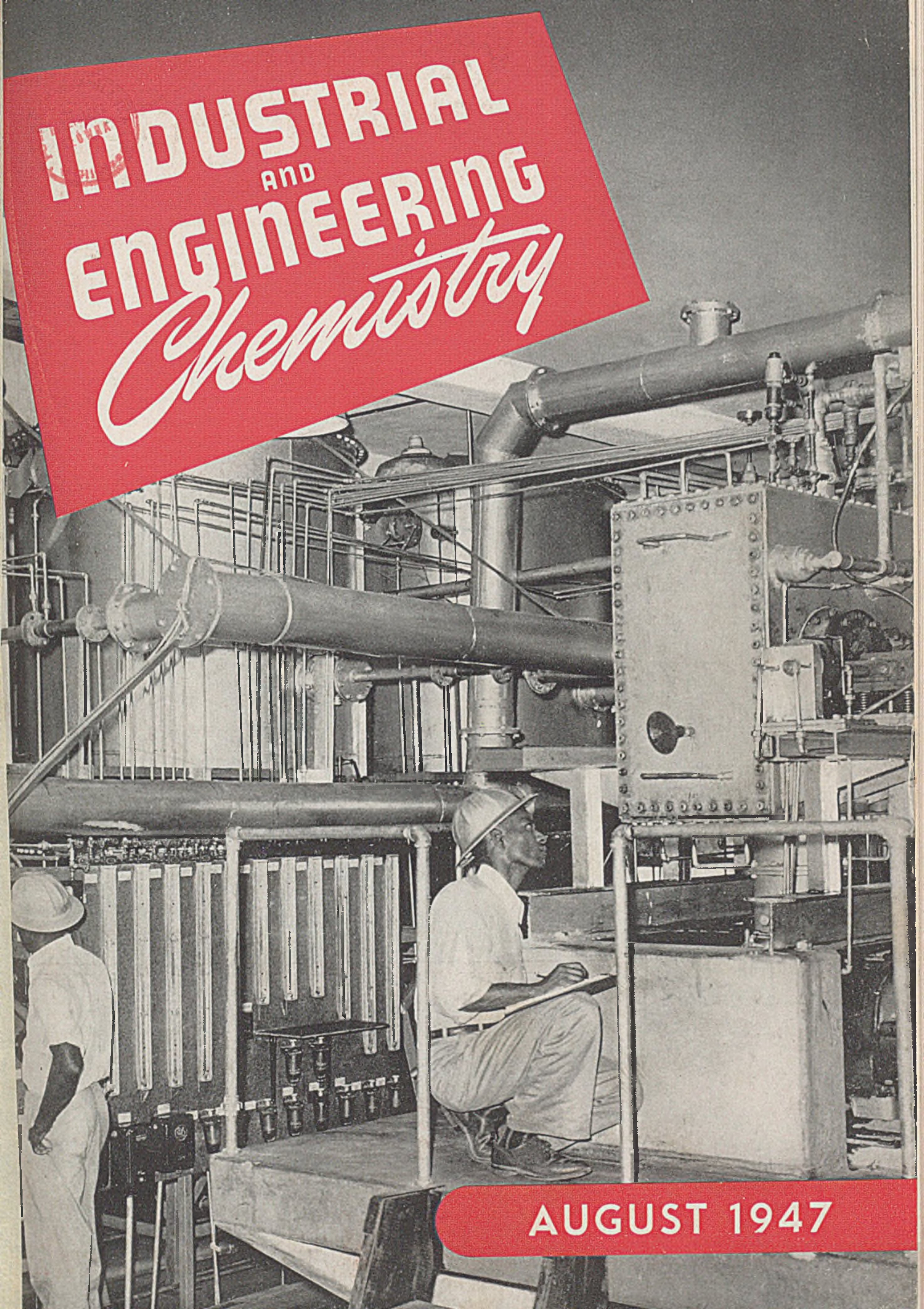
INDUSTRIAL AND ENGINEERING Chemistry



AUGUST 1947

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By transferring operations from laboratory glassware to Pfaudler acid-resisting glass-lined steel, you simulate exact conditions for *both* laboratory and plant. This enables you to plan procedures that will give you greatest yield at the smallest cost.

Service Flexibility

Pfaudler Glass-Lined Pilot Plant Kettles combined (when required) with Pfaudler glass-lined condensers, receivers, pipe and fittings give you maximum service range since they are resistant to all acids, except H F., at elevated temperatures and pressures.

