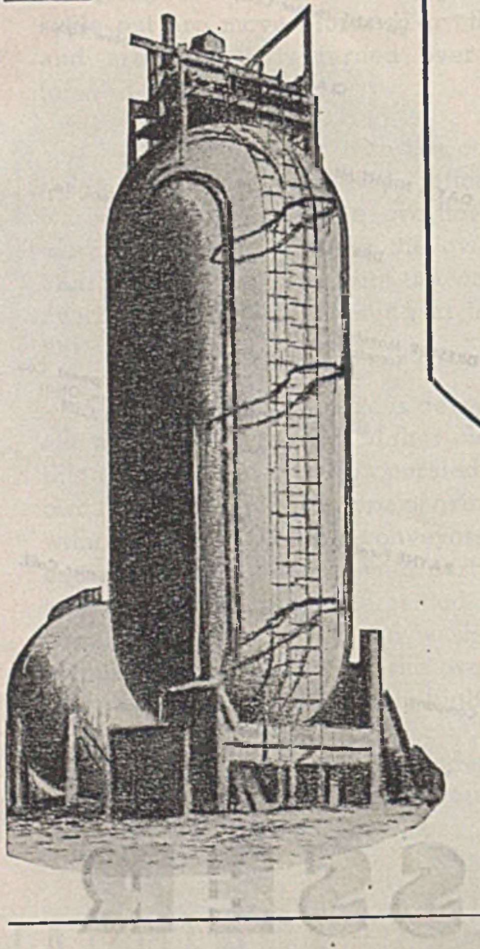
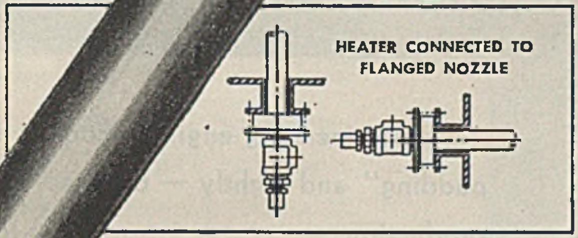
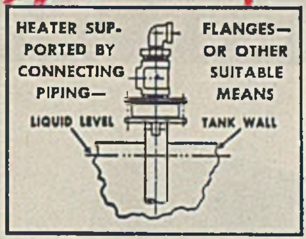
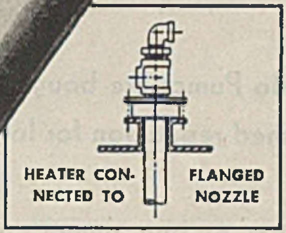
GEARED TO ANTICIPATE THE COURSE OF INDUSTRY
OIL AND GAS EQUIPMENT A SPECIALTY

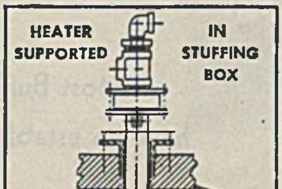


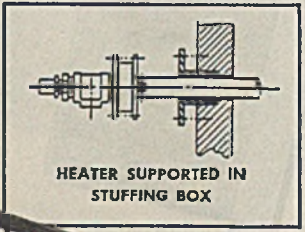

HOW DO YOU LIKE THAT?— IT DEFIES ME!
CRUSTY RUSTY


HEATER CONNECTED TO FLANGED NOZZLE

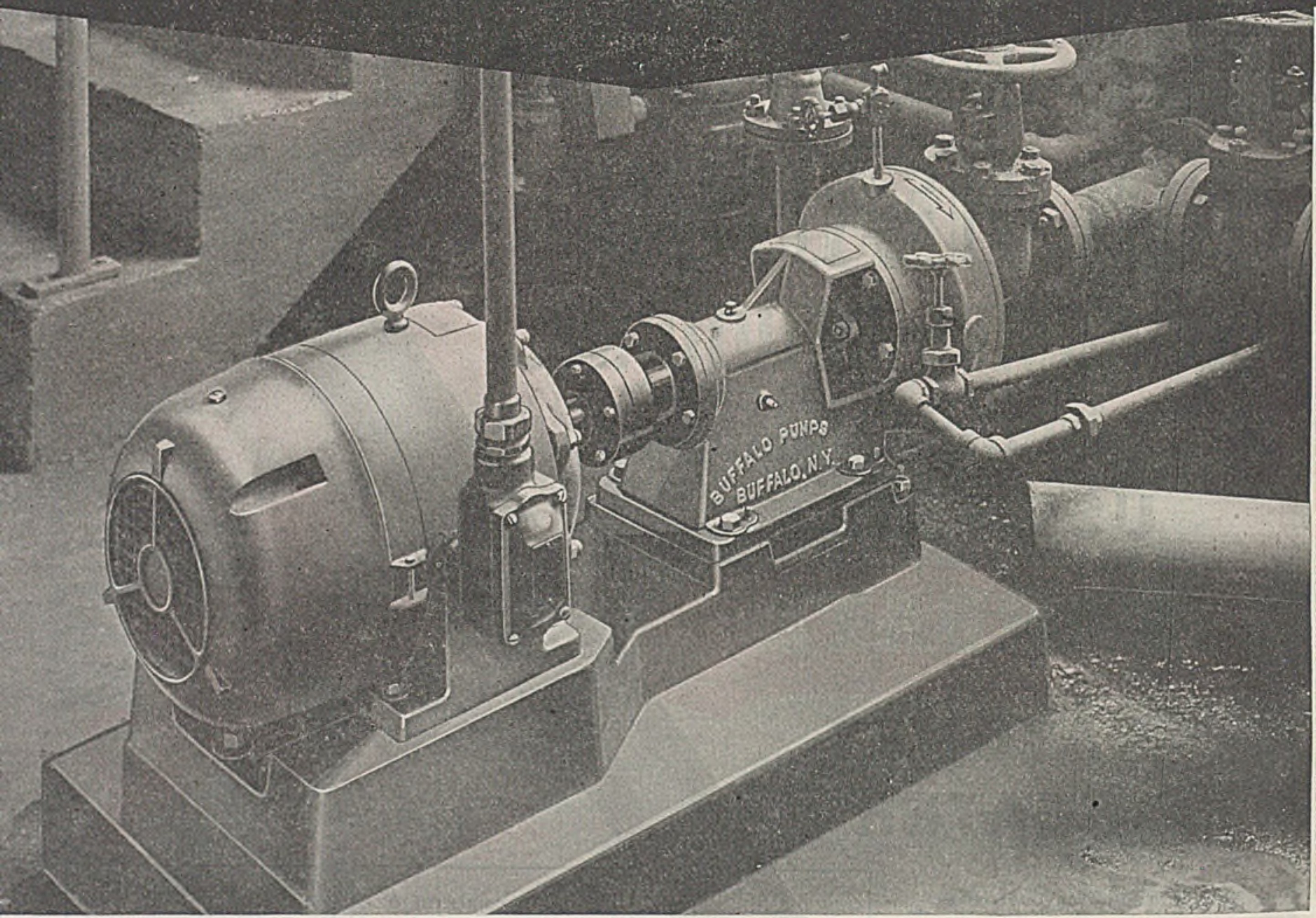

HEATER SUPPORTED BY CONNECTING PIPING—
FLANGES—OR OTHER SUITABLE MEANS
LIQUID LEVEL
TANK WALL


HEATER CONNECTED TO FLANGED NOZZLE

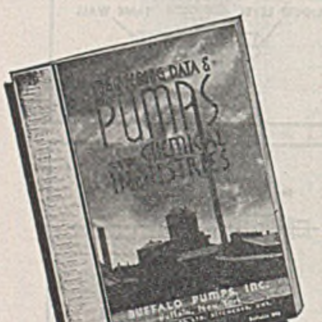

HEATER SUPPORTED IN STUFFING BOX


HEATER SUPPORTED IN STUFFING BOX


KARBATE HEAT EXCHANGERS

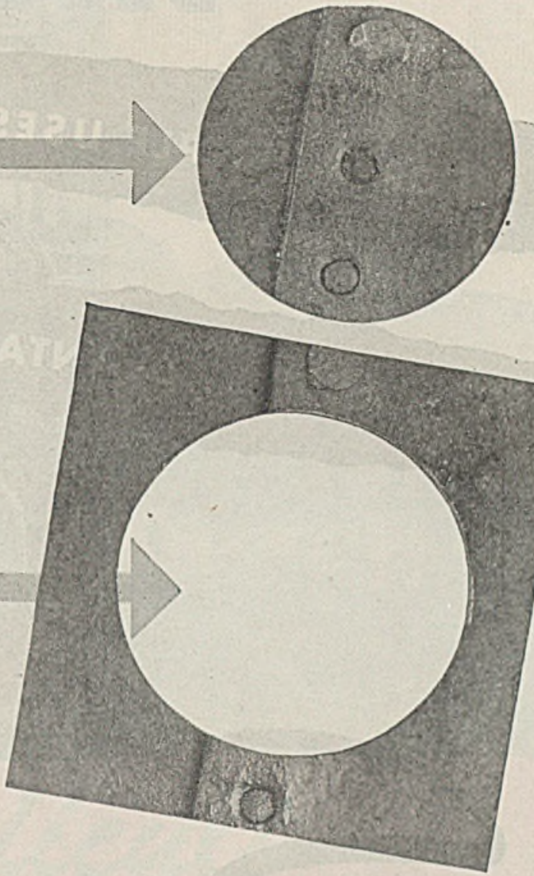


BUFFALO PUMPS
BUFFALO, N.Y.



DATA &
PUMPS
CHEMICAL
INDUSTRIES
BUFFALO PUMPS, INC.
Buffalo, New York

IT PAYS TO CUT THIS COUPON



Here's a coupon with top value for the holder—*your gas holder.*

From it you'll get *positive* information about the internal condition of your wet-seal gas holder—information that will save you money in reduced maintenance and replacement costs. You'll be able to safeguard failures due to corrosion, misalignment or improper lubrication.

The coupon method of internal inspection is only one of the steps in the Stacey Brothers Gas Holder Inspection Service. Based on scientific survey, thorough examination, laboratory tests and engineering study, we'll give you a comprehensive report and specific recommendations to help you insure maximum life for your holder.

Now's the time to let us give you this personalized annual inspection service. Many prominent operators already have entered their contracts with us for the 1946 season . . . and we've served some of them year after year. Their contract renewals are your best assurance of our ability to give you prompt, economical and efficient inspection. May we discuss your requirements with you?

STACEY BROTHERS GAS CONSTRUCTION CO.
One of the Dresser Industries
5535 VINE STREET · CINCINNATI 16, OHIO

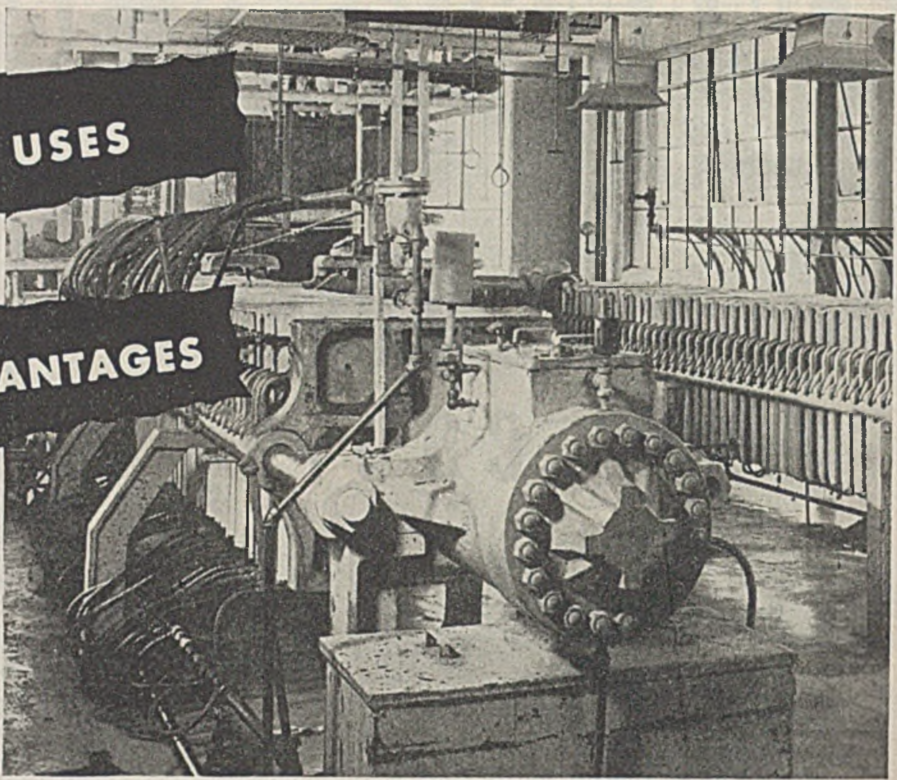
Coupons are cut with a special disc-cutter like this. An Archimedean screw holds the cutter in position, clamps the rubber sealing base ring tight against the holder shell, and prevents the coupon from falling into the holder after it is cut.

This and many other features of Stacey Brothers Gas Holder Inspection Service are described in a 16-page illustrated catalog, number 1-44. Write us for your copy.

Stacey Brothers
TANKS

FOR MULTIPLE USES

FOR MULTIPLE ADVANTAGES



Sperry PLATE FILTER PRESSES

There are many reasons — sound reasons — for the increasingly wide use of the Sperry Plate Filter Press. Industry has found that this filter press offers special advantages which increase the efficiency and reduce the cost of filtration.

One of the foremost is its versatility. The Sperry Plate Filter Press will handle any kind of filterable mixture, including viscous substances. It can perform low, medium or high pressure filtration. It can use wire, wool, asbestos, glass, vinyon, filter paper, pulp and virtually all types of filter cloths. The simplest type of filter cloth can be used — in fact the cloth can be cut direct from the roll. Cloths are easily removed and replaced.

Advantageous, too, is the simple construction of the Sperry Plate Filter Press. This means that its first cost is low, and that maintenance and operating expenses are kept to a minimum. It also assures ease of operation.

The Sperry Plate Filter Press can be used with precise temperature control. It can be used to separate emulsions. It will handle hot liquors without vaporizing. It will filter without exposing the liquid to the atmosphere.

If you have a filtration problem, why not discuss it with Sperry engineers? We invite you to submit samples of your material for a complete analysis, we will then give unbiased recommendations . . . all without obligation.

FREE . . . Valuable data and charts on industrial filtration in this booklet. Write Sperry for your copy — today!

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BATAVIA, ILLINOIS
Filtration Engineers for Over 50 Years

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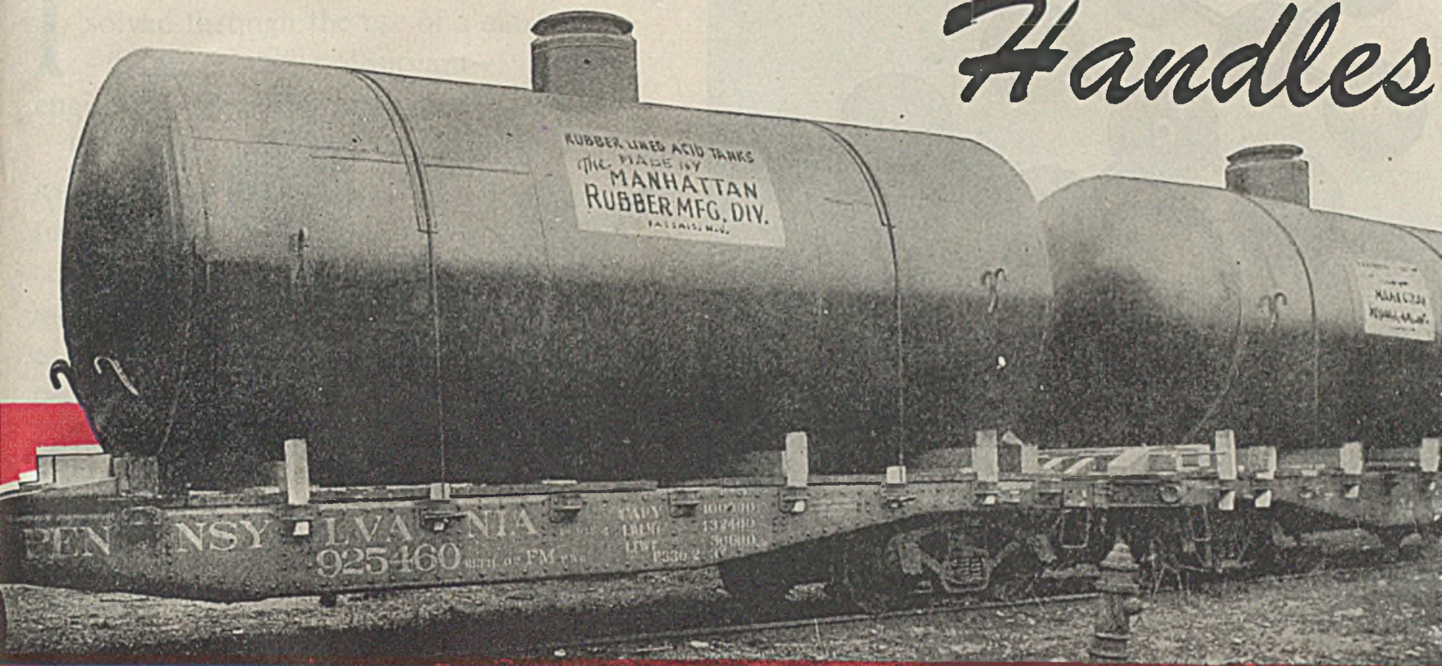
MANHATTAN *Handles*

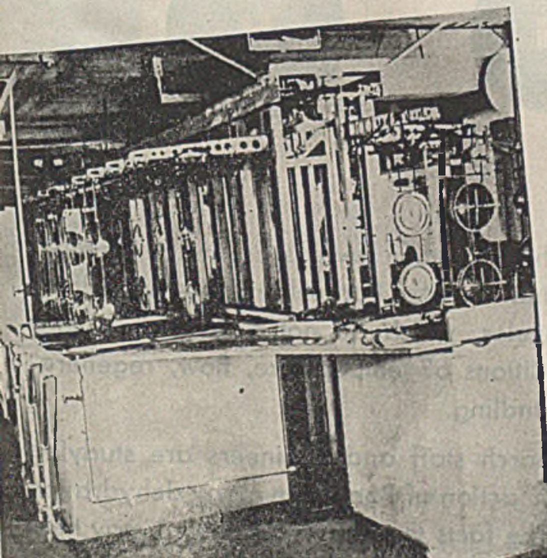


THE *Big* AND *Difficult* RUBBER LINING JOBS

Shown here are two 15,000-gallon rubber-lined barge tanks. 10 ft. in diameter x 27 ft. long. Weight 27,000 lbs. each. Rubber-lined by Manhattan with acid-proof rubber for conveying sulphuric acid solution.

Tanks like these are easily handled in Manhattan's giant tank-lining vulcanizer, which is 15 ft. in diameter and takes anything that can be shipped on a railroad flat car.

Below is an installation consisting of a number of rubber-lined plating, acid dip and rinse tanks lined by Manhattan for use with a Hanson-Van Winkle-Munning elevator-type, full-automatic conveyor.



Manhattan has developed a special rubber-to-metal bond that cannot be mechanically separated. Regardless of contraction and expansion of metal under radical temperature changes, Manhattan's rubber lining compound clings securely, does not crack or oxidize.

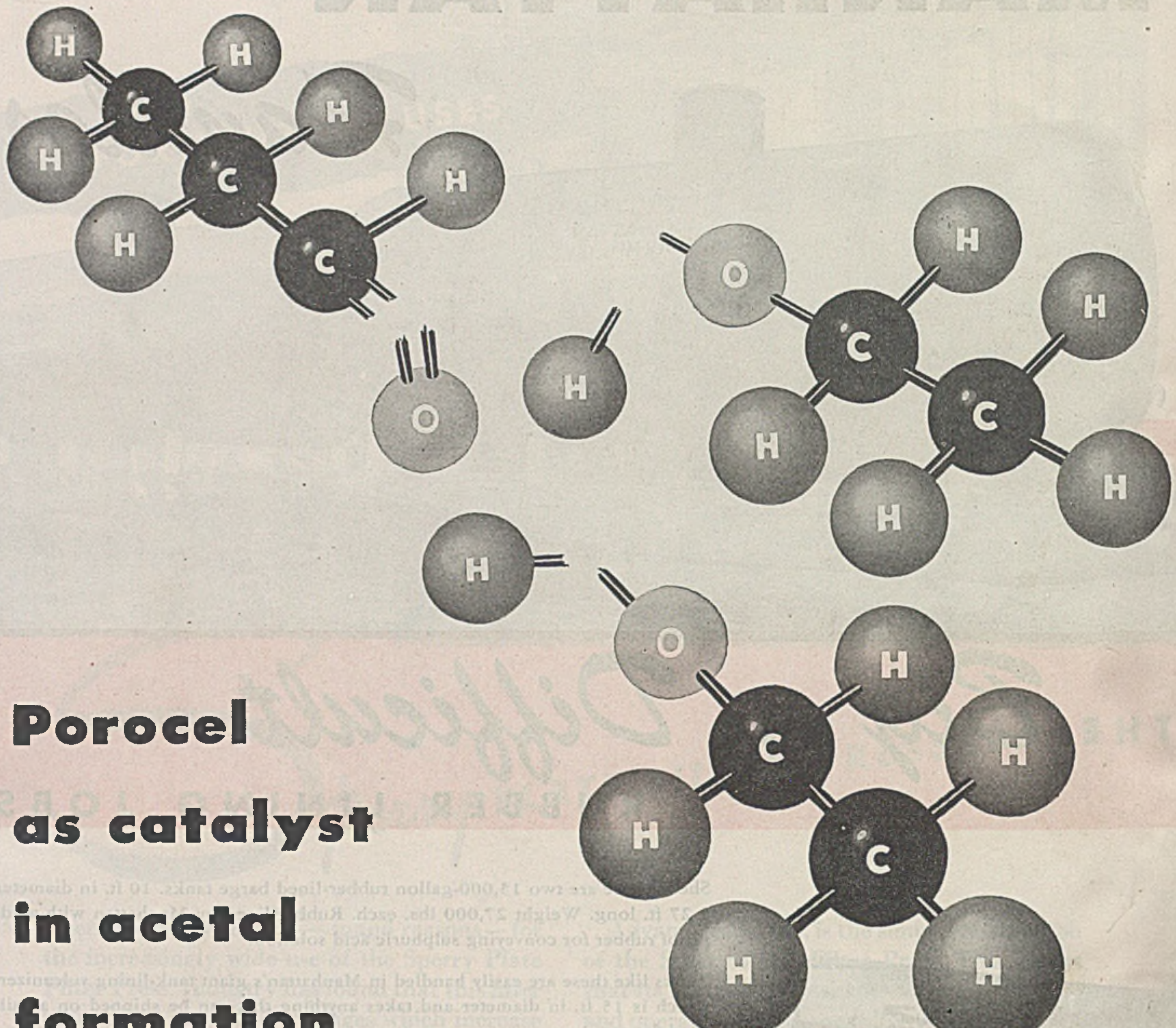
Manhattan rubber linings resist abrasion and shock and eliminate stray currents. They pay for themselves many times over in savings on maintenance. A textile finishing plant reports over 25 years constant service in a battery of 10 one-thousand gallon chemical storage tanks which are still giving satisfactory service.

LOWER YOUR OPERATING COSTS

Avail yourself of the services of Manhattan's 40 years' experience in rubber lining problems in the metal finishing, plating, chemical processing and allied industries.

RAYBESTOS-MANHATTAN, IN

MANHATTAN RUBBER DIVISION



Porocel as catalyst in acetal formation

The production of acetals by the reaction of alcohols with aldehydes has been successfully catalyzed by Porocel. Typical of these reactions is that of ethyl alcohol with propionaldehyde by the simple liquid phase percolation of the reactants through Porocel.

The ability of Porocel to promote dehydration reactions has been noted in many applications. Alcohols react with ammonia in its presence to produce amines. Porocel may also be used to convert glycerol to acrolein, acetone to mesitylene and fatty acids to esters or nitriles.

Dehydration with Porocel is a continuous process, giving the producer all the cost-saving advantages of this method. Further savings are made possible by the low initial cost of Porocel and the ruggedness of the granules, which do not deteriorate under severe conditions of temperature, flow, regeneration and handling.

Our research staff and engineers are studying the catalytic action of Porocel in many dehydration reactions. The facts they have assembled may help you improve your own process or reduce costs. We shall be glad to place them at your disposal without obligation. Just write Attapulgus Clay Company (Exclusive Sales Agent), 260 South Broad Street, Philadelphia 1, Pennsylvania.

POROCEL CORPORATION • BAUXITE ADSORBENTS AND CATALYSTS

If you have a problem that may be solved through the use of a catalyst—an adsorbent—a desiccant—Filtrol* engineers will gladly help you.

For years, Filtrol has maintained its leadership as the outstanding manufacturer of these highly activated, chemically treated materials for the petroleum industry, the fatty oil refiner, the drying of liquids and gases, and in protective packaging.

With vast new markets opening up to American business, based on the scientific advancements made during the war, we will gladly help you with our knowledge and manufacturing "know how" in the field of catalysts, adsorbents and desiccants.

OPENING NEW MARKETS

FILTROL CORPORATION

General Offices: 634 South Spring Street, Los Angeles 14,
California • *Plants:* Vernon, Calif., and Jackson, Mississippi

PRODUCT OF **Filtrol*** **CATALYSTS • ADSORBENTS • DESICCANTS**

RESEARCH AND DEVELOPMENT

*Reg. U.S. Pat. Off.

a.c.f.

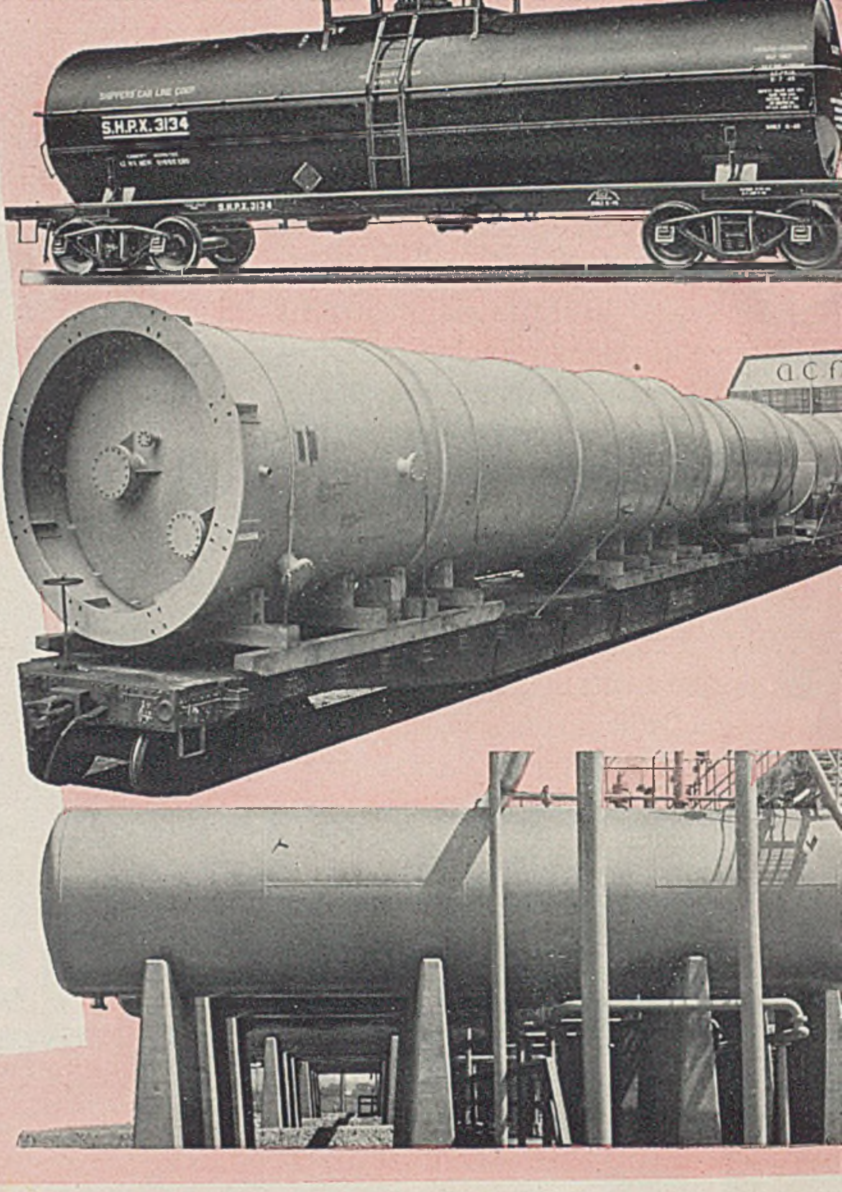
ADVANCED WELDING TECHNIQUE MEANS

BETTER

TANK CARS

PROCESSING EQUIPMENT

STORAGE TANKS



The service life you can expect from tank cars, processing equi
ment, and bulk storage tanks is in direct proportion to the lastin
qualities of the welding techniques employed in their manufactur

More than 30 years experience lies behind a.c.f. advanced weldir
methods — resulting in the development of precision machines ar
facilities today recognized as foremost in the industry.

a.c.f. "Unionmelt" submerged arc welding, for instance, is aut
matically controlled to produce smooth, consistent welds. Similarl
inner and outer welds are effectively joined and overlapped
provide greater strength and durability.

Stringent inspection in accordance with I.C.C., and A.S.M.E. U-
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that results in greater safety, longer service life.

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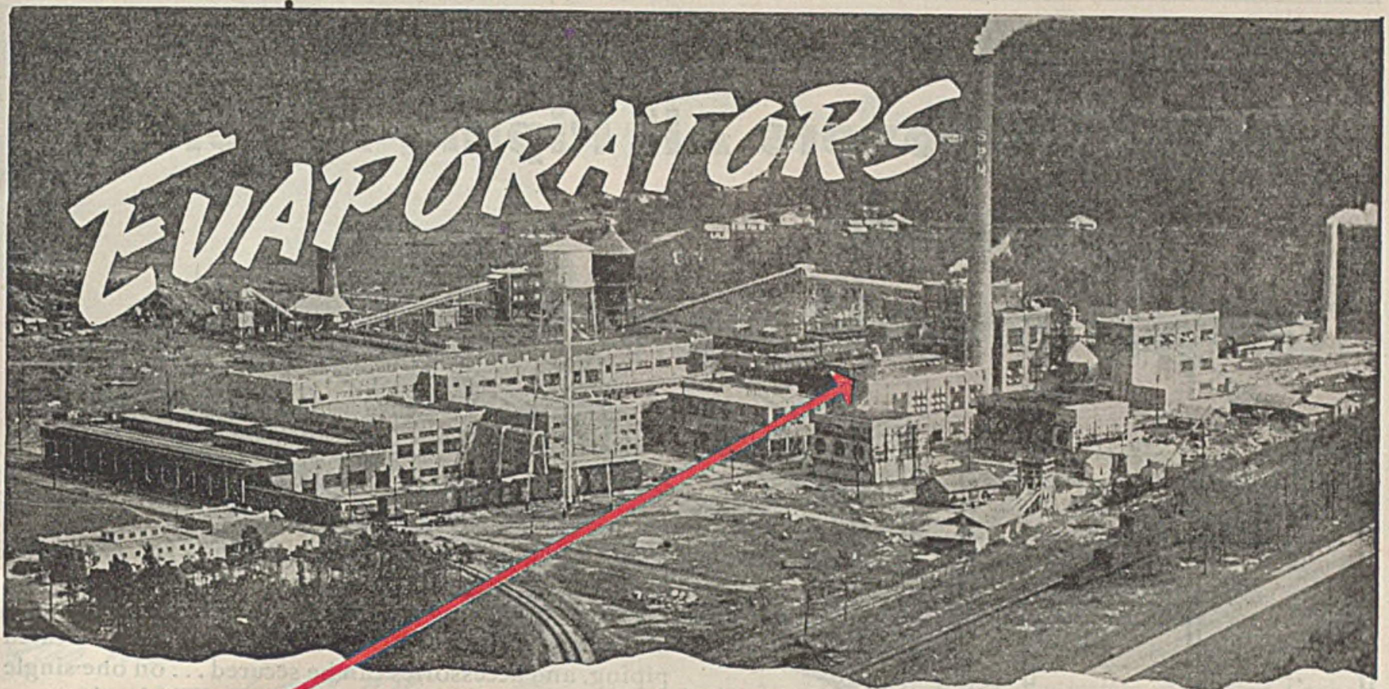
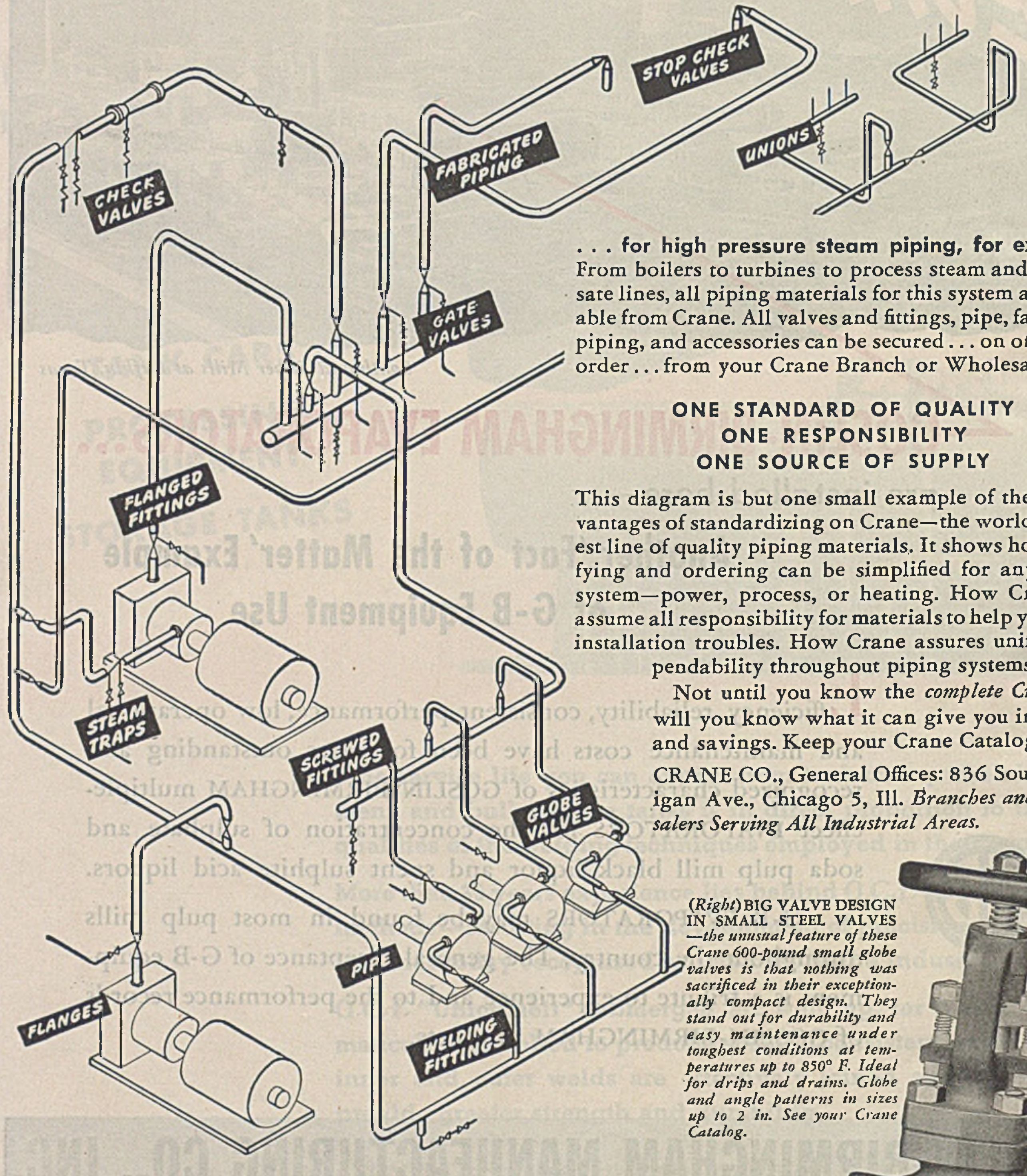


Southland Paper Mills at Lufkin, Texas

ONE ORDER TO CRANE...

Covers All Piping Materials



... for high pressure steam piping, for example. From boilers to turbines to process steam and condensate lines, all piping materials for this system are available from Crane. All valves and fittings, pipe, fabricated piping, and accessories can be secured ... on one single order ... from your Crane Branch or Wholesaler.

ONE STANDARD OF QUALITY
ONE RESPONSIBILITY
ONE SOURCE OF SUPPLY

This diagram is but one small example of the big advantages of standardizing on Crane—the world's greatest line of quality piping materials. It shows how specifying and ordering can be simplified for any piping system—power, process, or heating. How Crane can assume all responsibility for materials to help you avoid installation troubles. How Crane assures uniform dependability throughout piping systems.

Not until you know the *complete Crane line* will you know what it can give you in service and savings. Keep your Crane Catalog handy.

CRANE CO., General Offices: 836 South Michigan Ave., Chicago 5, Ill. *Branches and Wholesalers Serving All Industrial Areas.*

(*Right*) BIG VALVE DESIGN IN SMALL STEEL VALVES —*the unusual feature of these Crane 600-pound small globe valves is that nothing was sacrificed in their exceptionally compact design. They stand out for durability and easy maintenance under toughest conditions at temperatures up to 850° F. Ideal for drips and drains. Globe and angle patterns in sizes up to 2 in. See your Crane Catalog.*

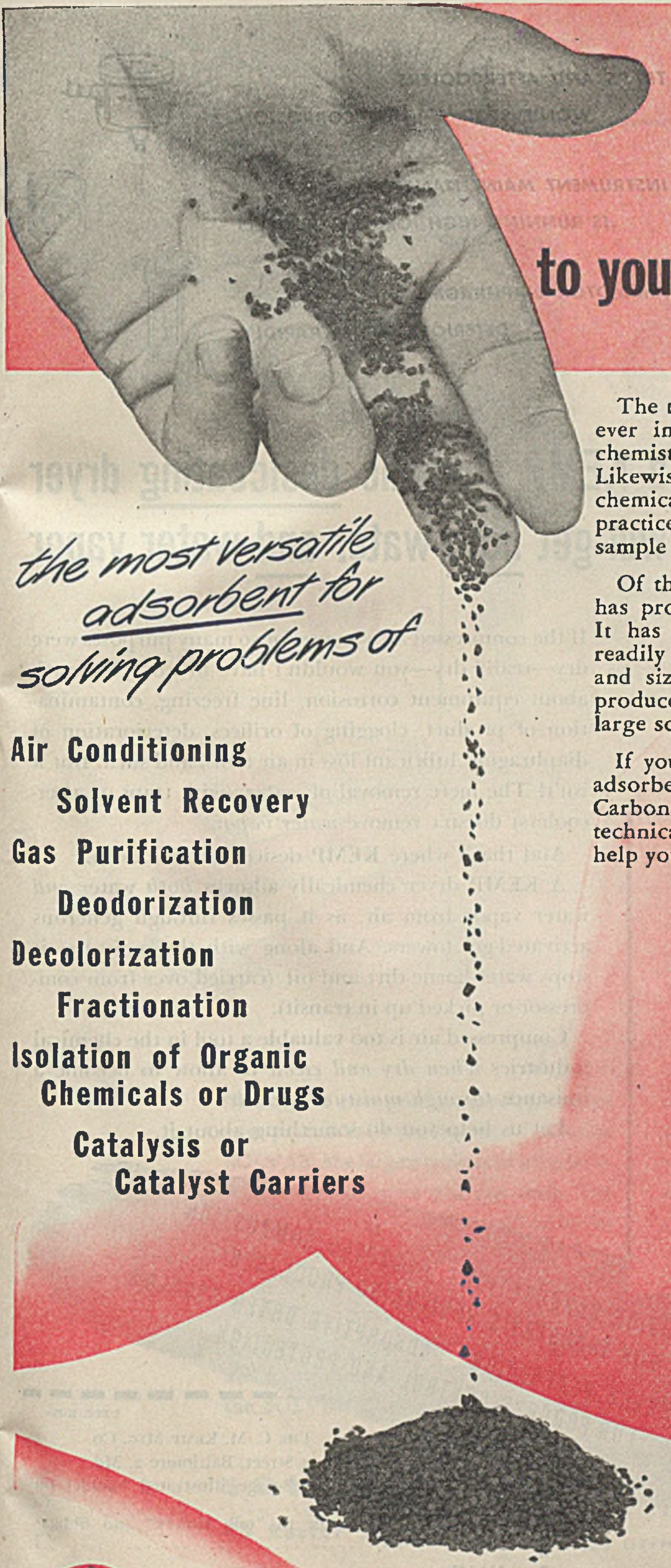
EVERYTHING FROM ...