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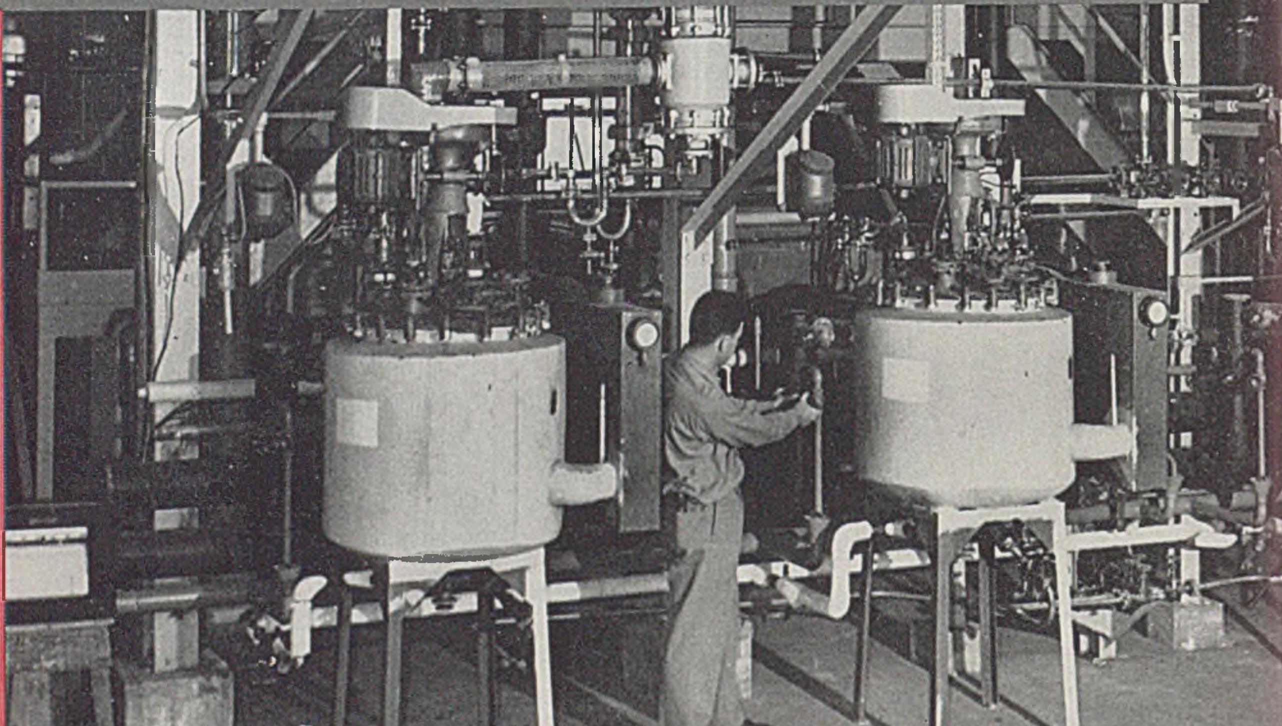
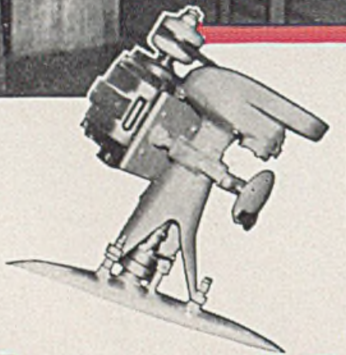
Available in various combinations in sizes ranging from 5 gallons upward, with or without steam jackets, top-heads, agitators and drives, you can select the exact unit for your particular problem. This gives you practically a custom made unit on a standard unit price scale. May we help you with your problem?





"Chemix" Agitator Drive—This new Pfaudler variable speed drive for Kettles over 30 gallons in size provides agitating flexibility. Its variable speed feature permits adjustment to comply with viscosity or specific gravity variations during reactions. It also may be used for many simple mixing jobs. It is inexpensive, sturdy, easy to attach for either vertical or angle mounting. Bulletin on request.

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ENGINEERS AND FABRICATORS OF CORROSION RESISTANT PROCESS EQUIPMENT

INDUSTRIAL and ENGINEERING *Chemistry*

AUGUST
1947

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Consecutive Number 15

Cover photo shows pilot plant at University of Texas for manufacture of acetylene from natural gas. It calls attention to a new pilot plant section starting with this issue. Photo by Will H. Shearon, Jr.

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Celite is amorphous diatomaceous silica, chemically inert, fire-resistant, highly absorbent, light in weight and has large surface area.

Celite Fillers are available in many grades at low cost. Why not discuss their application to your product with a Celite engineer. Address Johns-Manville, Box 290, New York 16, N. Y.

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Celite SSC	Light pink	Maximum 5% on 150 mesh	6-8 microns	Max. 1%	210	190	9	17	2.15
Celite HSC	White	Maximum 7% on 150 mesh	7-9 microns	Max. 1%	220	180	10.5	17	2.30
Snow Floss	Light buff	Maximum 0.5% on 325 mesh	1-2 microns	Approx. 4%	210	185	8	24	2.00
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* Gardner-Coleman Method—lbs. of liquid per 100 lbs. of Celite. ** lbs. per cubic ft.

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INDUSTRIAL and ENGINEERING CHEMISTRY....

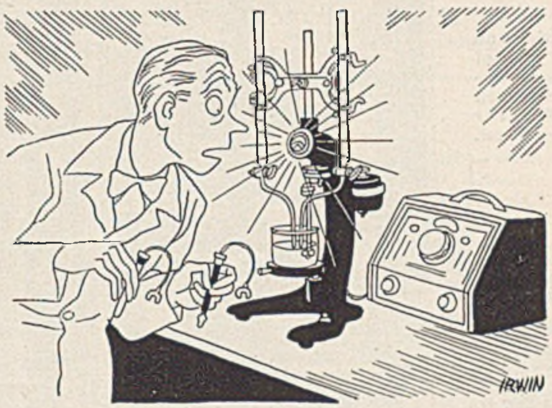
Reports

ON THE CHEMICAL WORLD TODAY

SUSIE Q

According to A.C.S. experts in the analytical field, few papers in the ANALYTICAL EDITION of I.&E.C. in the last year have attracted as much discussion and interest as that of Fred W. Jensen and A. L. Parrack of Texas A. & M. College entitled "Use of High Frequency Oscillators in Titrations and Analyses" (October, page 595). "Susie Q," as Jensen affectionately calls the instrument involved, has developed quite a bit since publication of the paper, and some of the questions and suggestions which have been received have opened up fields of possible usage far beyond the original thoughts of the authors.

The principle came to light when Jensen and a graduate student were doing some research work on dielectric constants. In the regular routine involving changing concentrations and the attainment of end points, it was noticed that in one particular case the end point was somewhat shaky and a little different from what might normally be expected. Checking to see what might be the cause of this not-too-satisfactory result, the student found that he had forgotten to put in the electrodes. What struck Jensen immediately was the fact that, shaky or not, the end point was there, even with no electrodes, and possibilities began to form in his mind. From this beginning came the Susie Q, based simply on the production of ionic or dipole motion without the introduction of electrodes, by using the field of a high frequency oscillator and measuring the change in oscillator current caused by the energy used in producing the motion. There was never much change from the original idea, since Jensen feels that almost any resonating circuit will exhibit the required characteristics to greater or less degree. With the theory in hand it became a matter of selection of the proper type of circuit to give the best results. The Engineering Experiment Station furnished A. L. Parrack to assist in the study of oscillators to be used for this type of work, and the tuned-plate tuned-grid type described in the paper was the one adopted.



Requests for reprints and additional information came pouring in, even from Russia. Angled from a "this is too good to be true" standpoint, many of the letters contained queries as to the possibility of adapting the instrument to certain specific types of titrations. Jensen's answer to any and all of these questions on titrations is simply this: The titrimeter will show any end point where there is a change in type or amount of ions at the end point, and titrations are not restricted to the use of reagents which are utilized in standard volumetric practices and which depend upon color changes or changes in hydrogen ion concentration.

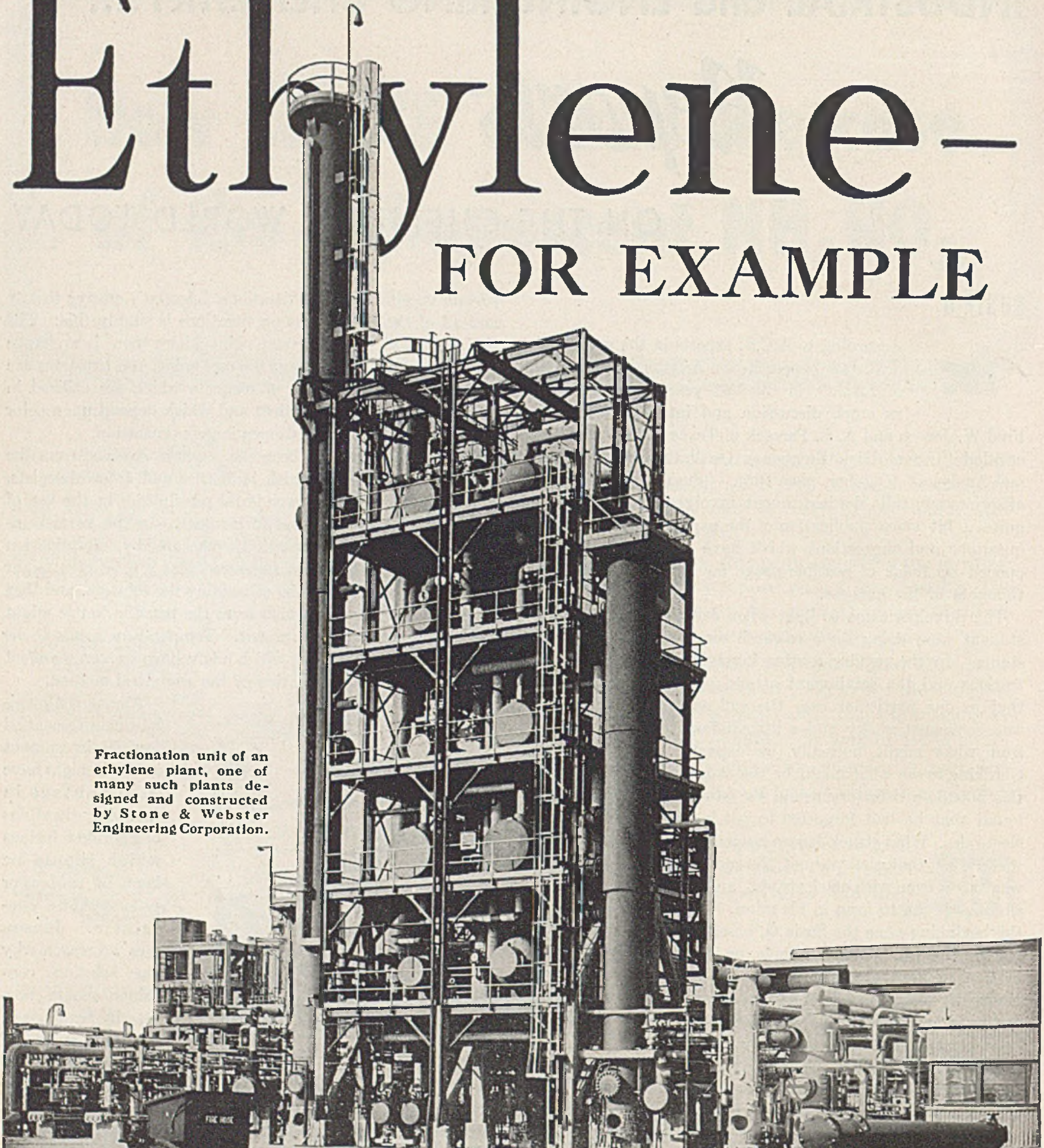
Most numerous have been the requests received from the plastics, paint, and varnish industries and from biologists, and the authors foresee wonderful possibilities in the use of the titrimeter as a control instrument. In the varnish industry, where degree of reaction is measured by determination of acid value, it has been suggested that a glass pipe might be substituted for the tube containing the solution, and that a continuous flow of varnish from the reaction kettle might be led through the instrument. Temperature seems to be the only important factor which might have an adverse effect on this particular application of the analytical method.

Among the possibilities suggested for the instrument is that it might have an advantage in following titrations of fluoride solutions which should be kept in rubber or polystyrene containers. Jensen sees no reason why the solution container should necessarily be of glass. Another angle of great research interest is Susie Q's application in following the course of reactions by changes in the number and type of dipoles. Inorganic solutions offer simple situations in all cases; the difficulty with organic solutions up to now is that, although changes in the solution and the resulting loading of the oscillator are evident, the causes to which this loading may be due are not always so obvious.