CRANE

FOR EVERY PIPING SYSTEM

VALVES • FITTINGS
PIPE • PLUMBING
HEATING • PUMPS

Is Activated Carbon the answer to your Adsorbent Problems?



the most versatile adsorbent for solving problems of

Air Conditioning

Solvent Recovery

Gas Purification

Deodorization

Decolorization

Fractionation

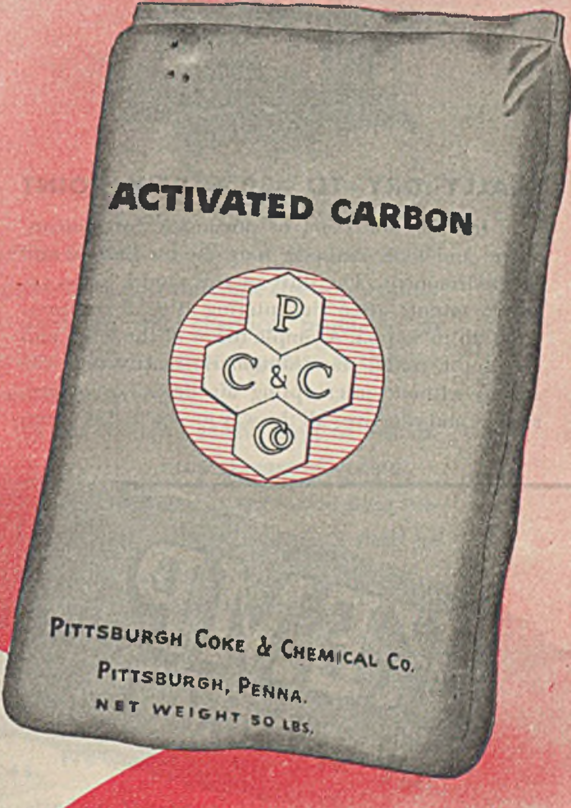
Isolation of Organic Chemicals or Drugs

Catalysis or Catalyst Carriers

The technology of modern manufacturing embraces, in ever increasing degree, application of the science of chemistry as well as the mechanical forces of physics. Likewise the accomplishment of a physical act through a chemical medium becomes more and more common practice. Solving problems of adsorption is a typical sample of this method.

Of the various adsorptive materials, Activated Carbon has proved to be exceptionally adaptable and versatile. It has high adsorptive capacity, is chemically stable, readily regenerated and can be made in a variety of forms and sizes to meet specific needs. Moreover it can be produced relatively economically on a tonnage basis for large scale applications.

If your manufacturing process requires the use of an adsorbent you should investigate the merits of Activated Carbon. Pittsburgh Coke & Chemical Company has the technical "know-how" and the production facilities to help you. Ask us to!



P C&C

Pittsburgh Coke & Chemical Company

Grant Building Pittsburgh, Pennsylvania

WHEN

TRAPS AND AFTERCOOLERS
WON'T STOP AIR-LINE CORROSION

INSTRUMENT MAINTENANCE
IS RUNNING HIGH (ORIFICE TROUBLE)

AIR-MOTOR DIAPHRAGMS
DETERIORATE TOO RAPIDLY

THEN

a KEMP dynamic desiccating dryer
will get both water and water vapor

If the compressed air you use for so many purposes were dry—really dry—you wouldn't have to worry so much about equipment corrosion, line freezing, contamination of product, clogging of orifices, deterioration of diaphragms, lubricant-loss in air tools, and such. But it isn't! The mere removal of *water* (with traps or aftercoolers) doesn't remove *water vapor*.

And that's where KEMP desiccation comes in.

A KEMP dryer chemically adsorbs *both* water *and* water vapor from air, as it passes through generous activated-gel towers. And along with the moisture, it stops water-borne dirt and oil (carried over from compressor or picked up in transit).

Compressed air is too valuable a tool in the chemical industries *when dry and clean* to allow to become a nuisance *through moisture and dirt*.

Let us help you do something about it.

REALLY DRY—TO −30°F DEW POINT

. . . for the protection of pneumatic instruments, valves and tools—however long the air line or cold its environment. The duty of this model is 100 cu. ft. per minute (free air) entering at 70°F and pressures up to 80 p.s.i. A simple throw of the lever, and set of the timer, starts automatic reactivation (by steam) without interrupting air flow. Economical, simple, and effective—all the way to −30°F dew point.

PRECISION CARBURETION + ADAPTED COMBUSTION
FOR INDUSTRY'S HEAT-USING PROCESSES
ATMOSPHERE GENERATION & ADSORPTIVE DRYER SYSTEMS
FOR PROCESS CONTROL AND PROTECTION

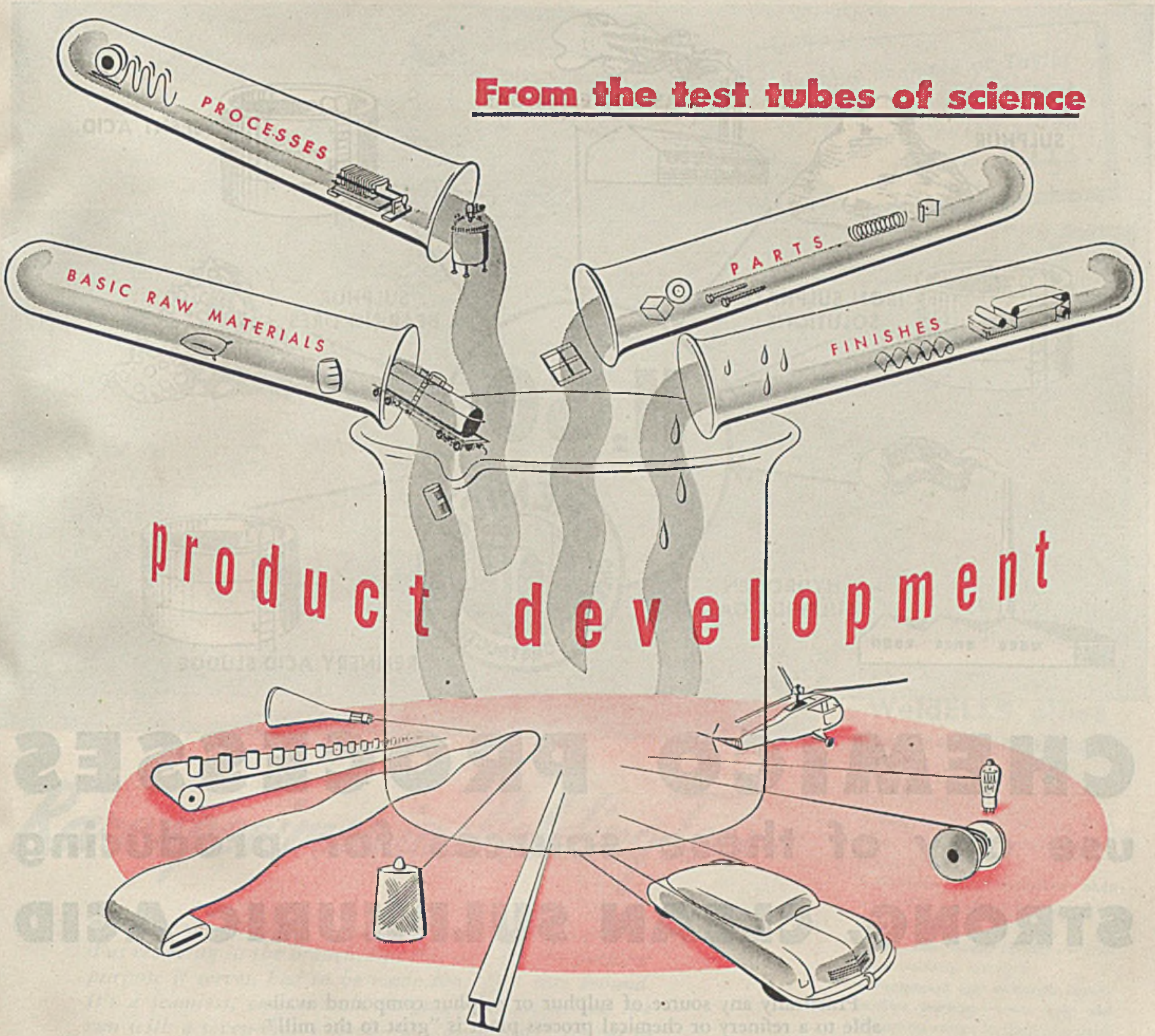
KEMP
OF BALTIMORE

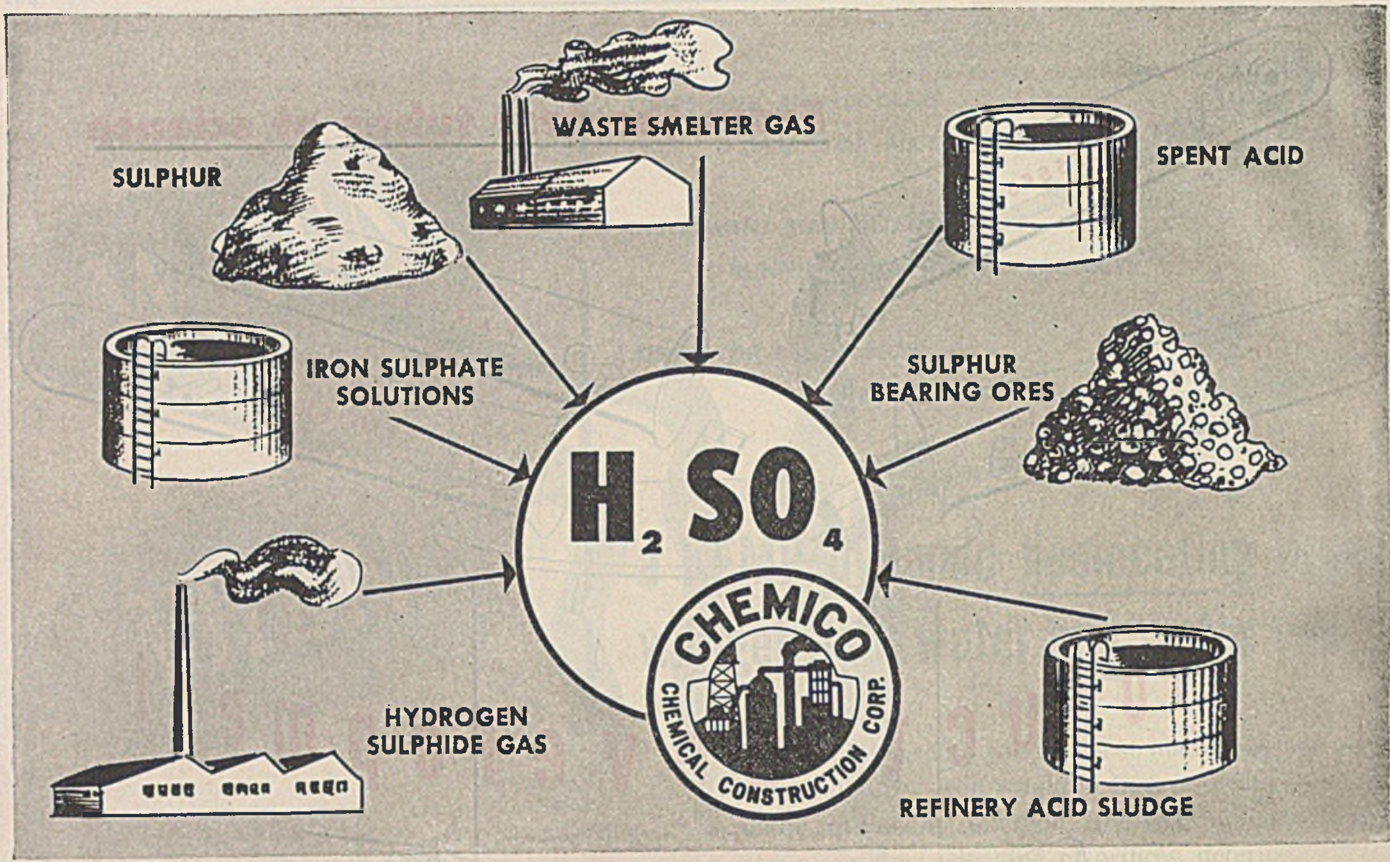
DEPT. K-File

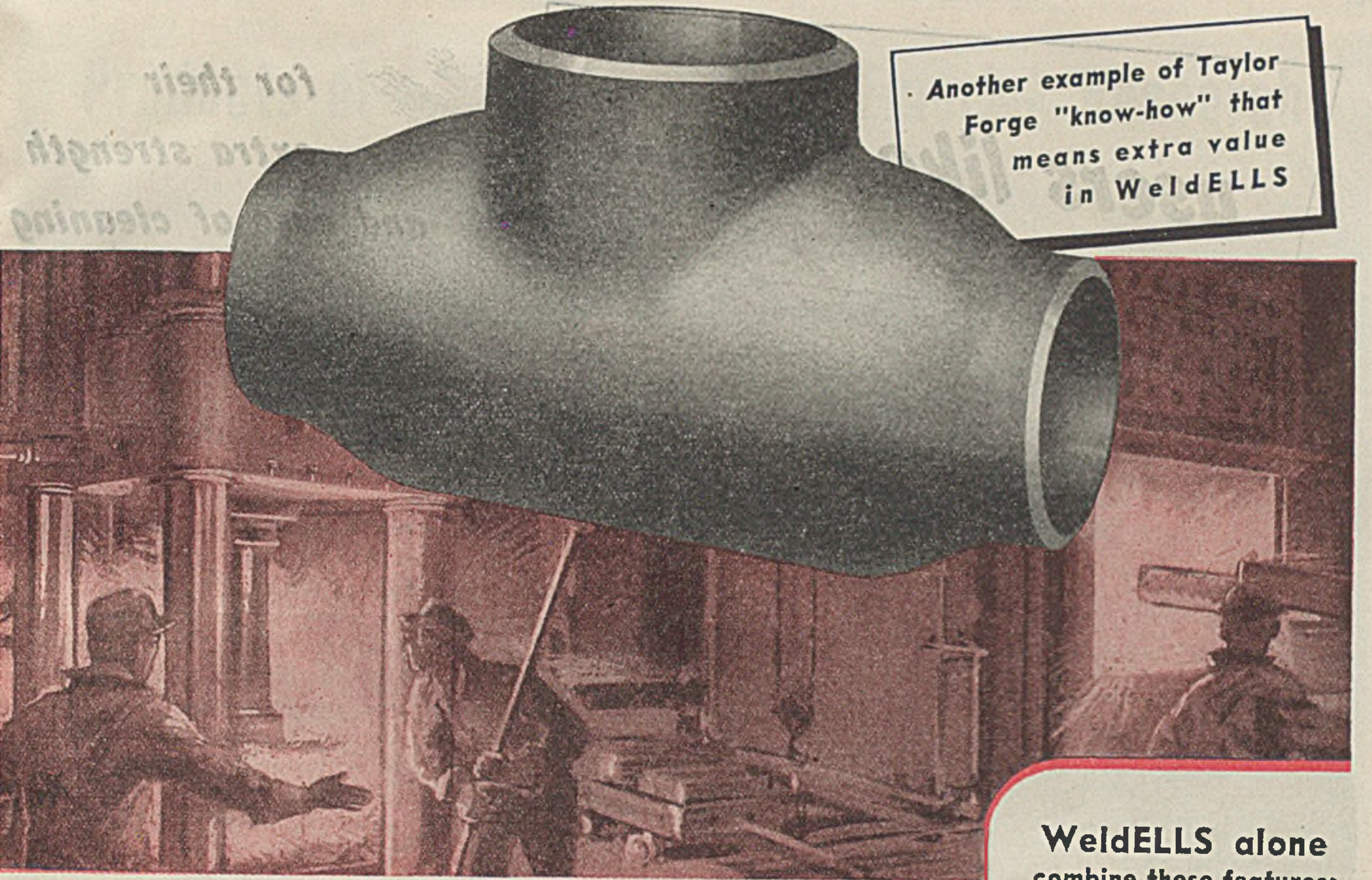
THE C. M. KEMP MFG. CO.
405 E. Oliver Street, Baltimore 2, Md.

Send me your new 48-page illustrated booklet on "Dynamic Dryers"........ ☐
Send a field-enginer to "talk turkey" (no obligation, of course)........ ☐

NAME__________
POSITION__________
COMPANY__________
PLACE__________


From the test tubes of science
PROCESSES
BASIC RAW MATERIALS
PARTS
FINISHES
product development


SULPHUR
WASTE SMELTER GAS
SPENT ACID
IRON SULPHATE SOLUTIONS
SULPHUR BEARING ORES
H_2SO_4
CHEMICO
CHEMICAL CONSTRUCTION CORP.
HYDROGEN SULPHIDE GAS
REFINERY ACID SLUDGE



Another example of Taylor Forge "know-how" that means extra value in WeldELLS

WeldELLS alone combine these features:

- **Seamless**—greater strength and uniformity.
- **Tangents**—keep weld away from zone of highest stress—simplify lining up.
- **Precision quarter-marked ends**—simplify layout and help insure accuracy.
- **Selective reinforcement**—provides uniform strength.
- **Permanent and complete identification marking**—saves time and eliminates errors in shop and field.
- **Wall thickness never less than specification minimum**—assures full strength and long life.
- **Machine tool beveled ends**—provides best welding surface and accurate bevel and land.
- **The most complete line of Welding Fittings and Forged Steel Flanges in the World**—insures complete service and undivided responsibility.

Rare specimen in Welding Tees-

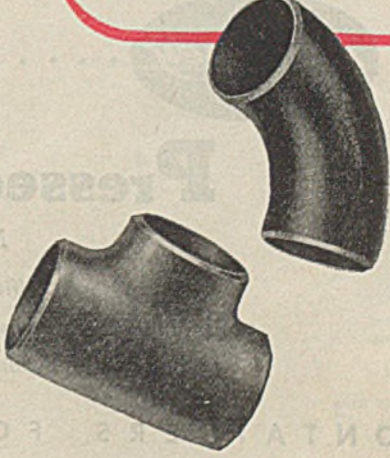
● *When you think of a reducing tee you always picture it as reducing in the branch. But this one, for the peculiar purpose it serves, had to be made the other way around. It's a seamless, carbon-moly forging, five inches in the run with a seven-inch branch—an "increasing" tee, so to speak; one more example of those kinks that are found so abundantly in the Taylor Forge bag of tricks.*

The "know-how" acquired during many years of performing these special—often extremely difficult—manufacturing operations, has a mighty important bearing on our standard line of WeldELLS, Welding Tees and other Taylor Forge Welding Fittings.

It means that in developing WeldELLS we did not have to ask what kind of fitting is easiest to manufacture. Instead we asked what comprises the ideal fitting, and then, with every special facility and process at our command, made that conception a reality.

That is why WeldELLS have tangents . . . why they have extra reinforcement where service stresses are greatest . . . why they have such extremely accurate dimensions . . . why they have the features listed opposite . . . why, in short,

WeldELLS have everything



TAYLOR FORGE & PIPE WORKS, General Offices & Works: Chicago, P.O. Box 485
New York Office: 50 Church Street • Philadelphia Office: Broad Street Station Bldg.

users like them..

for their extra strength and ease of cleaning

Where shipping requirements demand durability, strength and ease of cleaning . . . you'll find the Hackney Removable Head Seamless Steel Barrel. This sturdy container is made from a single sheet of open-hearth steel, pressed and cold-drawn into a seamless shell with integral bottom. It is bilged to shape by the Hackney Method, increasing its rigidity and making it more resistant to blows and abuse.

This bilged shape makes the Hackney Barrel easy to handle, too—while the Toggle-tite or Bolt closure permits easy, quick opening and closing of the removable head. With such outstanding features, it is only natural that Hackney Removable Head Barrels should be first choice with shippers for the transportation and storage of paints, varnishes, inks, chemicals, greases, soaps, etc. Be sure to write for full details—and see how your handling and shipping can be improved, too.

The Hackney Barrel above is equipped with bolt-type closure. This single bolt of alloy steel results in a strong, rigid closure—easily and quickly operated with speeder wrench. Cadmium plating prevents rusting.

Barrel Cover at right illustrates the Hackney Toggle-tite closure. The handle permits quick opening and closing. When handle is in closed position, barrel is locked positively air-tight. Closing mechanism is cadmium plated to prevent rusting. Rolling or stacking is not interfered with by locking mechanism.

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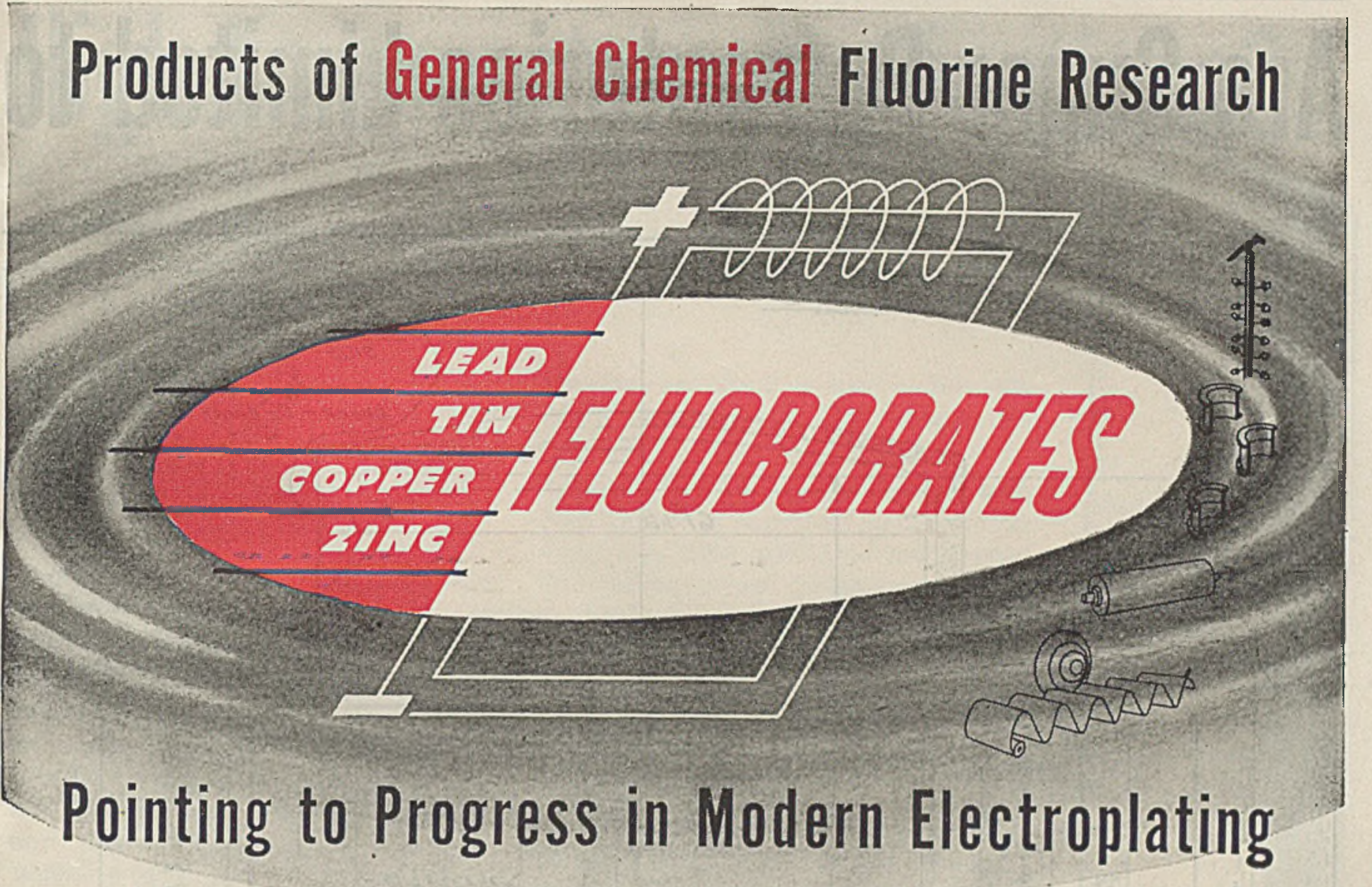
CONTAINERS FOR GASES, LIQUIDS AND SOLIDS

Products of General Chemical Fluorine Research



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Progress and important advancements in modern electroplating lie ahead with the broadening use of General Chemical Metal Fluoborate Solutions. Today—fluoborate baths are proving outstanding for many lead, tin, lead-tin alloy, copper, zinc and other applications. Tomorrow—Metal Fluoborates hold still greater promise since their superiority to ordinary baths is indicated both by the unusual characteristics of the fluoborate electrolyte and by the type of deposits obtained.

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

These advantages can mean real economy, efficiency, and convenience in your plant. So investigate the Metal Fluoborates now by writing for technical data and trial samples of the products that interest you. As always, General Chemical's skilled Engineering and Technical Servicemen are available to assist you in preparing for test or full-scale runs.

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Available now . . . extensive operating data on the Metal Fluoborates in the technical manuals outlined here. For copies, write or phone the nearest General Chemical Sales and Technical Service Office listed above.

Lead-Tin Alloy Plating MANUAL LT-1
Full description of the practical, economical fluoborate method for plating lead-tin alloys in any desired ratio (particularly low-tin ranges) with high degree of uniformity and minimum of control measures.

Zinc Fluoborate MANUAL ZF-1
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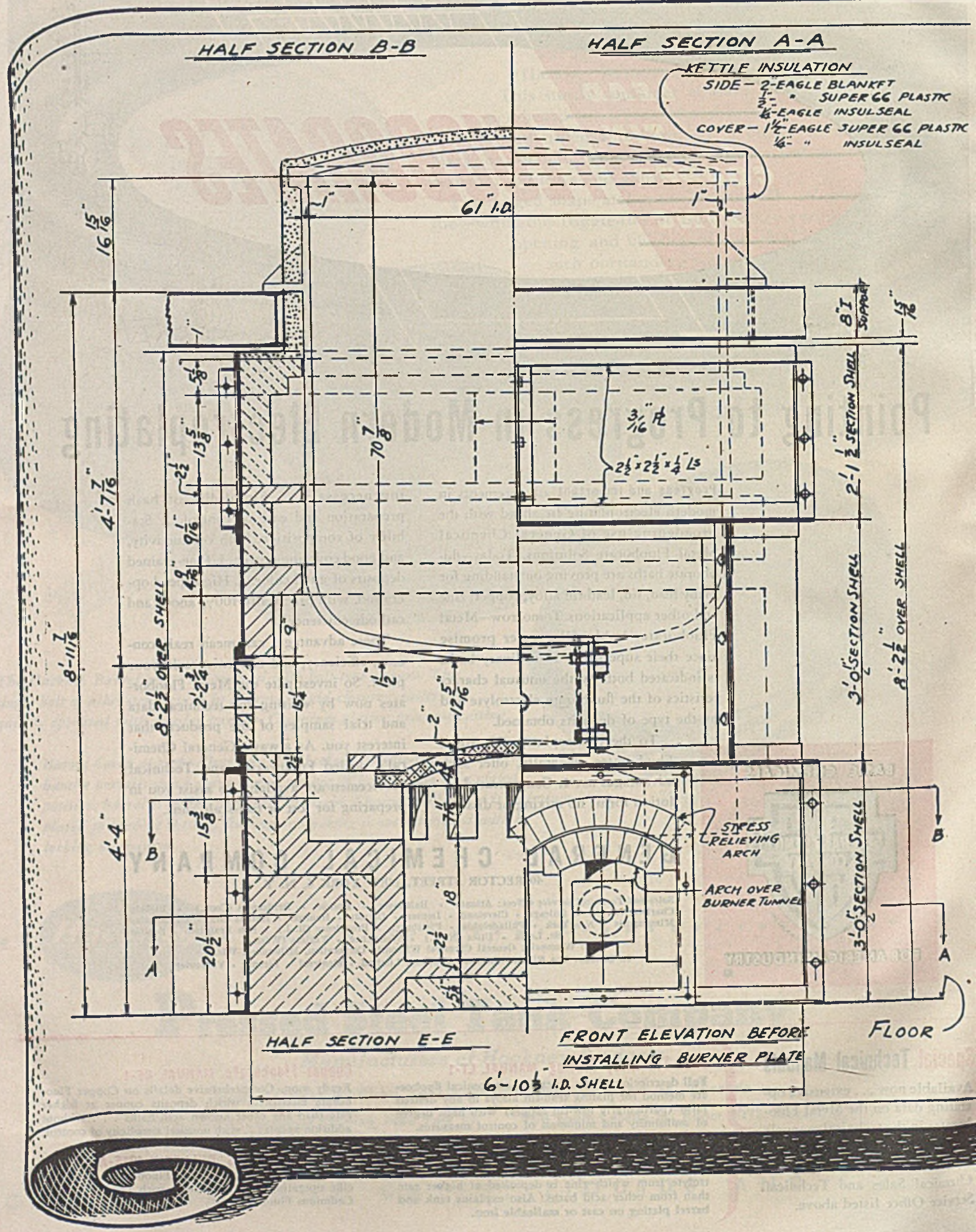
Metal Fluoborates BULLETIN 1015-A
General information on Metal Fluoborates plus specific operating data on plating with Lead, Tin, and Cadmium Fluoborate.


HALF SECTION B-B
HALF SECTION A-A
KETTLE INSULATION
SIDE – 2" EAGLE BLANKET
1/2" – " SUPER 66 PLASTIC
1/4" EAGLE INSULSEAL
COVER – 1 1/2" EAGLE SUPER 66 PLASTIC
1/4" – " INSULSEAL
1"
61" I.D.
1"
16 15/16"
8" I SUPPORT
1 5/16"
5 5/8"
13 5/8"
70 7/8"
3/16" PL
2 1/2" x 2 1/2" x 1/4" LS
2'-1 1/2" SECTION SHELL
2 1/2"
9 11/16"
4'-7 7/16"
4 1/16"
9
1 1/2"
8'-11 1/16"
8'-2 3/4" OVER SHELL
2'-2 1/4"
12 5/16"
2
2 1/2"
3'-0 1/2" SECTION SHELL
8'-2 1/2" OVER SHELL
STRESS RELIEVING ARCH
ARCH OVER BURNER TUNNEL
B
B
15 1/8"
4'-4"
18
20 1/2"
2 1/2"
5 1/2"
A
A
3'-0 1/2" SECTION SHELL
FLOOR
HALF SECTION E-E
FRONT ELEVATION BEFORE INSTALLING BURNER PLATE
6'-10 3/8" I.D. SHELL

High Temperature Applications?

SUPER refractories are usually considered in terms of super heats. Often overlooked is the fact that unique properties of super refractories by CARBORUNDUM are an advantage in low temperature applications.

The oil fired vacuum still shown here, with its 500 gallon cast iron pot, is one of many examples. A low 350°C. is the temperature to which charge is heated.

With a thermal conductivity 11 to 12 times that of ordinary refractories, the CARBOFRAX silicon carbide arch radiates heat to the pot far faster. Combustion chamber temperatures are lower. Working temperature is reached with a reduced heat head. Gases surrounding the kettle are not destructive as they, too, are at lower temperatures. Heat control is greatly simplified and the setting life is extended materially.

Having a mechanical strength seven to eight times greater than fireclay a CARBOFRAX arch usually can be made half as thick—often less. This provides a further aid to rapid heat transfer and heating up speed.

An exceptional resistance to spalling and cracking assures long service from the CARBOFRAX arch. Replacements are few—maintenance expense is low.

Controllable off-take ports are lined with MULLFRAX-S converted kyanite brick. They, too, easily withstand temperature fluctuations without cracking or spalling.

To provide additional improvements, our engineers recommended the judicious use of insulating firebrick. This reduced the overall weight of the setting, cut heat capacity and shortened time of heating and cooling.

In service over five years the pot is still in use. Formerly, pots lasted about six months. The setting remains untouched. Speed of heating and cooling is under absolute control at all times. Worthwhile fuel savings, too, have been effected.

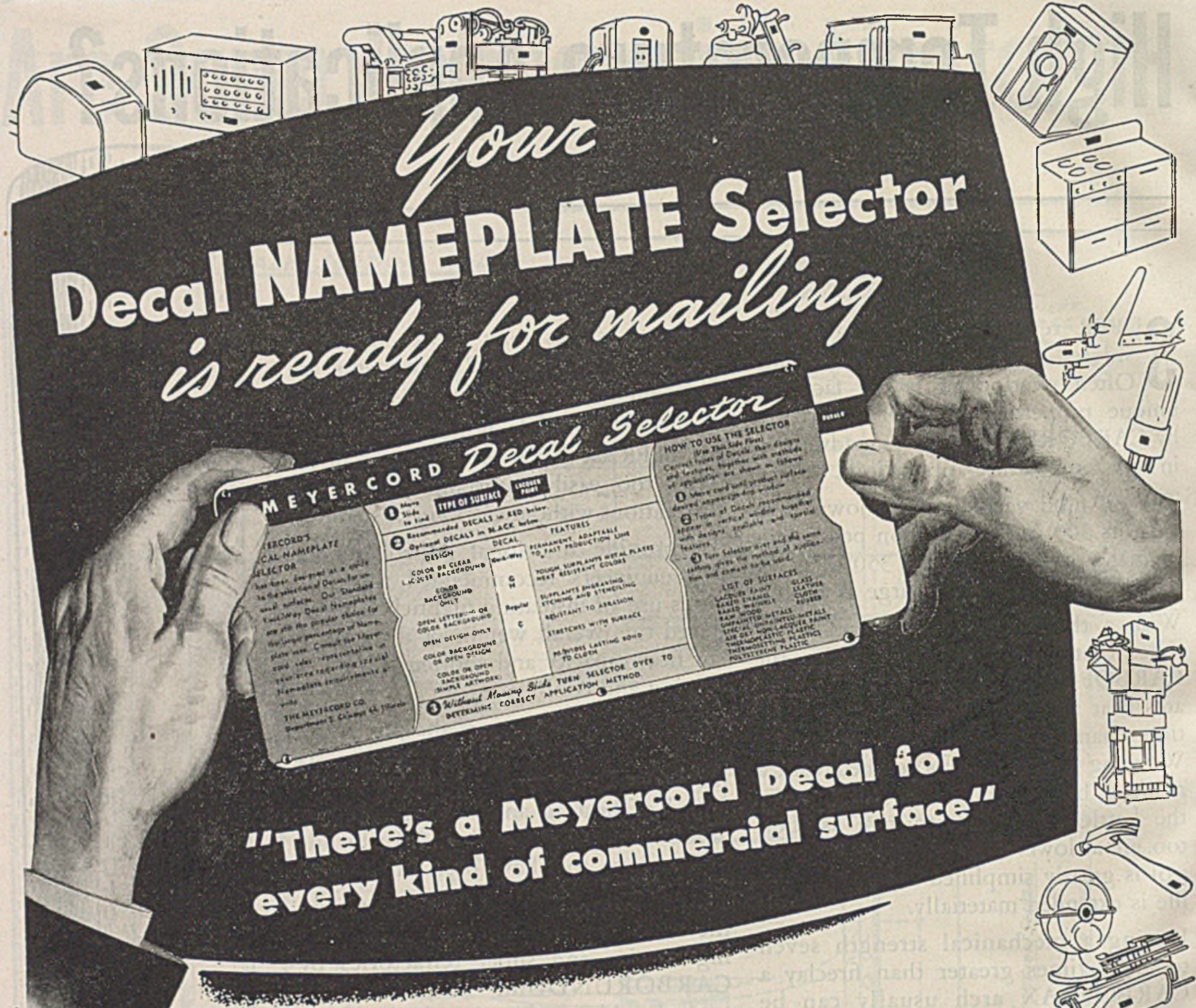
Here is another case clearly illustrating the benefits achieved through engineering service and super refractories by CARBORUNDUM. You, too, may profit by this combination for low temperature operating ranges. Write Dept. E-66, The Carborundum Company, Refractories Division, Perth Amboy, New Jersey.

SUPER REFRACTORIES

BY CARBORUNDUM

TRADE MARK

"Carborundum", "Carbofrax" and "Mullfrax" are registered trademarks which indicate manufacture by The Carborundum Company



THIS PRACTICAL "SLIDE-RULE"
WILL HELP YOU SELECT THE RIGHT

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Don't take a chance on just "any Decal" to do your product identification job. Conditions, type and use of surface should determine the kind of Decal and adhesion method. Meyercord technicians have prepared this Decal Selector to assist in the selection of the right Decal...for use as trademarks, instructions, patent data, etc....particularly on difficult surfaces. There's a Meyercord Decal for every surface, from standard Kwik-Ways to highly specialized types resistant to acid, abrasion, temperature extremes, moisture...: for application on any shape or kind of commercial surface. No rivets, bolts or screws required. They can be produced in any size, design or number of colors. Write today for the new Meyercord Decal Selector to help you specify the right Decal. Please address your inquiries to Department 90-6.

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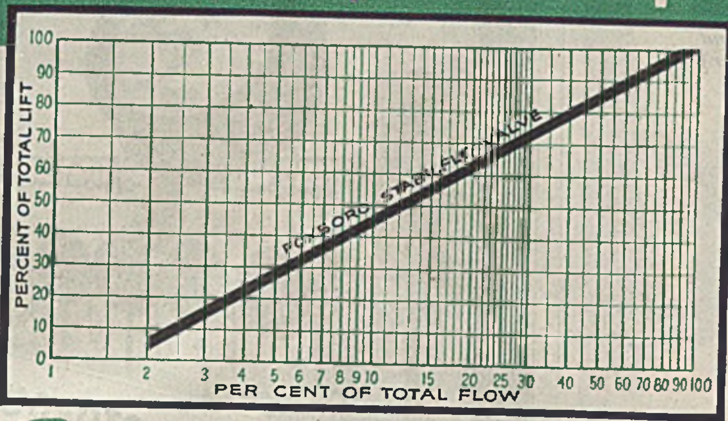
Only Stabilflo Valves will give you this remarkable performance



50 to 1 RANGEABILITY WITH UNIFORM CHARACTERISTICS

With this unique valve, you now can be sure that the extraordinary sensitivity, accuracy, and dependability of precision-engineered controllers are translated into matching valve performance.

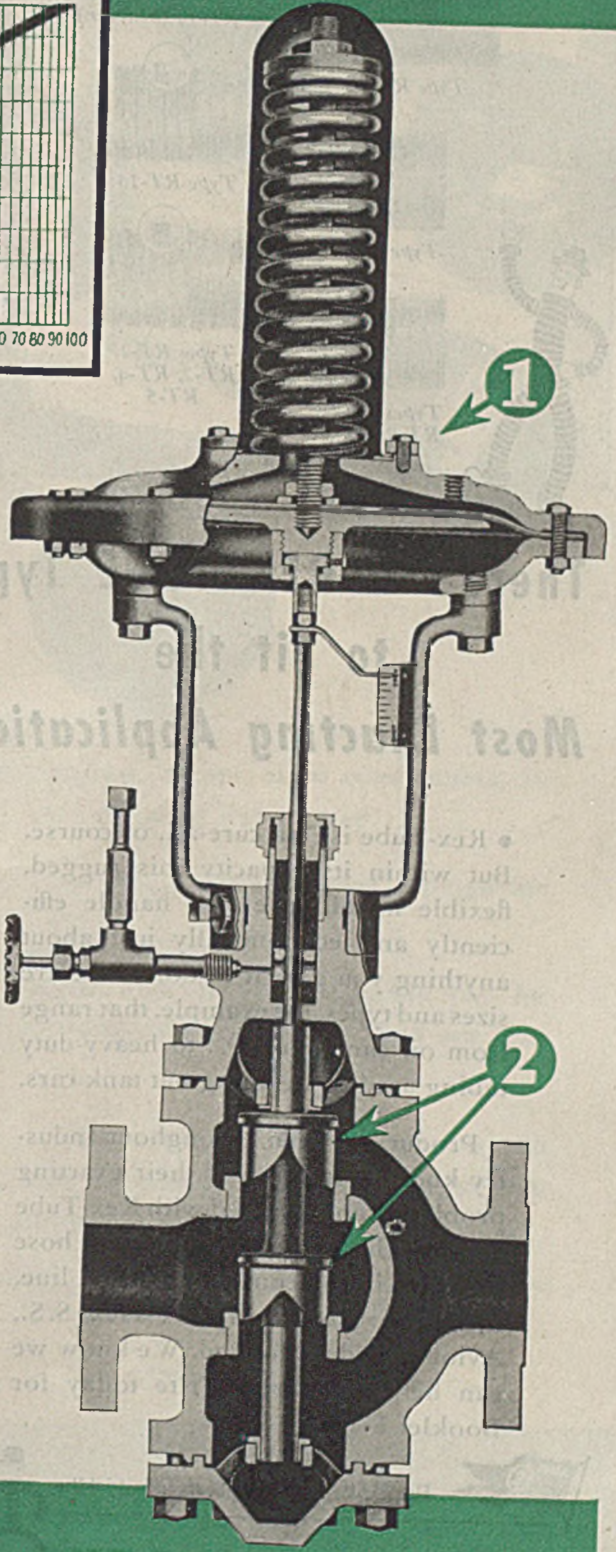
The unique characteristics of the Foxboro Stabilflo Control Valve are graphically revealed in the chart above; . . . *equal increments in controller output (and valve lift) produce equal percentage changes in flow.* Thus under constant pressure drop conditions and on a semi-logarithmic scale, the line plotted is straight.

This achievement was made possible by two major Foxboro developments in valve design. . . .

① **THE INVERTED TYPE MOTOR . . .** By reversing the usual position of diaphragm and spring, Foxboro engineers practically eliminate all sources of friction in the action of the motor. Anti-friction bearings are unnecessary. The suspended construction of the valve motor requires no guides. A special flexible coupling between the valve stem and the diaphragm motor allows the stem to establish normal alignment.

This self-aligning motor with its floating action is an exclusive feature of Foxboro Stabilflo Valves.

② **WIDE RANGE V-PORT VALVES . . .** This outstanding development corrects the common faults of control valves of conventional types. Almost any kind of port opening can produce equal percentage flow changes within a limited range, but Foxboro's WIDE RANGE V-PORT VALVE extends the limits to the full stroke of the motor. The greater the rangeability possessed by a valve, the greater its ability to handle unusual conditions. Hence, the 50 to 1 rangeability means that the Stabilflo Valve insures satisfactory control at all demands.



Since the success of any control system may depend as much on the performance of the valve as on the control instrument, it will pay you to investigate the advantages of Stabilflo Valves. Write for complete information. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U. S. A. Branches in principal cities.