Colloidal systems are also being investigated. Although the tuned-plate tuned-grid oscillator is not particularly adapted to this type of work because the frequency range is so narrow, it is thought that projection of the theory into the colloid field will open up

(*Continued on page 8 A*)

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



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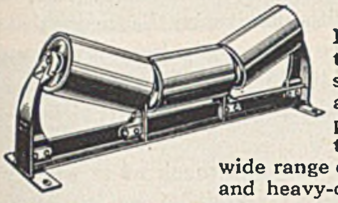
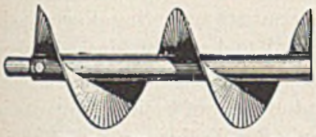


BELT CONVEYORS

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

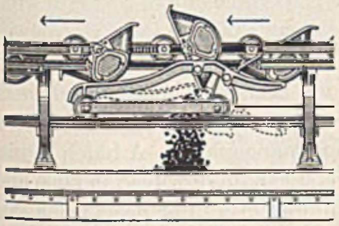
BUCKET ELEVATORS

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. Included are all accessories—chain, buckets, casings, take-ups, drives, etc.



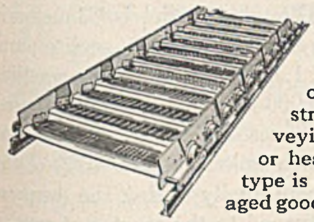
SCREW CONVEYORS

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



BUCKET CARRIERS AND ELEVATORS

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



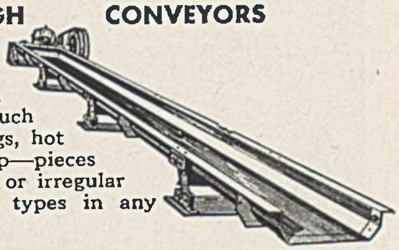
APRON & SLAT CONVEYORS

The steel-pan type, consisting of pans mounted on multiple strands of chain, is ideal for conveying fine or lumpy materials, light or heavy-duty service. The wood-slat type is recommended for handling packaged goods, parts, crates, barrels, boxes, etc.

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

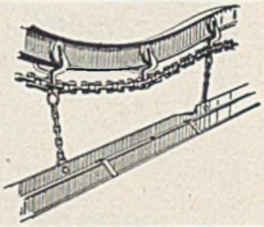
BULK-FLO Conveyor-Elevator-Feeder

Simple . . . Versatile . . . Compact . . . Enclosed. Economically handles flowable, granular, crushed, ground or pulverized materials of a non-abrasive, non-corrosive nature in a continuous mass, horizontally, vertically or on an incline, in a single unit. Bulk-Flo is easily adaptable to practically any surroundings.



OSCILLATING-TROUGH CONVEYORS

An economical conveyor for handling sharp, abrasive, hot materials, such as castings, metal turnings, hot shakeout sand, steel scrap—pieces that are hot, oily, jagged or irregular in shape. Made in two types in any length, for any capacity.

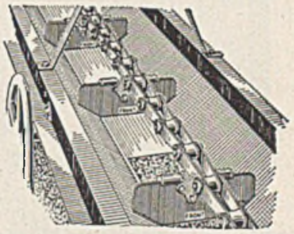


OVERHEAD CONVEYORS

Link-Belt overhead conveyors put ceilings to work, save valuable floor space, prevent congestion, interference and damage to materials in transit. Can be installed in existing plants without costly remodeling.

SKIP HOISTS

The skip hoist is especially well adapted for making high lifts, elevating abrasive or corrosive materials, and the handling of large lumps, as well as fines. Link-Belt skips are economically applicable to large or small capacities.

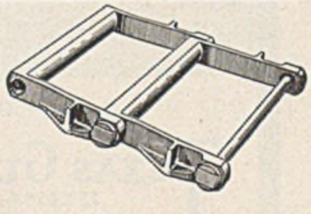


FLIGHT CONVEYORS

Made in many types for fine or lump materials in single or double chain designs, some arranged to slide, others carried on rollers, for horizontal or inclined operation.

CHAIN CONVEYORS

The most complete line of chains, sprockets and attachments of all types and sizes for every conveying, elevating and power transmission service.



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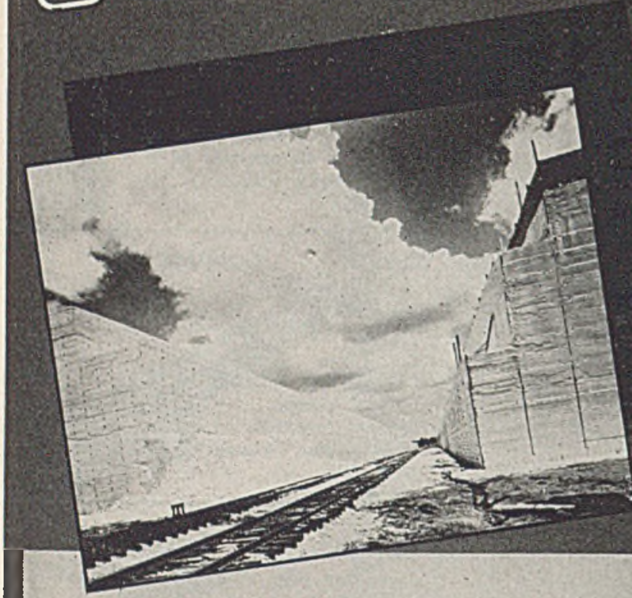

some very interesting avenues. The method may well be important in drilling mud analyses, where conductometric methods have not proved satisfactory because of fouling of the electrodes.

Citrus fruit growers and packers have been trying for a long time to find a satisfactory and not too costly method for the detection of internally crushed or frozen fruit; they have picked up the idea with alacrity, on the theory that the energy required to produce ionic or dipole motion in sound fruit is probably measurably different from that required for crushed or frozen fruit. Work on this project is already proceeding.

In the meantime there has been much more activity at Jensen's laboratory, and two additional models of Susie Q, smaller and more compact, have already appeared. One operates entirely on alternating current, and the other is a portable, direct current instrument which will interest those who have field analyses to perform. W.H.S.

PERMANGANATES VIA ION EXCHANGE

The German war machine's search for suitable oxidizing agents for its self-propelled missiles sent German scientists scurrying down the byways of chemical technology after syntheses which could be carried out with the limited mineral resources available. One of the most interesting of their discoveries is a zeolite process for the manufacture of sodium and calcium permanganate, which went into small scale plant production at the Elektrochemische Werke at Hollriegelkreuth in 1940. The plant produced 60 tons of permanganate a month with a crew of nine men working in three shifts and was the only one of its kind ever completed.