FOXBORO
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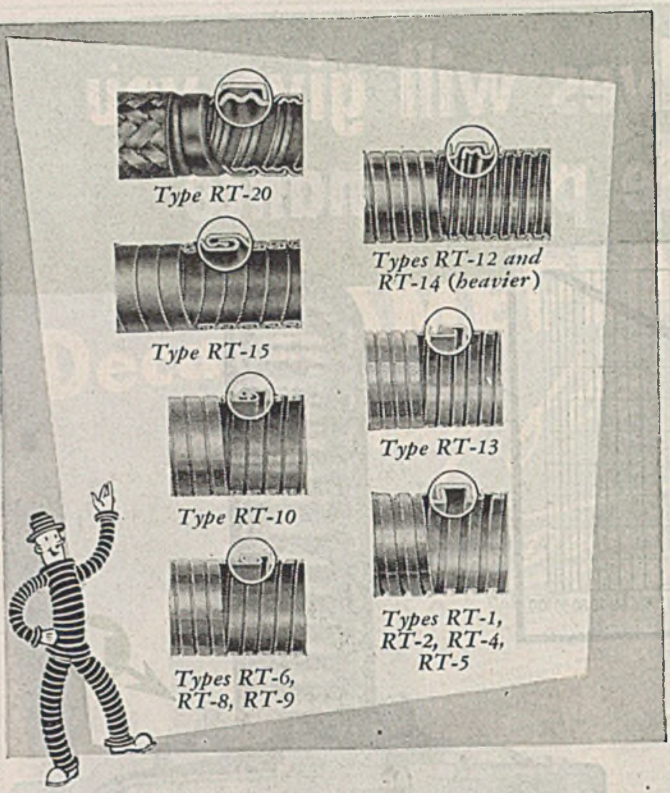
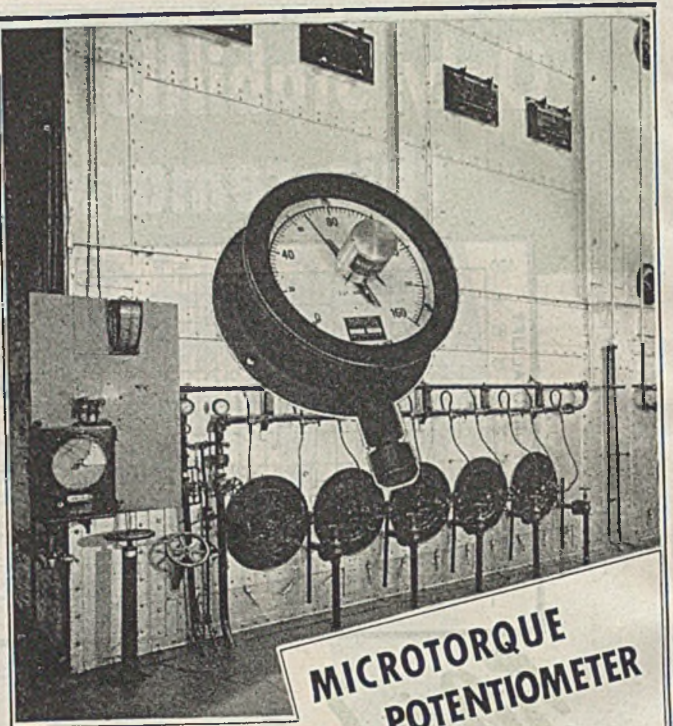
AUTOMATIC CONTROL VALVES


Type RT-20
Types RT-12 and RT-14 (heavier)
Type RT-15
Type RT-13
Type RT-10
Types RT-1, RT-2, RT-4, RT-5
Types RT-6, RT-8, RT-9

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Name it and we make it!
Three Stage Oil Condenser
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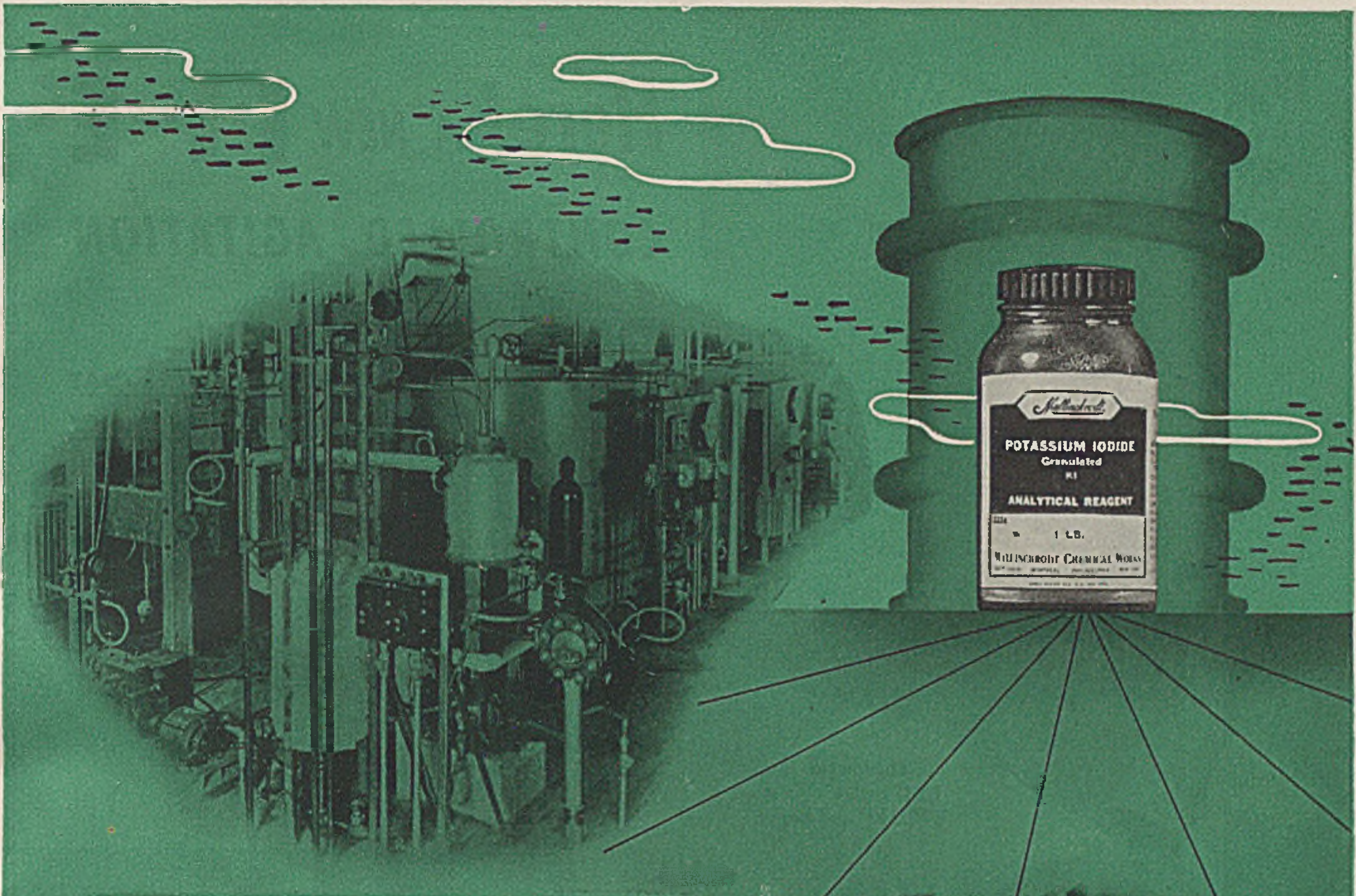
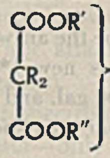
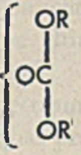
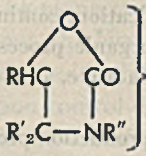


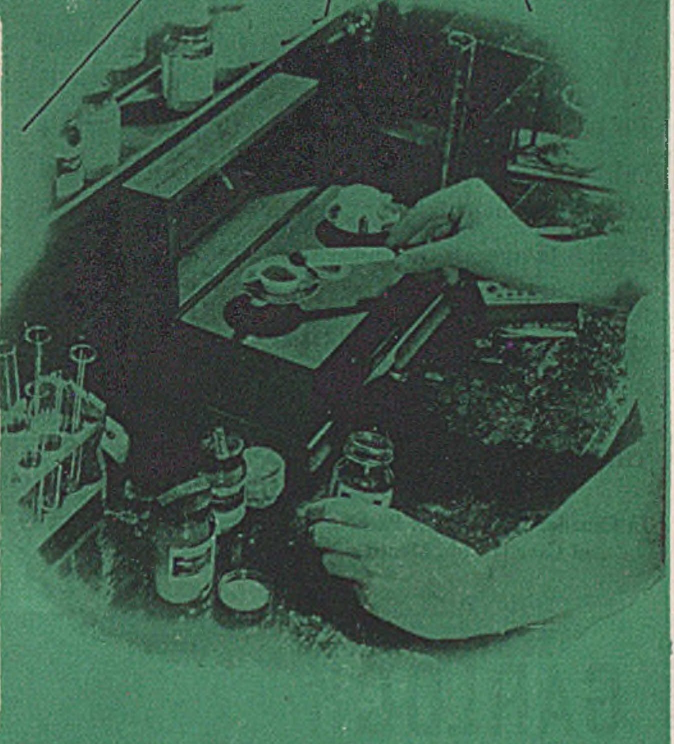


$$\left.\begin{array}{l} COOR' \\ | \\ CR_2 \\ | \\ COOR'' \end{array}\right\}$$



$$\left\{\begin{array}{l} OR \\ | \\ OC \\ | \\ OR' \end{array}\right.$$





For
HIGH Temperatures
and EXTREME
Pressures

Thicknesses from
1/64″ to 1/4″. Sheets
40″ x 40″ and larger.

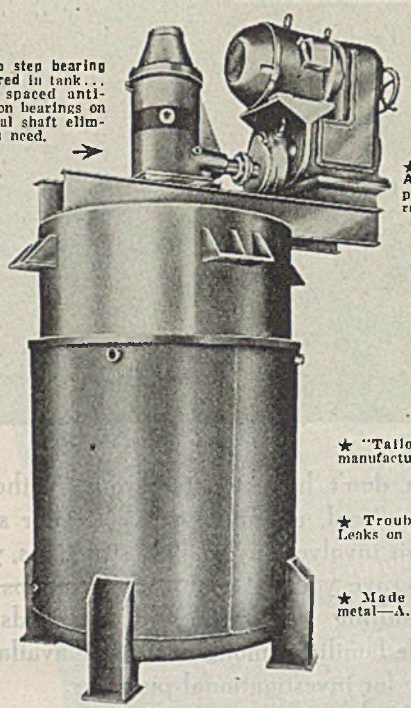
WHEN temperatures are extra high and pressures are excessive, that's the time to use GARLOCK 7021 Compressed Asbestos Sheet Packing. Gaskets cut from 7021 give superior service on pipe lines and other equipment handling gasoline, oil, gas or steam at high temperatures and extreme pressures. Tough, yet resilient, GARLOCK 7021 is economical and efficient under severe conditions.

THE GARLOCK PACKING COMPANY
PALMYRA, NEW YORK
In Canada: The Garlock Packing Company
of Canada Ltd., Montreal, Que.

GARLOCK
7021
COMPRESSED ASBESTOS
SHEET PACKING

Here! A NEW I★P★E
CONTROLLED AGITATION
REACTOR FOR PRODUCTS THAT
CHANGE CONSISTENCY
DURING PROCESSING!

★ No step bearing required in tank... wide spaced anti-friction bearings on vertical shaft eliminates need.



★ Variable Speed Agitation allows processing over wide range of viscosities.

★ "Tailored" to your own manufacturing process.

★ Trouble-free! No Oil Leaks on Vertical Shaft.

★ Made of any weldable metal—A.S.M.E. Code.

Variable speed agitation may be the answer to *your* processing problem!—This new I★P★E kettle is built in sizes up to 3000 gal. and each installation is engineered to *your own* specific manufacturing requirements.

I★P★E also designs and builds complete equipment—for resin esterification, continuous neutralization, continuous organic processing, paint and varnish manufacture, etc.—and DELIVERS ON TIME.

Let I★P★E analyze your production process, make suggestions to help step up your output. We can point to engineering problems solved, attempted by few other manufacturers. Write, phone, wire today!

INDUSTRIAL
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*"Special and Standard Process Equipment
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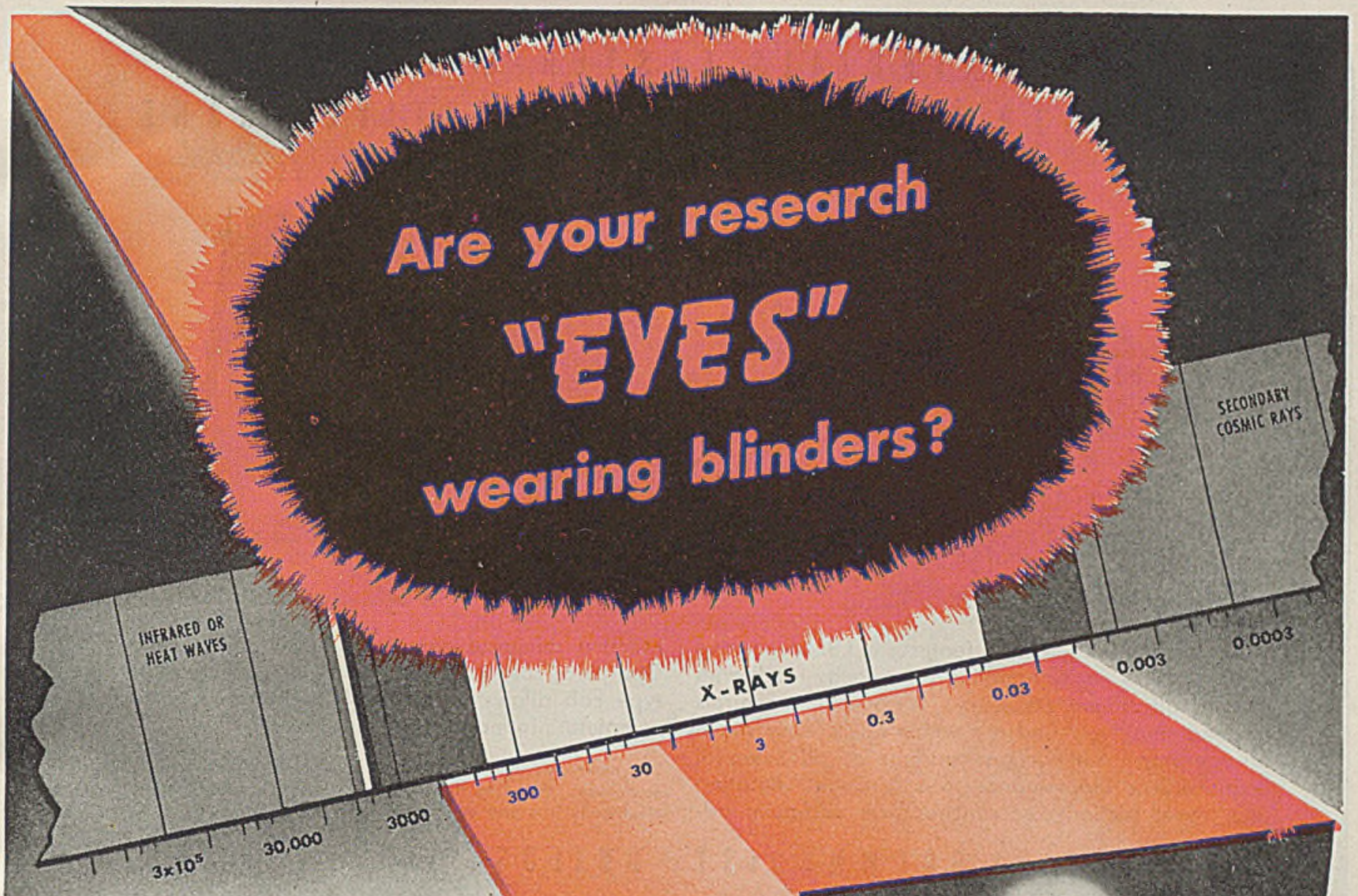
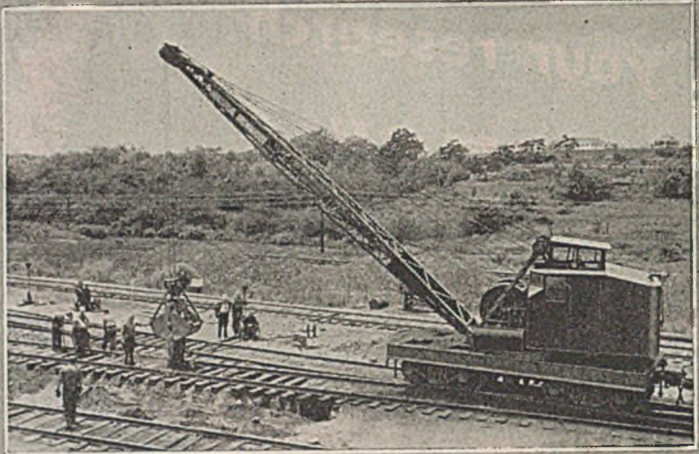
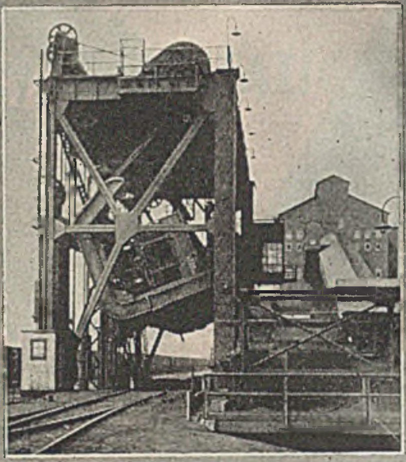
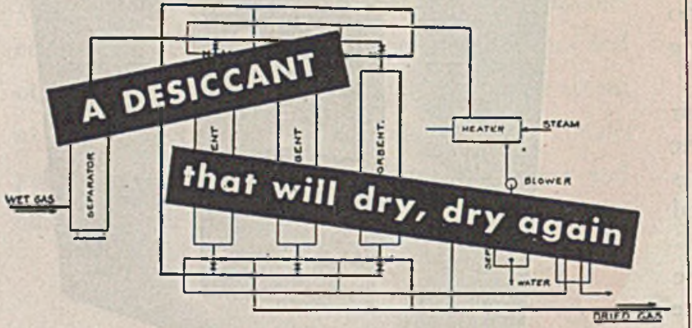
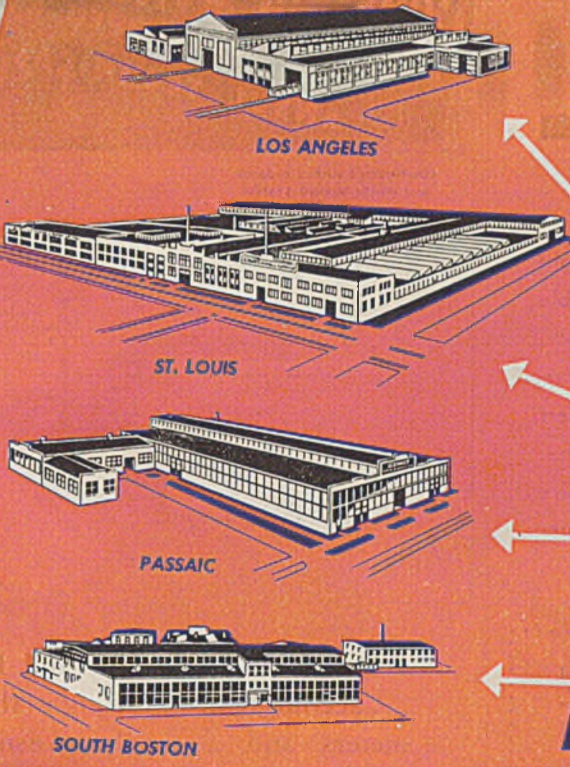

Are your research
"EYES"
wearing blinders?
INFRARED OR HEAT WAVES
X-RAYS
SECONDARY COSMIC RAYS
3x10⁵
30,000
3000
300
30
3
0.3
0.03
0.003
0.0003






A DESICCANT
that will dry, dry again
WET GAS
SEPARATOR
HEATER
STEAM
BLOWER
WATER
DRIED GAS


LOS ANGELES
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PASSAIC
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INDOPOL

(INDOIL Polybutene)

The INDOPOLS are synthetic high molecular weight mono-olefins. They are light in color—stable—compatible with waxes, natural and synthetic rubbers, solid polybutenes, etc.—miscible with hydrocarbon and chlorinated hydrocarbon solvents—miscible with many ethers and esters—insoluble in the lower alcohols and ketones. Uses include electrical insulating compositions, adhesive products, coating and laminating compositions for paper and other films.

Brand Name	Indopol L-10	Indopol H-100	Indopol H-300
Mean molecular weight	330	780	940
Viscosity S.U. seconds			
at 100°F.	114	—	—
at 210°F.	40.6	942	3330
Specific gravity 60°/60°F.	.831	.881	.894
Refractive index (20/d)	1.4655	1.4918	1.4959
Color, N.P.A.	2	2	3
Pour point (ASTM)°F.	—65	+20	+35
Weight, lbs./U.S. gallon	6.92	7.34	7.44

Intermediate grades are also available.