The process is a simple ion exchange in which potassium permanganate is passed through a sodium or calcium zeolite to produce the corresponding permanganates. A batch consists of 290 kg. of potassium permanganate dissolved in 4000 liters of water at 35° C.; this is filtered in a filter press using chlorinated polyvinyl chloride fiber filters and is introduced into a conventional zeolite tower. The tower, which is 1.3 meters in diameter, 3 meters high, and filled with 3-mm. zeolite particles, retains the solution for 1.5 to 2 hours. The resulting solution is concentrated in 40,000-liter lots at 100 mm. pressure and temperatures not exceeding 60° C. Unreacted potassium permanganate, which amounts to 5–10% of the original charge, precipitates continually during the evaporation and is filtered off and returned to the reactor at regular intervals.

When the volume of the product solution has been reduced to about 5%, it is removed from the evaporator and subjected to a series of cooling and filtering operations in Schumacher-type filters, ultimately reaching −10° C. This removes the remaining potassium permanganate which is practically insoluble at this temperature. The solutions are then rediluted to the commercial strength required and transferred to large iron storage tanks or 295-kg. iron shipping drums. Iron has been found suitable for handling permanganate solutions and is used for tanks, pipe, the evaporator, and the pumps. The zeolite towers, however, are made of iron lined with Oppanol

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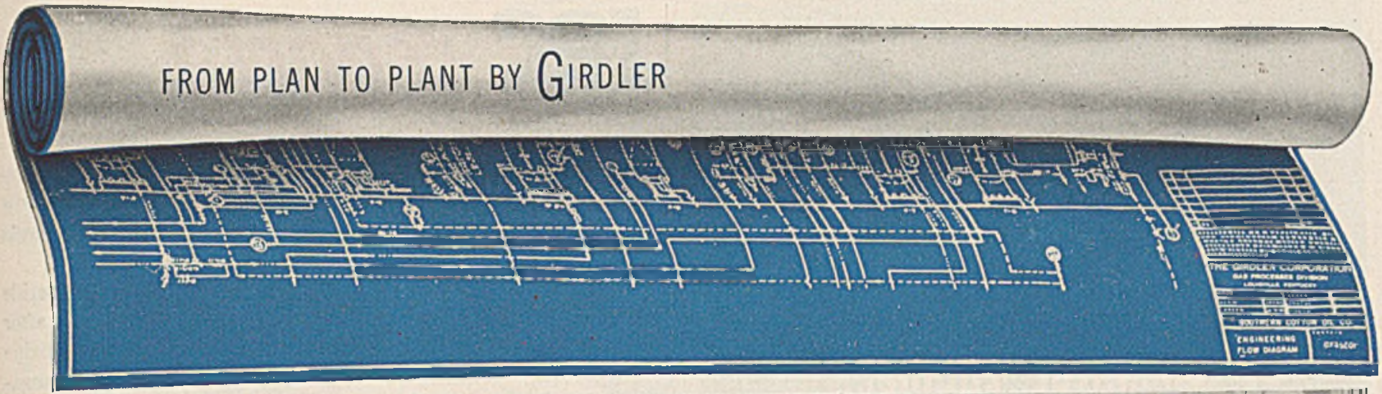

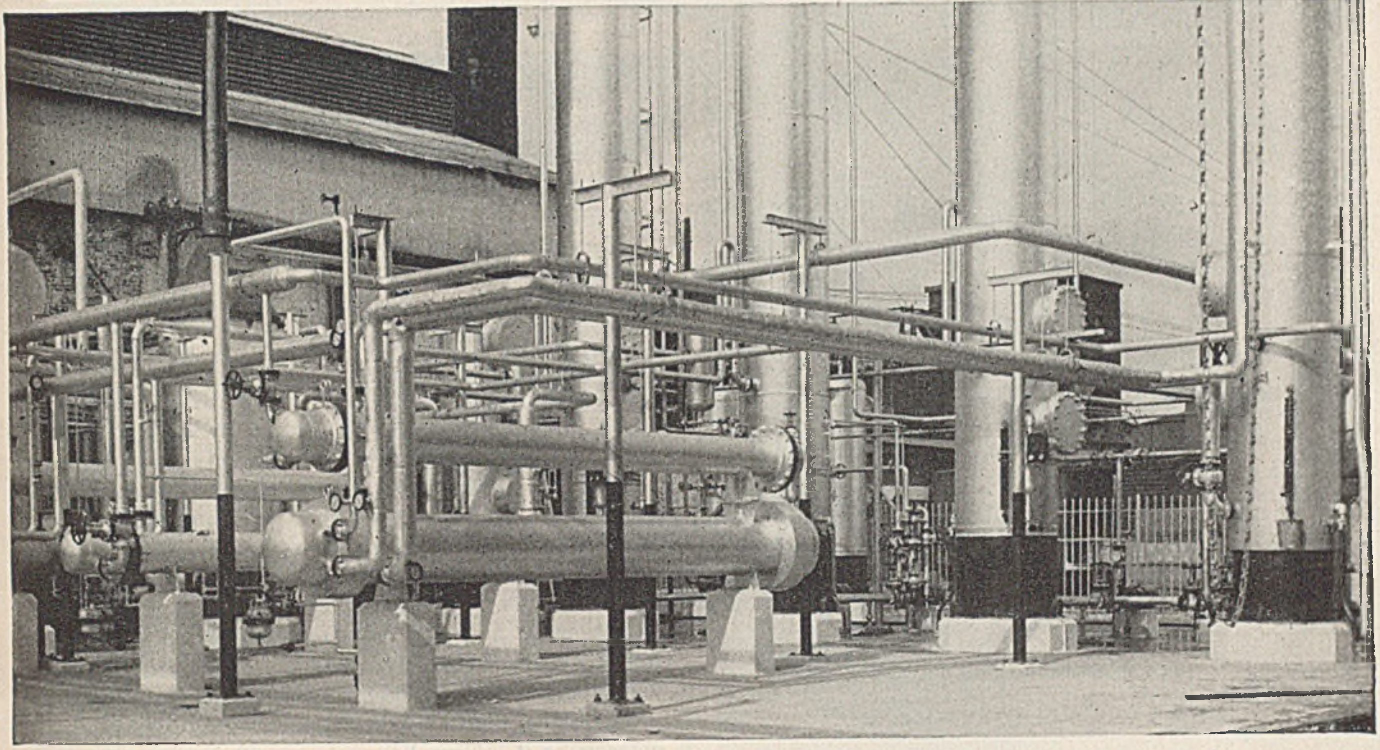

The complete job well done

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It was designed, engineered, and constructed by the Gas Processes Division of The Girdler Corporation, turned over to the customer "on stream" . . . meeting all guarantees. Advertising superlatives aside, it is typical of the neat, compact, efficient plant installations assured when Girdler does the complete job.

Girdler's complete service in gas processes covers all types of gas process plants—for gas manufacture, purification, separation, and dehydration. Girdler's versatile, practical experience includes processes dealing with hydrogen sulphide, carbon monoxide, carbon dioxide, inert and controlled atmospheres, natural gas, synthesis gas, refinery gases, liquid hydrocarbons, hydrogen, nitrogen.

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(a butadiene copolymer) since the free chlorine which is present would attack iron. It is believed that low phosphorus steel would also be suitable, but the austenitic VA steels were found to be unsatisfactory.

The zeolite is regenerated with a 22° Bé. calcium chloride solution or a 200 gram per liter sodium chloride solution after each run. Every four or five days the manganese dioxide formed from the reaction of residual chloride and permanganate must be removed by purging the tower for two to three hours with an 80 gram per liter sodium bisulfite solution. It has been suggested that calcium nitrate rather than the chloride be used to regenerate the zeolite and thus avoid the reduction of the permanganate. However, it is feared that the ammonium nitrate present in commercial calcium nitrate would react to form dangerously explosive ammonium permanganate.

The potassium chloride formed in the regeneration was not recovered. M.L.K.

OLD SOFTIE

The housewife's prime criterion in the selection of a good loaf of bread is freshness, which she judges almost entirely by its softness. As everyone knows, once bread becomes hard or "dry" its desirability suffers seriously. There are few people, other than baking experts, who know that staling is not caused by loss of moisture—experimental study has shown that there is no appreciable reduction in water content—but by a change in the state of starch, called retrogradation.

Although staling has been a problem since the inception of breadmaking, until recently there had been little progress in overcoming it. Now, however, according to a technical report by H. H. Favor and N. F. Johnston of the R. T. Vanderbilt Company, an organic compound has been found which strongly retards this process of retrogradation. The compound is polyoxyethylene stearate, a reaction product of ethylene oxide and stearic acid containing an average of eight oxyethylene groups per stearic acid radical. It is reported to be a nontoxic material, partially water soluble, stable to heat and aging, hydrolyzable by pancreatic lipase in vitro, and is said to impart no flavor or odor to products in which it is used.

In laboratory and bakery examination, polyoxyethylene stearate in quantities up to 2% of the flour weight showed no significant effect in bread doughs on condition of gluten, diastatic activity, or rate and amount of gas produced by the yeast. The only effect found in the bread was improved retention of softness and tenderness on aging. Bread containing 1% of this material, compared with bread prepared from the same formula without it, was found to be at least as soft after three days of aging as the control loaf had been after one day.

When added to starch paste, this compound increased the temperature of gelation but did not prevent complete gelatinization at the higher temperatures. The pastes containing it showed much less "setback" or stiffening after cooling and storage for one day, with no tendency to increase in viscosity or to retrograde in aging tests lasting as long as five days.

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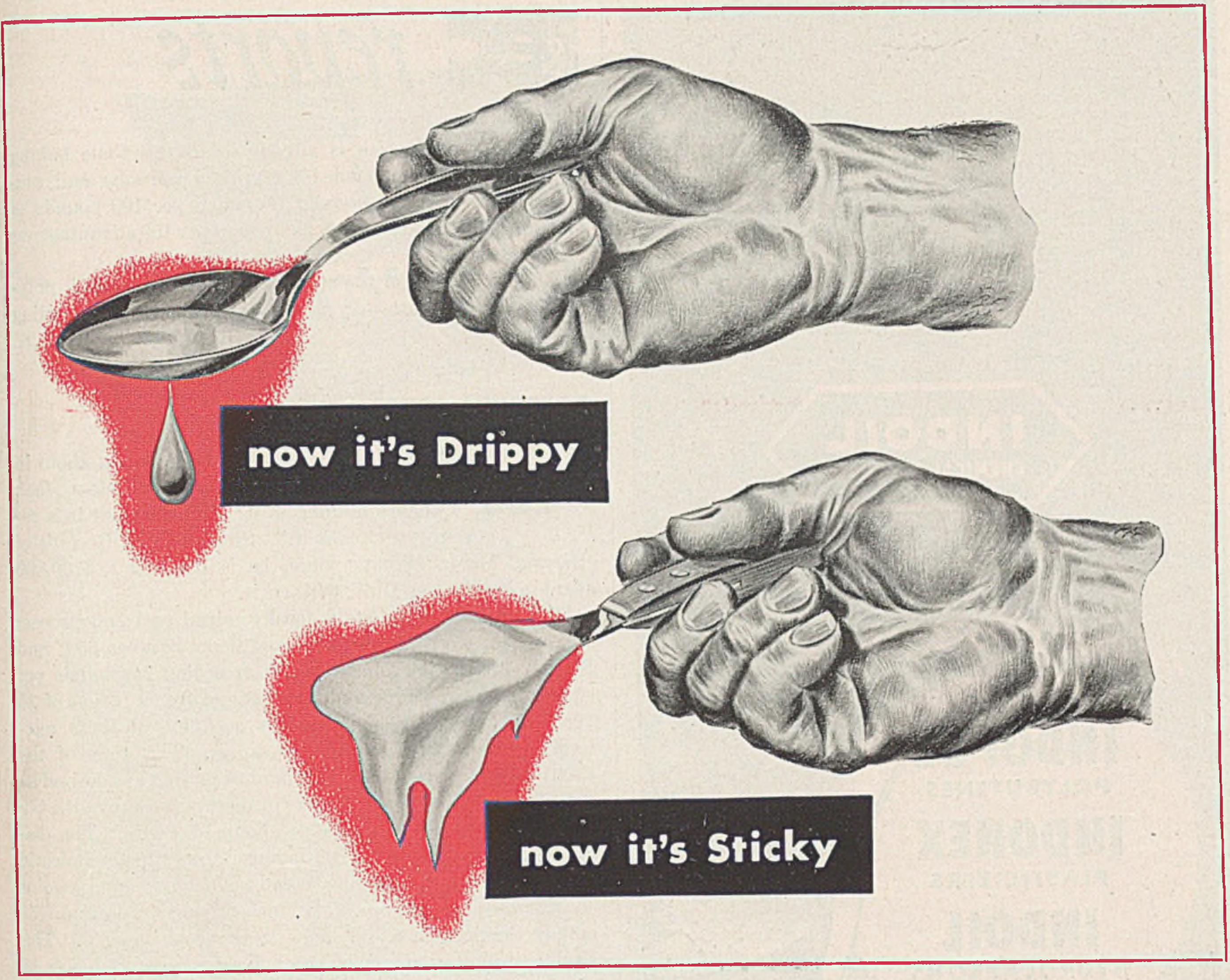