SEND FOR BULLETIN 12

It describes the above and
other grades.

ALSO AVAILABLE

Aliphatic Hydrocarbons—Bulletin 10
INDONEX Rubber Plasticizers—Bulletin 13
Petroleum Sulfonates

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Chemical Products Department

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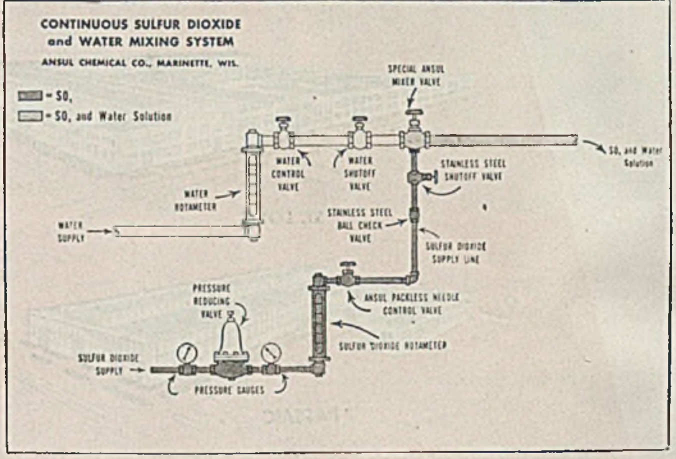
DEVELOPED BY ANSUL TECHNICAL STAFF



- Pre-mixing of water and liquid SO_2 . . . accomplished through the use of meters and a single, Ansul-designed valve installed at the juncture of the water and SO_2 supply lines . . . permits constant control of the H_2SO_3 at any desired concentration.

If you have need for an SO_2 mixing system for a specific application in your business, Ansul technicians will plan one for you.

LIQUID Sulfur Dioxide* ANSUL

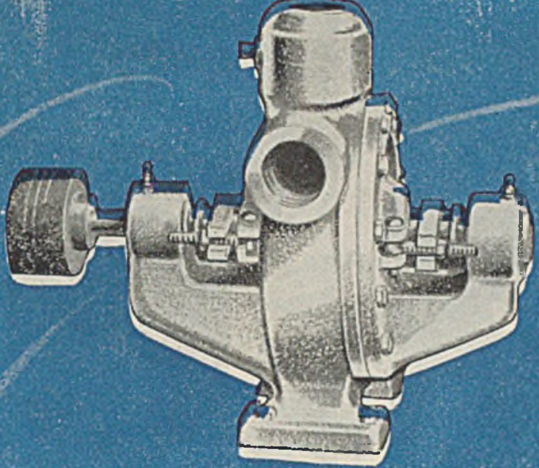
PHYSICAL PROPERTIES

Chemical formula................SO_2
Molecular weight..............64.06
Color (gas and liquid)......Colorless
Odor........Characteristic, pungent
Melting point −103.9° F. (−75.5° C.)
Boiling point.....14.0° F. (−10.0° C.)
Density of liquid at 80° F.
(85.03 lbs. per cu. ft.)
Specific gravity at 80° F.........1.363
Density of gas at 0° C. and 760 mm:
2.9267 grams per liter
(0.1827 lb. per cu. ft.)
Critical temperature
314.82° F. (157.12° C.)
Critical pressure
1141.5 lbs. per sq. in. abs.
Solubility...........Soluble in water
Purity.........99.9+% (by wt.) SO_2
(H_2O less than 0.01%)

*REG. U. S. PAT. OFF.

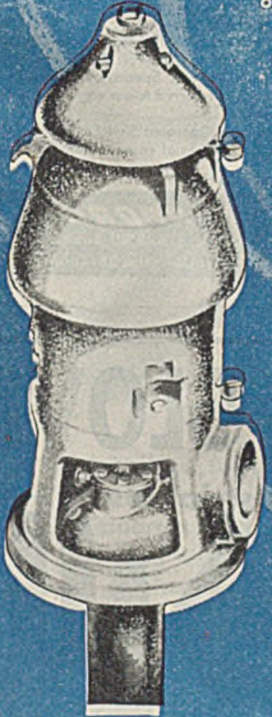
Send for your copy of "Liquid Sulfur Dioxide" —a treatise on the properties, characteristics, and industrial uses of Liquid Sulfur Dioxide—written by the Ansul Technical Staff.

ANSUL CHEMICAL COMPANY
INDUSTRIAL CHEMICALS DIVISION, MARINETTE, WIS.
Eastern Office: 60 E. 42nd St., New York City



THE WESTCO LINE of precision-built pumps: unique advantages in long-life and varieties of use for small-capacity pumping of all types of liquids. High heads, low speeds.

FAIRBANKS-MORSE split-case centrifugals are first in their class for sustained high efficiency.



FOR VERTICAL TURBINE WORK—the complete line of Fairbanks-Morse and Pomona turbine pumps. At home—and well-proved—in farm or factory.

Impartially Yours . . .

for lower cost fluid-handling

When you are after lower cost liquid-moving, you want 100% impartial advice from men with second-to-none records of applying the right pump to all types of water-handling jobs! For this kind of engineering service—*and for a complete line from which you may choose*—there's no substitute for Fairbanks-Morse. Here's a single source for all your centrifugal, turbine, and special pumping needs—one "pump store" to simplify your pump-selection and servicing problems to the vanishing point!

IF YOU'RE AFTER any of these advantages, see your Fairbanks-Morse dealer or call the nearest Fairbanks-Morse office.

FAIRBANKS-MORSE

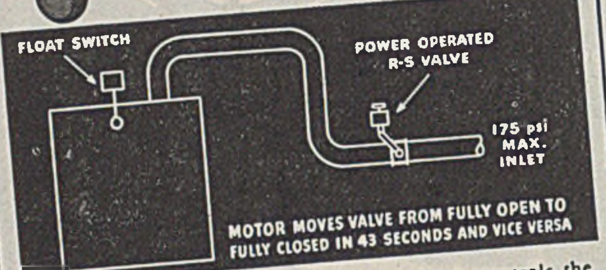
F M

A name worth remembering

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

R-S
QUALITY PRODUCTS SINCE 1908

FLOAT SWITCH CONTROL

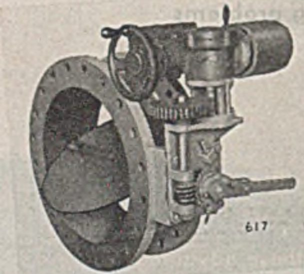


As indicated by the diagram, the float switch controls the power-operated, slow-acting R-S Valve which maintains a constant water supply in the storage tank.

Similar applications of automatically operated R-S Valves can be equipped with an air diaphragm, oil or hydraulic cylinder for the control and shut-off of a multitude of materials. The result is simplified performance, prevention of water hammer and line damage, unexcelled flow characteristics and reduced maintenance.

R-S Valves are used advantageously to reduce, regulate and shut off pressure whether above or below atmosphere; to control liquid level; to relieve and control back pressure; to maintain a constant differential pressure; to control rate of flow; to control combustion and govern the output of pumps, fans, engines and turbines.

No. 617 Extremely slow-acting valve equipped with electric motor control. The hand wheel on a gear reduction drive is for manual operation in case of power failure. Note the extended lever for operation of sister valve in parallel line.



Can be adapted to elevated or subzero temperatures. 15 to 900 psi.

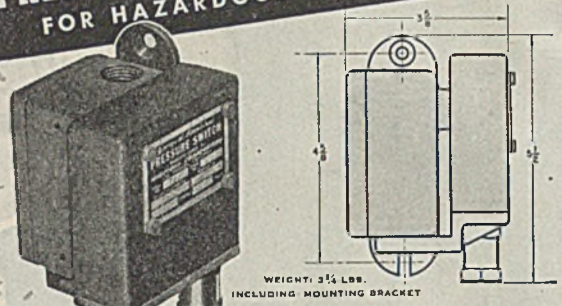
Write for detailed information and Catalog No. 14-B.

VALVE DIVISION
R-S PRODUCTS CORPORATION
Germantown Ave. & Berkley St. • Phila. 44, Pa.

R-S *Streamlined* BUTTERFLY VALVES

GEORGE A. STARBIRD EQUIPMENT

NEW EXPLOSION-PROOF PRESSURE OPERATED SWITCH FOR HAZARDOUS LOCATIONS



WEIGHT: 3¼ LBS.
INCLUDING MOUNTING BRACKET

COMPACT—LIGHTWEIGHT

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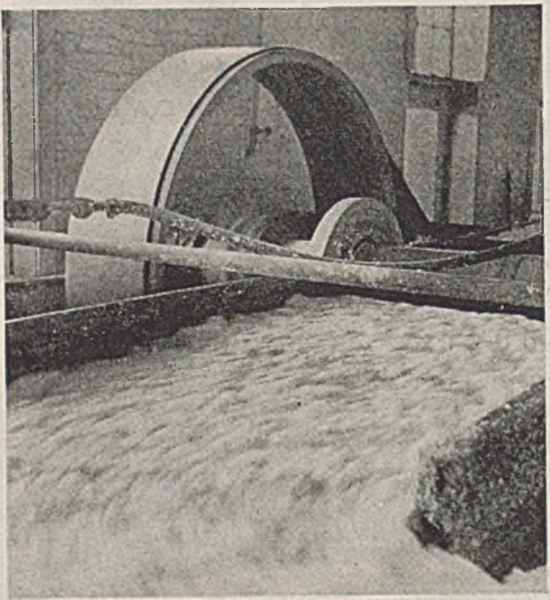

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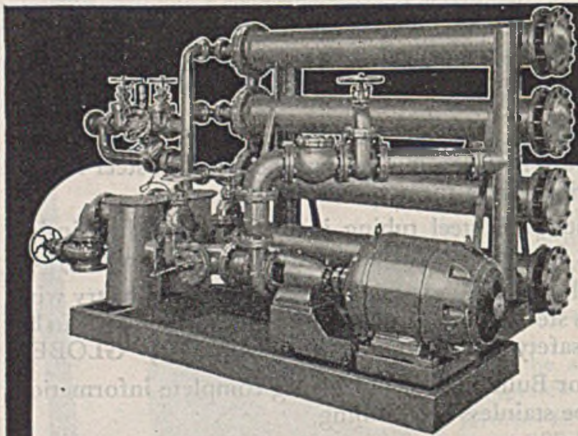

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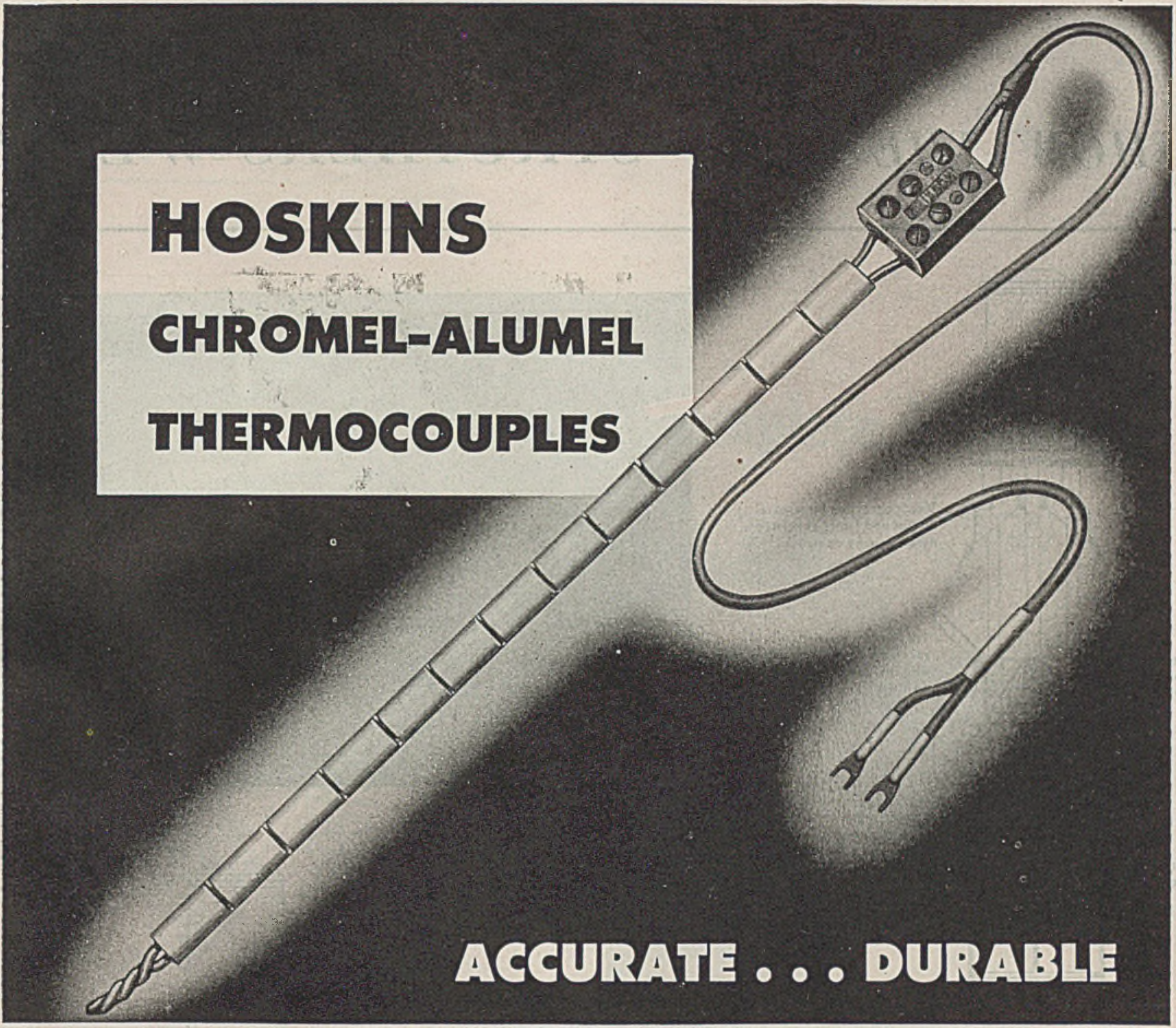

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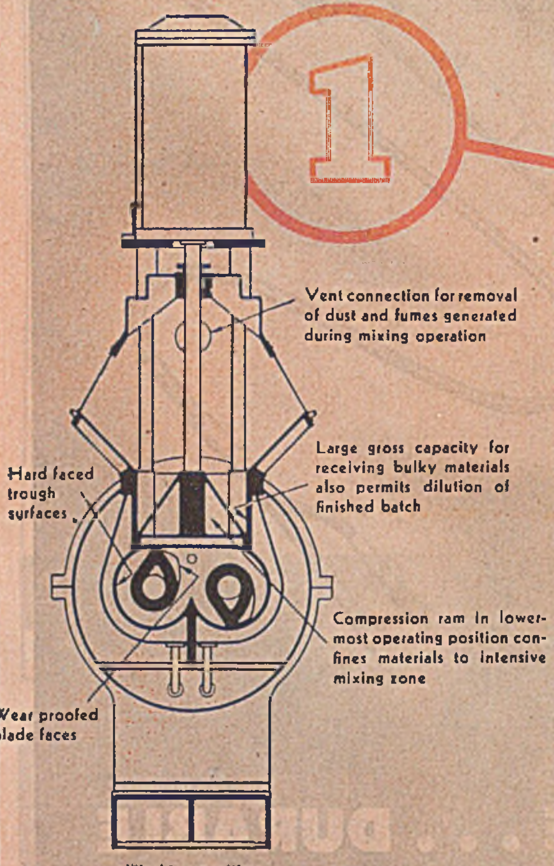
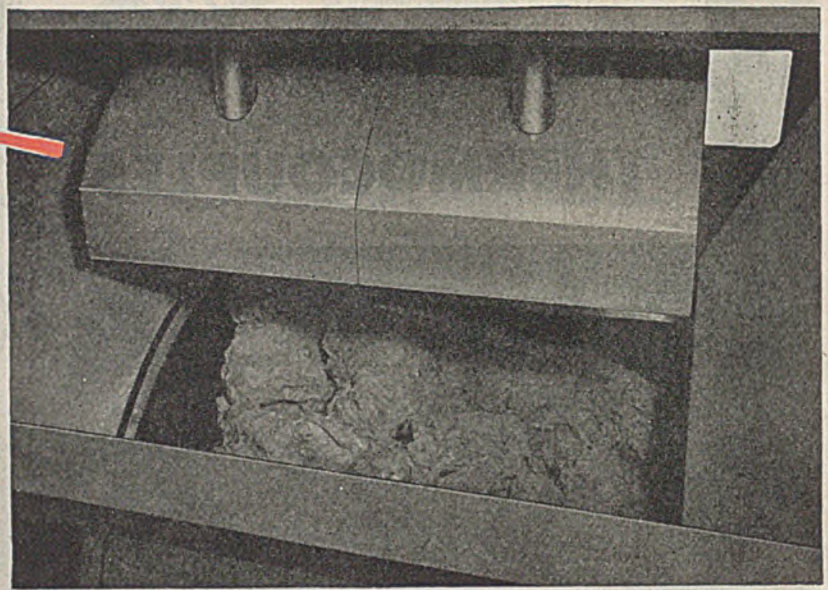
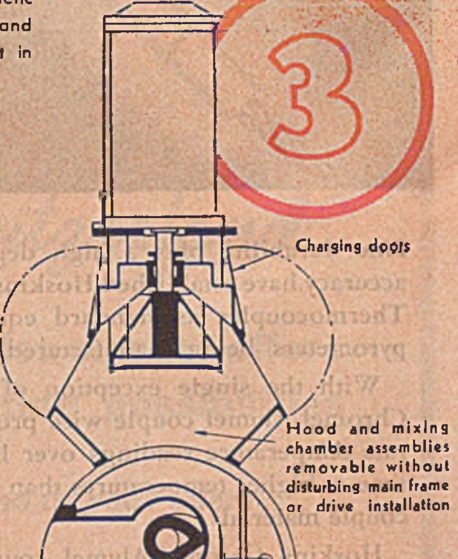


Working position





Cleaning position

This diagrammatic view shows the mixing chamber in position for cleaning or inspection. Chambers can be rotated to any position within 180° limits.

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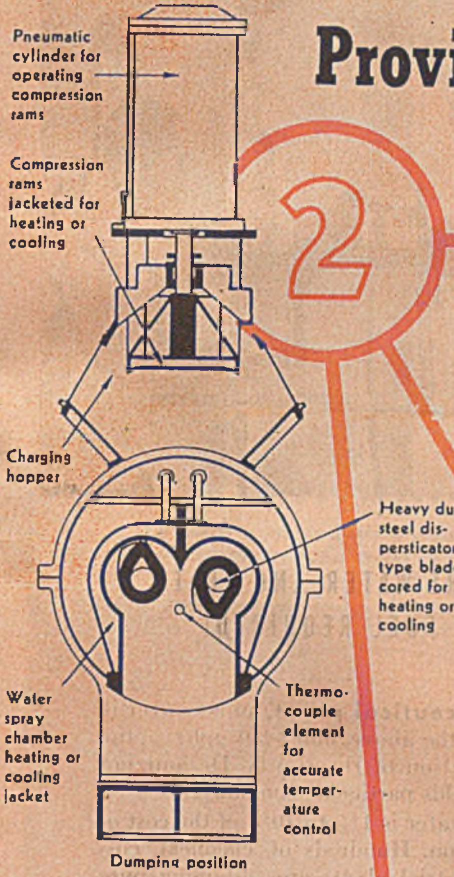
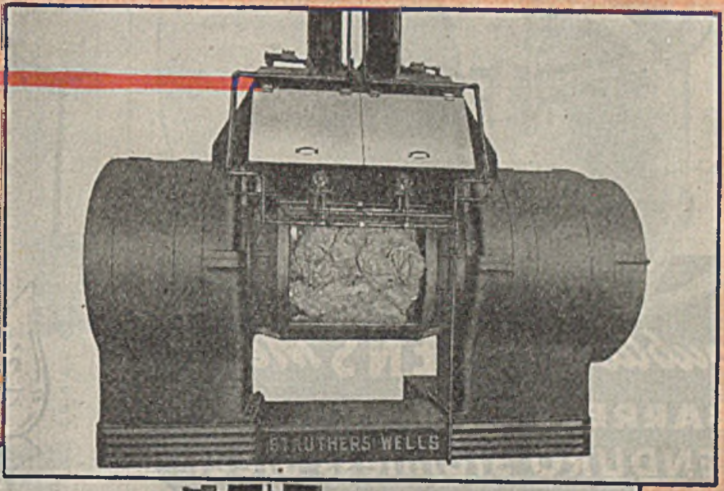
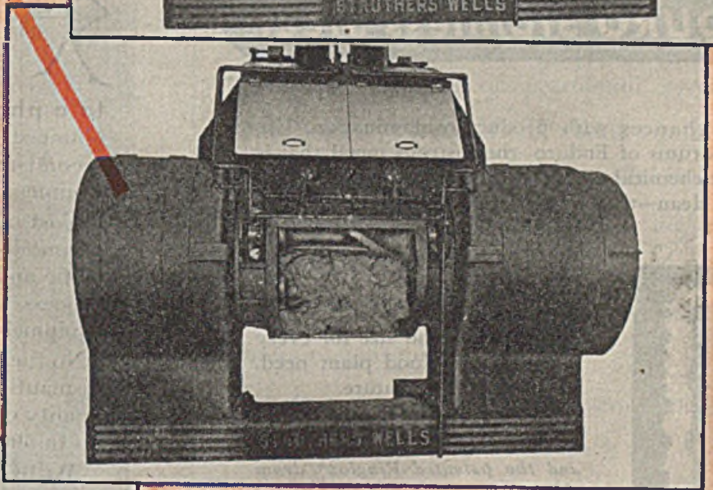
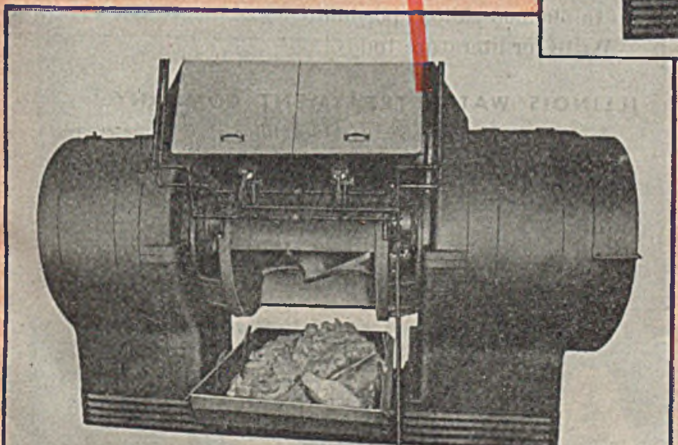


The above diagrammatic view and the three actual photographs show how the mixing chamber is rotated to an upside-down position or to any other position within 180° limits for discharging, inspection and cleaning operations.