THE LIQUID-TOWARD-SOLID TRANSITION

Billion dollar processing problem solved by Continuous, Closed operation

MARGARINE, or lubricating grease, or shaving cream . . . Dozens of food, petroleum, and chemical products have this in common: They originate as a *liquid* which must be properly *congealed* with heat transfer and manipulation.

That's a billion dollar processing problem for a vast cross section of industry, most efficiently solved by continuous, closed VOTATOR operation.

The material is heated and/or cooled in seconds, safe and sanitary, *as it flows through the* VOTATOR *processing apparatus.* Scientifically determined agitation and perfect control over time and temperature precisely fix product texture, plasticity, and viscosity. Uniform quality is assured, at reduced processing cost.

VOTATOR apparatus does the work in often less than half the floor space required by open and batch methods, uses heat transfer medium with economy.

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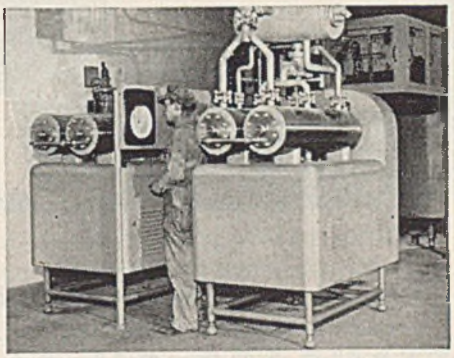

Typical Votator processing apparatus, for industrial starch. On a continuous, closed basis, variations of this apparatus handle heat transfer and plasticizing problems involving temperatures up to 400° F and down to —70° F, in connection with highly viscous products as well as the more liquid.

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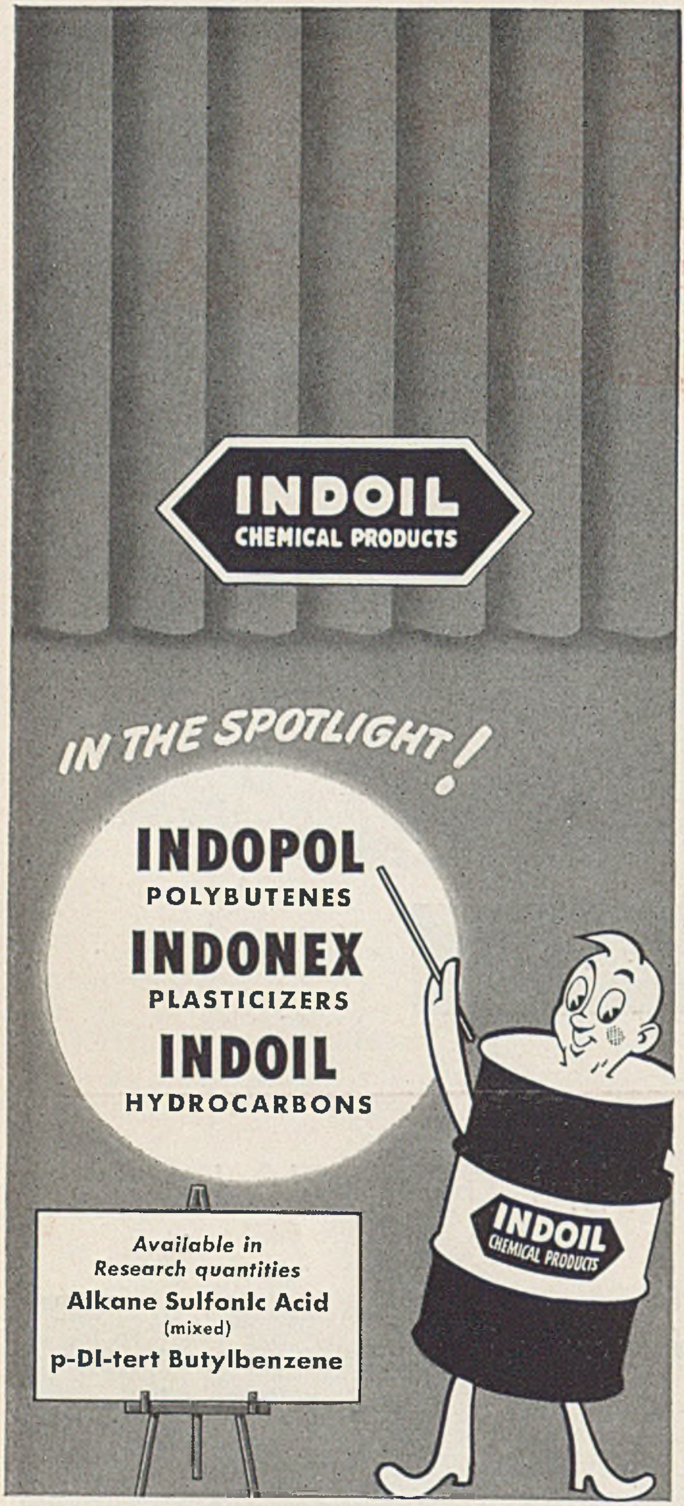
Votator PROCESSING APPARATUS