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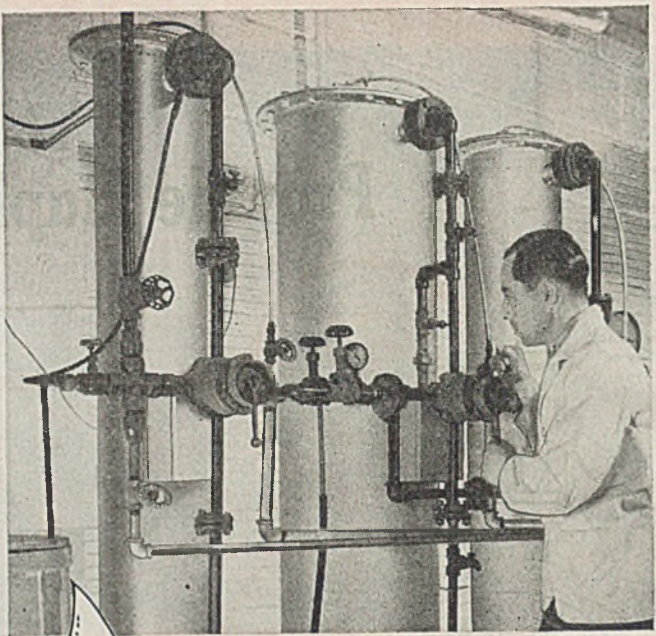

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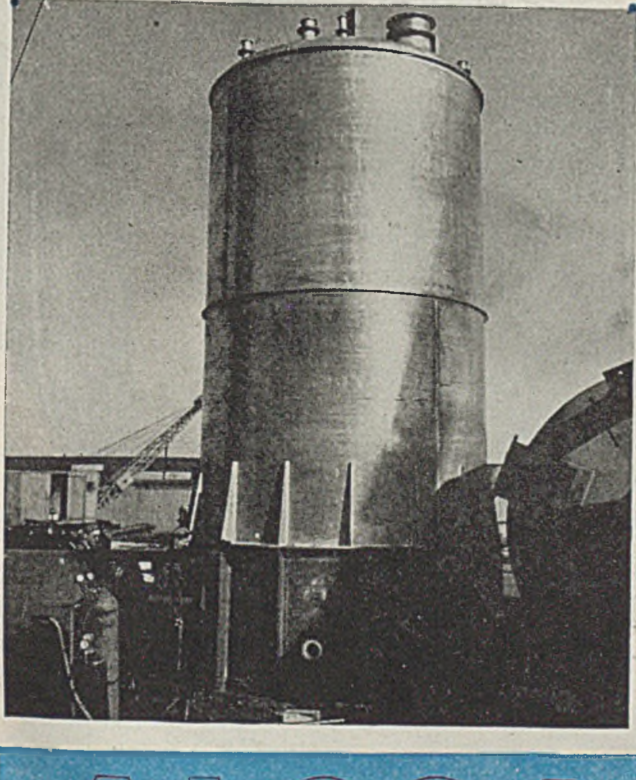

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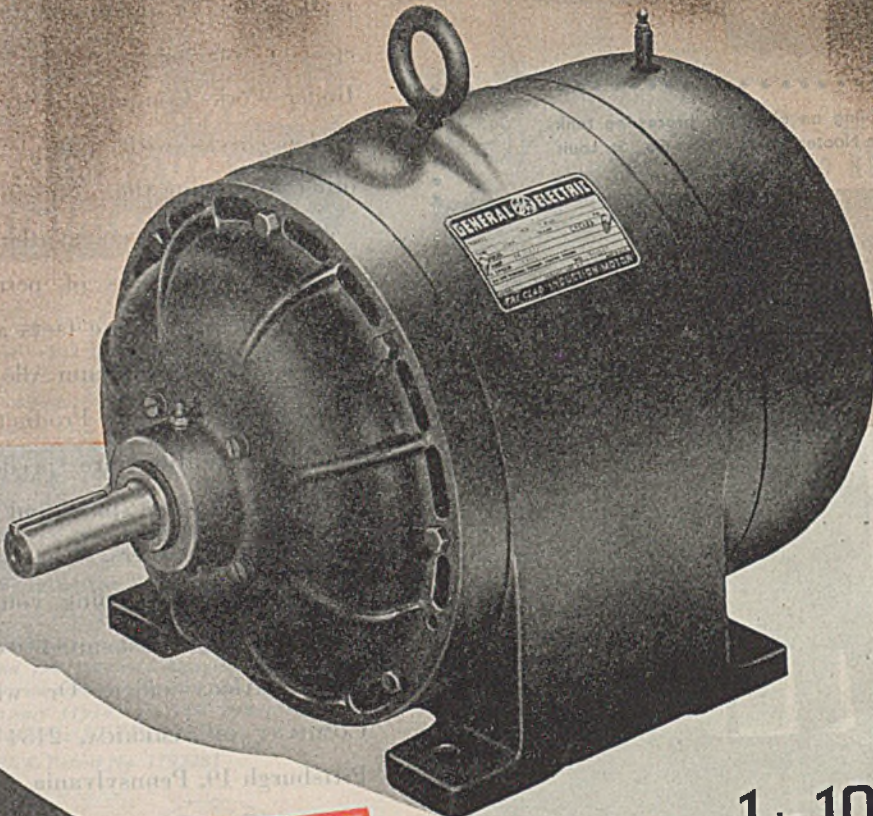
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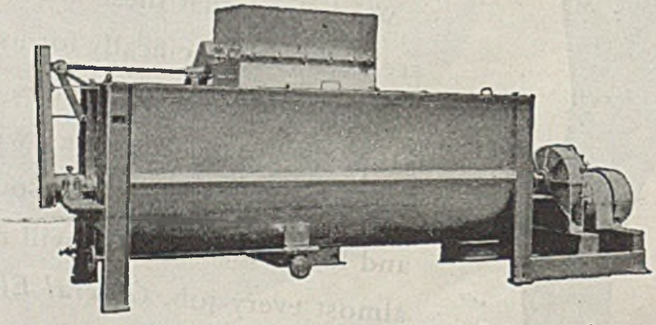

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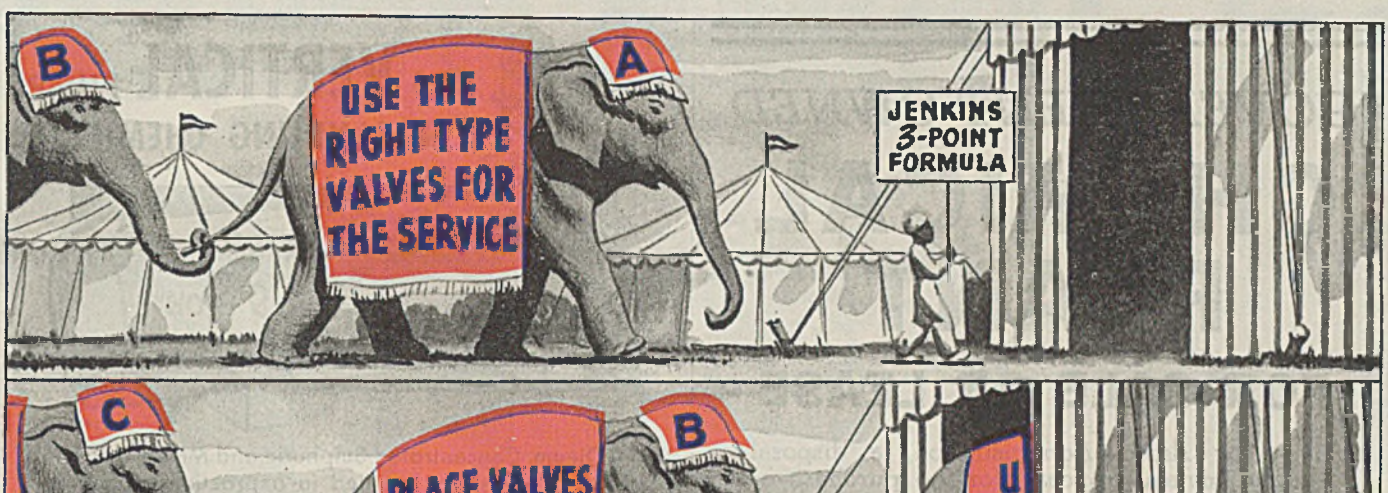

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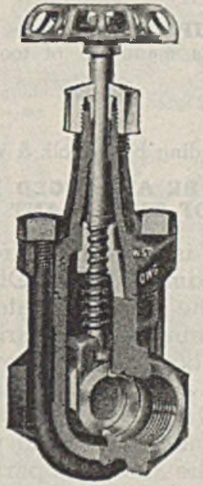

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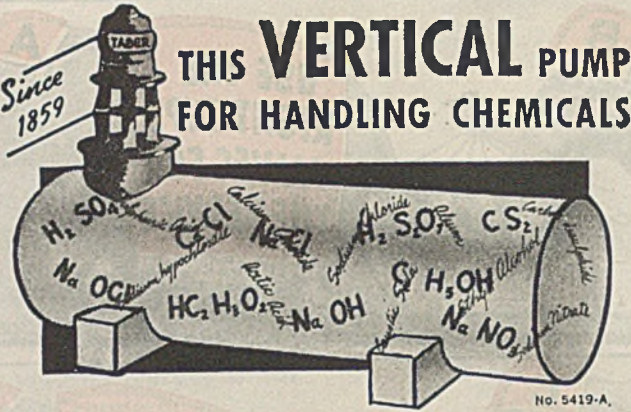
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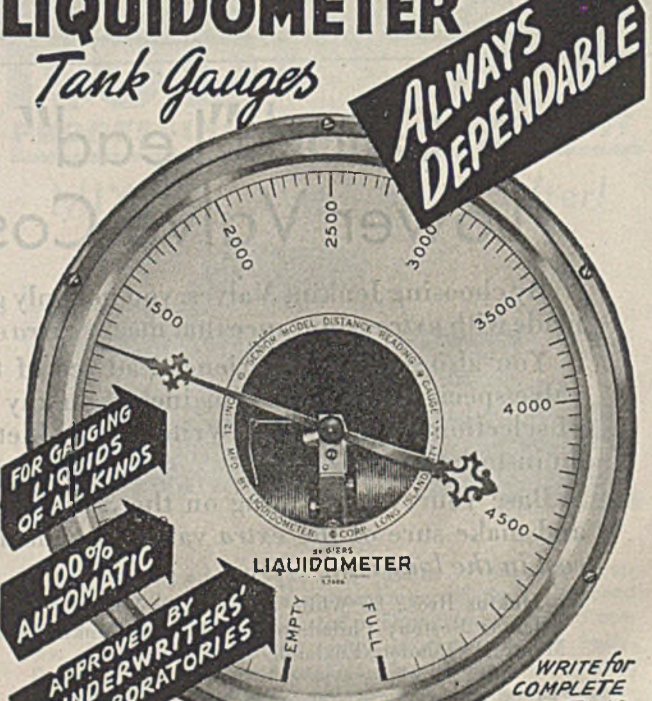
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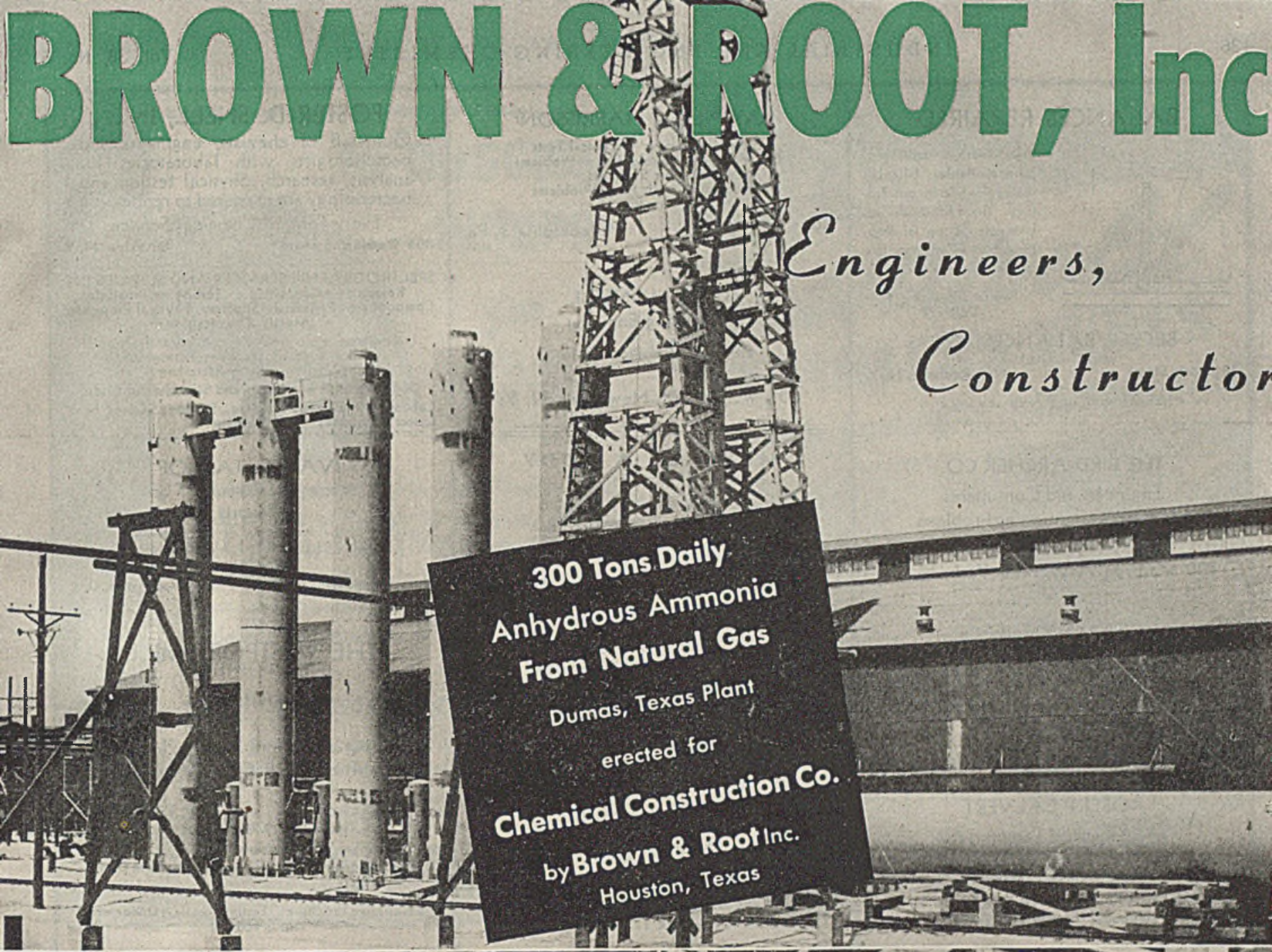

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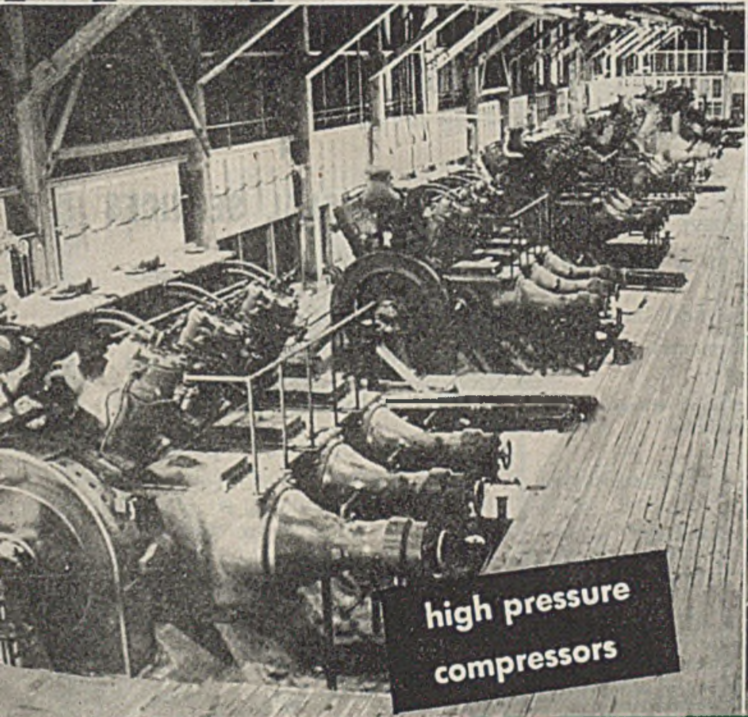

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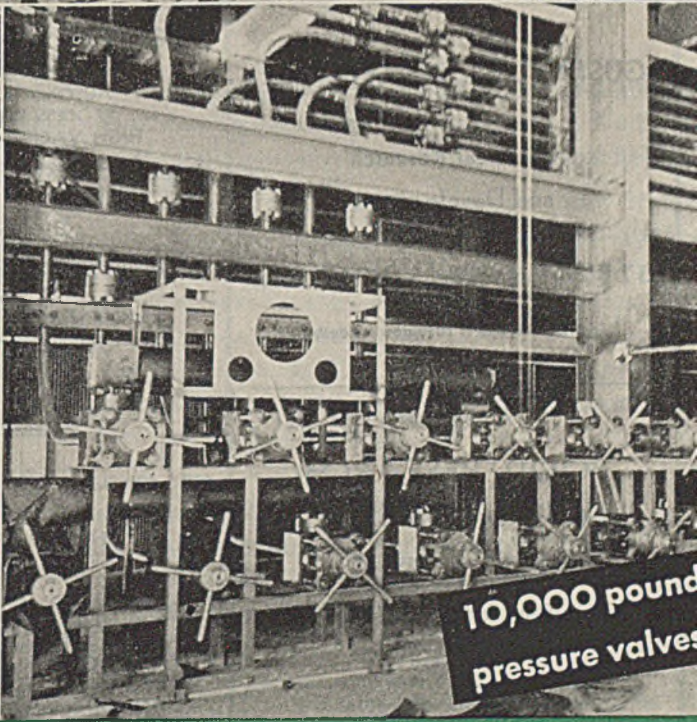

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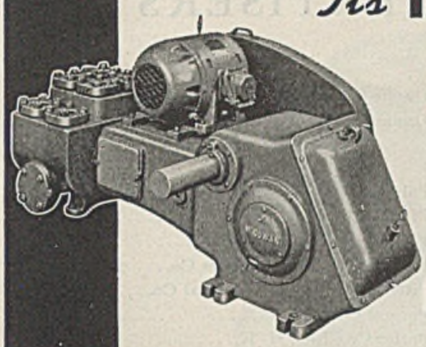


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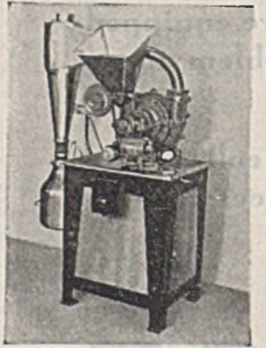


From the Editor's Desk

The 100-ounce pyramid of aluminum that caps the Washington Monument was placed there in 1884. Two years later Charles Martin Hall discovered the cryolite electrolysis process that changed aluminum's status from precious metal to commercial material.

★ A plastic compound now marketed by General Electric is used to join and seal tubes of various materials. Tubes made of the compound are swelled in a "dilator" solution and then applied, when they shrink to form a tight fit.

★ Army research is accorded top-level status in a recent reorganization, and now ranks alongside the Personnel, Intelligence, Supply, and Training and Operations sections of the General Staff.

★ Production of nylon stockings in February, 1946, was more than 2.25 million dozen pairs as compared with a total of only about 3.25 million in the last four months of 1945. Exports were less than 2% of the output.

★ Synthetics are being used to some extent in the manufacture of straw hats, but more sisal, baku, and ballibuntl must be imported before straws again become plentiful.

★ Previous estimates that this nation's potash reserves will last only 100 to 150 years are based on the amount of soluble salts in the fields now developed, according to the American Potash Institute. Estimated reserves, that include potential resources of soluble salts in other fields and insoluble ores, would be enough to last more than 1000 years at the present rate of consumption.

★ In a typical year United States cemeteries purchase between 20 and 25 million dollars worth of fertilizer, greenhouse stock, and insecticides.

★ Production of cast iron soil pipe, indispensable in the construction of new housing, fell from 565,000 tons in 1941 to 165,000 tons in 1944. Forecast for 1946 is 330,000 tons, less than the estimated need.

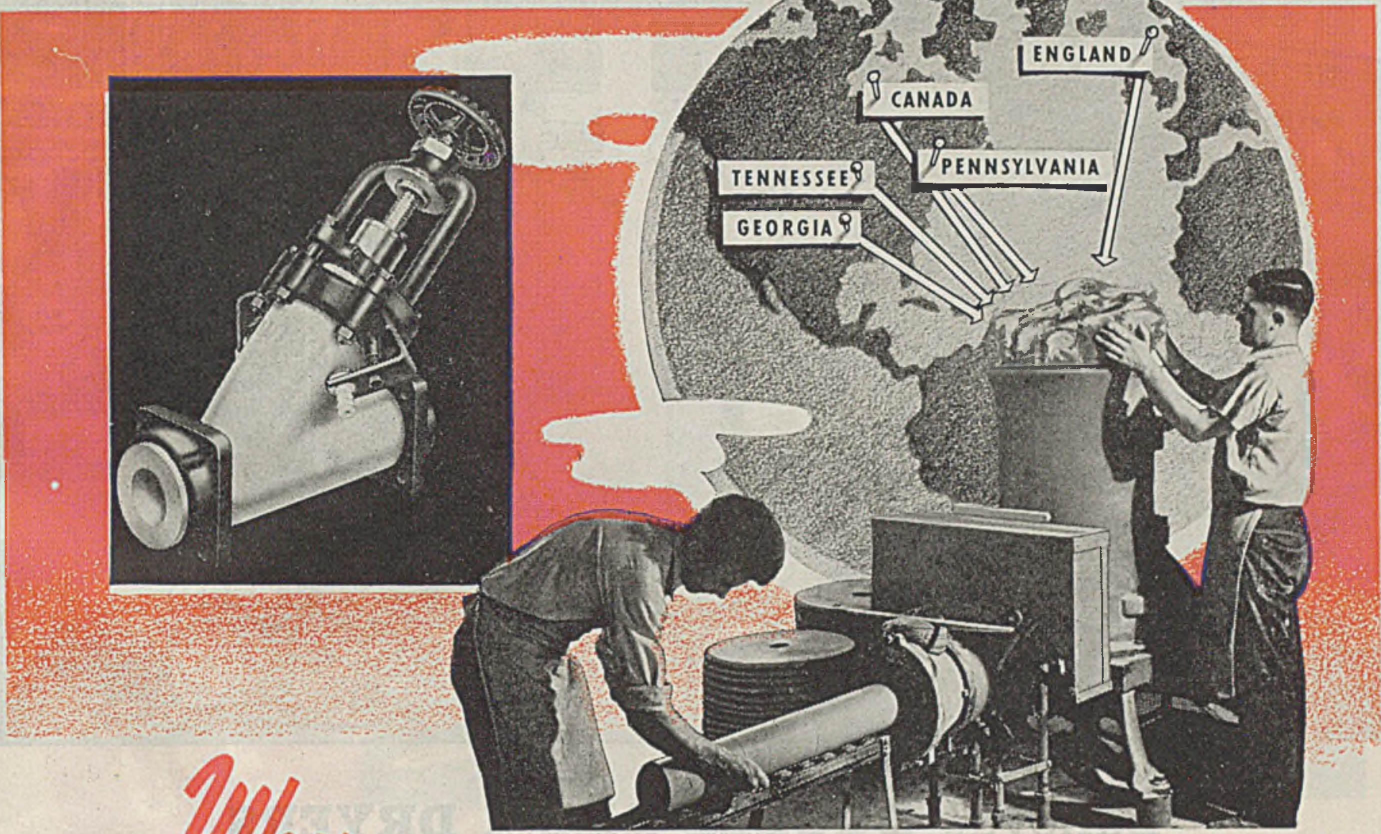
★ Rubber estates of the future, planted entirely with high yield trees, would have a reasonable chance of producing rubber for 4 cents a pound and selling it profitably at 7 to 8 cents plus transportation costs, based on present monetary exchange. Present price of natural rubber f.o.b. the United States is 22.5 cents a pound. Synthetic prices at the end of 1945 were: GR-S, 18.5 cents; neoprene, 27 cents; and Butyl, 15.5 cents (now up to 18.5).

★ Dried streptomycin is obtained by vacuum evaporation of an aqueous solution of the product at a pressure of 0.0005 to 0.00005 atmosphere (0.007 to 0.0007 pound per square inch).

★ Ten to twenty gallons of sap ordinarily can be obtained from a sugar maple tree in a season, and 25 to 50 gallons of sap are required to make 1 gallon of maple sirup.

★ The Patent Office maintains a register of patents offered by the owners for sale or license. Simplified descriptions of the invention are printed in *The Official Gazette of the U. S. Patent Office.* Eleven thousand patents have been placed in the register, which is operated without charge, since June, 1945.

★ Fifteen per cent of United States rubber requirements can be satisfied only with natural rubber; 75% can be satisfied either with natural or synthetic.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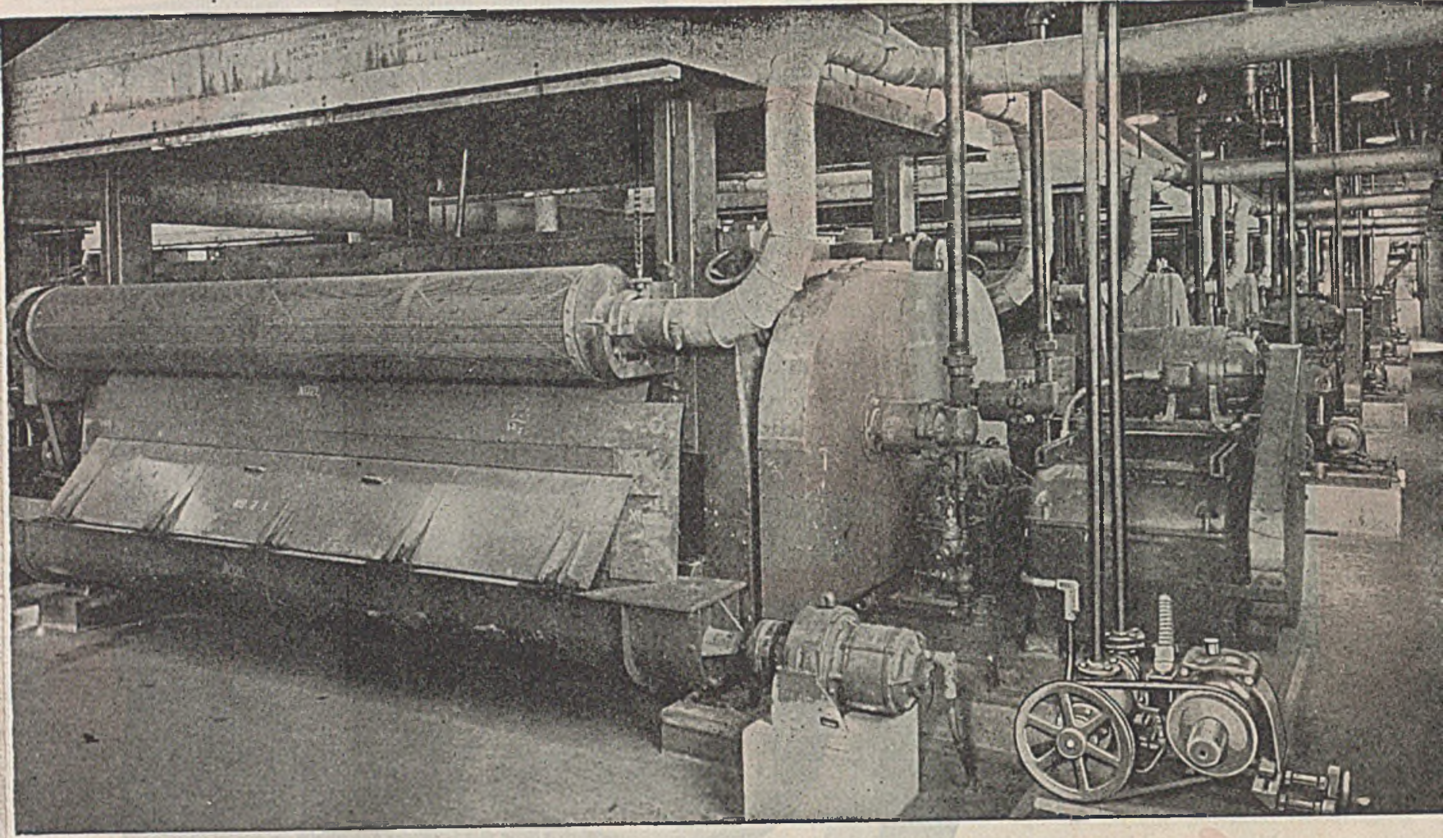

Buflovak DOUBLE DRUM DRYERS

a continuous low cost method of drying liquid materials

FROM the drums of these BUFLOVAK Dryers, a valuable food material comes in continuous sheets, reclaimed from a by-product.

Other installations, serving many industries have proven that drum drying is *easier, quicker*, more *profitable*, and occasionally the *only practical* way of drying liquid materials.

It is a continuous, direct, one-step operation from liquid to dry material, that may be profitably applied to a wide range of products, including chemicals, pharmaceuticals, dyes and food products. The materials are almost limitless in their physical characteristics ranging from dilute, heat-sensitive pharmaceuticals to corrosive crystal-forming chemicals. Such a range requires many types of dryers with special modifications in feeding devices, drives and material handling.

Among the many important BUFLOVAK wartime developments of drum drying is an Automatic Control, that increases drying capacity and further simplifies operation by maintaining the correct-liquid level between the drums.

Another development is the new Vacuum Double Drum Dryer that accomplishes entirely new results for many heat-sensitive materials.

In ever increasing variety, products are being dried profitably on drum dryers. The BUFLOVAK Research Department will gladly conduct a drying test of your material and recommendations can then be made on proven performance facts.

Send for Bulletin No. 316.

BUFLOVAK EQUIPMENT DIVISION of BLAW-KNOX CO.

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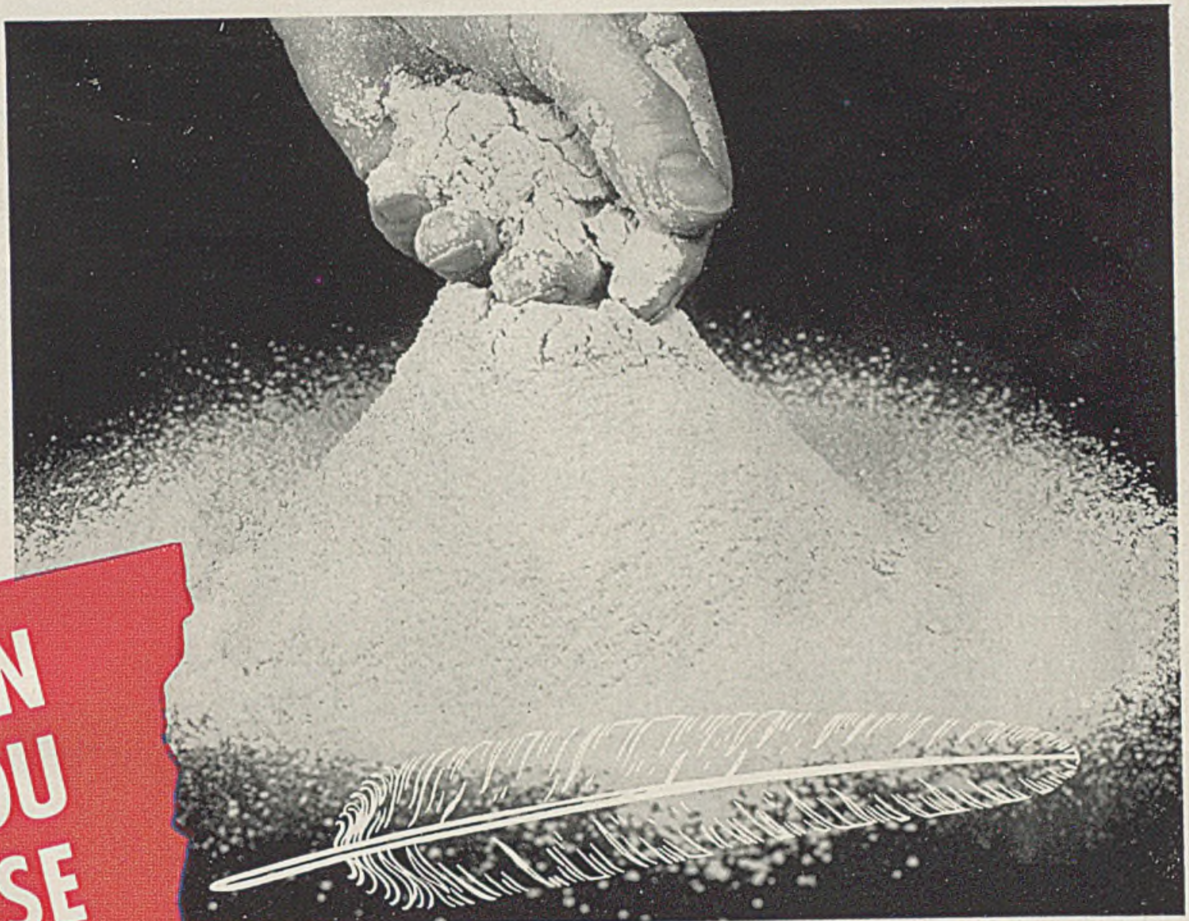

CAN YOU USE

Lightweight

HIGH VOLUME FILLERS – BULKY – FINELY DIVIDED

RANGE OF PROPERTIES DICALITE FILLERS

Colors . . . gray white, buff, white

Particle Size . . . from all through 150 to trace on 325 screen

Weight (loose) . . . 8-13 lbs. cu. ft.

Surface area . . . 20,000 to 100,000 sq. ft. per lb.

Porosity . . . approximately 90%

The above data gives the ranges of the many grades of Dicalite available for filler use. Complete data on specific materials on request.

Dicalite mineral fillers supply needed bulk without material weight increase. They can add strength, toughness, and abrasion resistance to a product; can reduce the heat and electrical conductivity. Besides these physical effects, Dicalite fillers very often aid in manufacturing operations as well. Two typical examples: they improve pigment dispersion and speed grinding in paint manufacture; they improve fiber formation and increase the drying rate in making paper and paperboard products.

Note the range of properties at left. A wide range of standard grades of Dicalite are available. A Dicalite Engineer will gladly analyze your filler needs and tell you how to take advantage of the economy and operating benefits offered in so many cases by Dicalite materials.

THE DICALITE COMPANY

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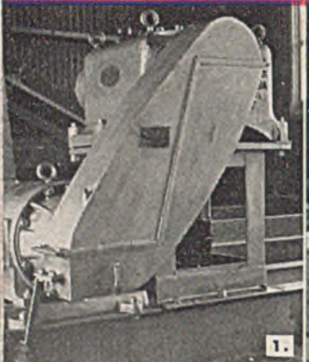
DICALITE MINERAL FILLERS

Process Adapted Agitation FOR YOUR PARTICULAR Open Tank Job..



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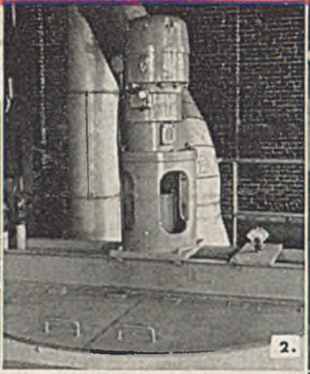

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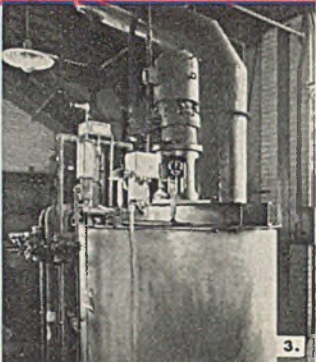

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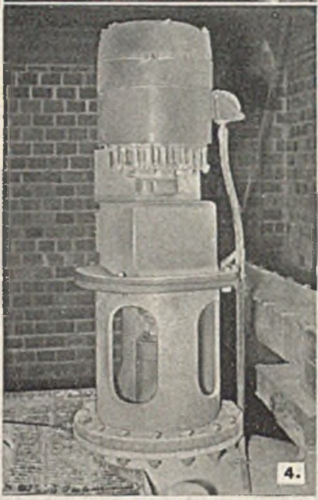

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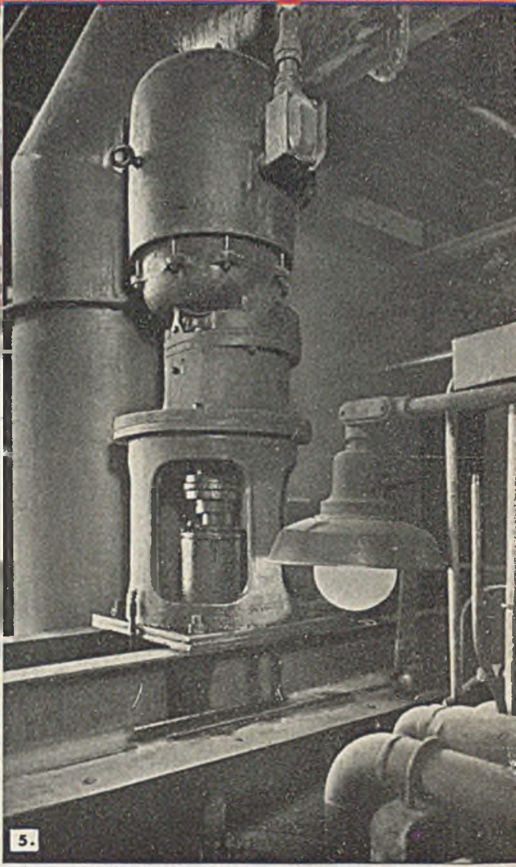


5.

1. Right angle reducer shown with chain drive from standard motor, bolted to common support. Can be furnished with Vee-belt drive or direct connected. **2.** For loose covered tanks with bent stacks—note neat accessible construction and heavy Timken bearing member. **3.** Compact vertical design permits location of other fittings on tank top. May be furnished with other types of speed reducers. **4.** Usually furnished with square base for open tanks. Also furnished for nozzle mounting (also usual style for pressure vessels) where external steel supports are not wanted. **5.** Note simple—"4 bolt" mounting and separately supported shaft—connected to speed reducer by FLEXIBLE COUPLING.

MIXCO AGITATORS

Where to use them—Wherever you have a job of mixing or agitation in an open tank of any practicable capacity, by all means let Mixing Equipment Co. Engineers assist you in engineering a *"Lightnin"* or *"Mixco"* Top Entering Mixer specifically to your job. That is the one positive way in which you can be sure that all factors (such as specific gravity, viscosity of materials, time and power consumption, results required, etc.,) will be taken into consideration to determine the proper equipment for an efficient, economical installation.

Available in 1 to 50 H.P. for agitating liquids up to 20,000 centipoises at mixing temperatures, *"Mixco"* Turbine—Agitator Mixers are the most complete line of mixers available. These extend the scope and range of the well-known *"Lightnin"* Propeller type mixers. A wide variety of propellers and turbine type impellers are available to obtain maximum efficiency on various materials under specific conditions and requirements.

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.

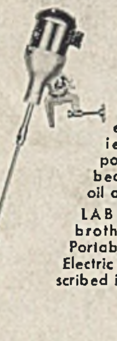
MIXING EQUIPMENT COMPANY OFFERS

Complete coverage of industrial areas with service for both individual users and engineers or equipment manufacturers.

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

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.



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direct drives. Man
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positioning. Extende
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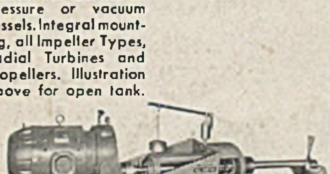

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☐ B-78—Top Entering Mixers
☐ B-75—Portable Mixers (*Electric and Air Driven*
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet

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