for products such as Industrial Starch, Chemicals, Lard, Paraffin Wax, Vegetable Shortening, Lubricating Grease, Shaving Cream



This material, which is already in use by some baking companies, is recommended for optimum results and economical use in proportions of $^1/_2$ pound per 100 pounds of flour, with quantities as high as 1 pound per 100 advantageous in some formulas.

Thus by control of the state of the starch in bread, polyoxyethylene stearate may preserve the appeal of the aging loaf. R.L.K.

PRESSURE COKER

"I don't know what all the secrecy is about in making low temperature smokeless fuel. There's nothing to it. You just put in a retort and cook it." So says E. H. Records of Tacoma, Wash. What's more, he is building a $100,000 plant in Wellington, Utah, to prove it.

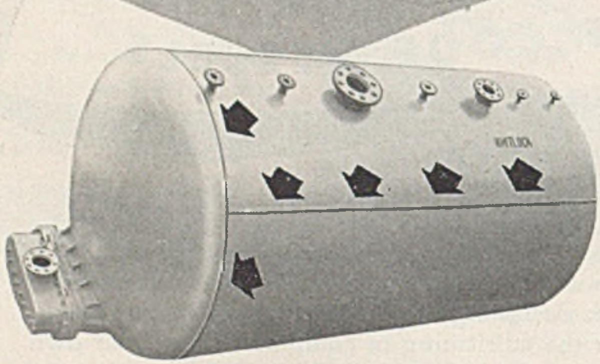
The Utah plant will take locally mined coal and process it in sealed retorts with superheated steam between 650° and 800° F. and at low pressures not exceeding 25 pounds per square inch. Experimental installations over a period of 25 years have experienced no serious corrosion at these relatively low temperatures and pressures. The time of the treatment will vary with the amount of tar and gas desired as determined by the relative prices of these substances with the smokeless fuel, but will average about 1.5 hours. The distillation can be effected in continuous retorts when nonplastic coals are used, but coking coals tend to "hang up" and require an intermittent process. The fuel produced has approximately the same size and shape as the coal charged. The Utah coal to be used at Wellington averages about 3 inches in diameter and undergoes about 10% size degradation in the retorts.

The steam-tar mixture which is distilled off is easily separated by drawing off the aqueous layer. The tar fraction is fractionated to yield 6 gallons of motor fuel spirits boiling below 180° F. for each ton of coal processed. The material has definite antiknock properties and can be used as a motor fuel additive without further fractionation. The total tar yield on Utah coal runs between 32 and 52 gallons per ton. The heavy residue is used for the manufacture of creosote, and the aqueous solution contains ammonium salts and soluble coal tar acids in concentrations which, it is believed, will make the solution suitable for sheep dip. About 75 gallons of this sheep dip solution are obtained from a ton of coal.

Pilot plant runs on coal samples obtained from all over the world indicate that this process will work on any known type of coal. It has the added advantage o being adaptable to the recovery of shale oil. By charging the retorts with an asphaltic rock, available at Sunnyvale, Utah, and adding certain natural mineral fluxes, 39 to 55 gallons of oil have been recovered for each ton of rock used in sample runs. This oil, if steam-distilled in pressure stills at 800° to 900° F., gives an almost 100% yield of an oil which, with the addition of cobalt or resin driers, compares favorably with linseed oil as a paint vehicle. We know this is impossible, but they are painting buildings with it in Tacoma, and it drys hard in 24 hours and weathers satisfactorily.

The yield from this oil process is almost one third greater that that obtained by any

(Continued on page 14 A)



other shale process and even exceeds the total oil content as determined by conventional dry analysis. Recent investigations using solvent method analysis on shales have confirmed the fact that the older analytical method was consistently low in the oil content indicated.

The process gives about 1300 pounds of smokeless fuel, that looks like coke but is not, out of a ton of high moisture Utah coal at an estimated gross processing cost from $0.75 to $1.25. This fuel burns to produce a light fly ash and no smoke, according to E. H. Records. Maybe it will help to retard the trend initiated by oil salesman Lewis. M.L.K.

TRAFFIC IN TRACERS

There is little doubt but that tracer techniques have now become integral parts of the scientist's tool kit. Although their ultimate potentialities in industry, agriculture, and physical and chemical research have been tapped only slightly, the results where they have been employed have given them secure footholds. A corresponding increase in instrumentation has accompanied this increase in interest of tagging molecules with radioactive or stable isotopes of constituent elements. This is especially true in the case of the radioactive tracers, where established companies have created special departments to meet the demand for constantly improved instruments for the detection and measurement of radioactivity.

Many new companies owe their birth to this same reason. An interesting example of this latter category of enterprise is that of Tracerlab Inc. of Boston, Mass., which was founded in March 1946 by a group of Massachusetts Institute of Technology scientists and engineers. Its original purposes were to manufacture and sell instruments, supply laboratory and consulting services, and develop commercial and industrial applications of radioactivity.

In late 1946, when radioactive isotopes from the atomic pile were made available for nonmilitary use, Tracerlab created a chemical division to purify, standardize, dilute, and store the radioactive materials for its clients, the ultimate users. This arrangement has the obvious advantage of placing the processing work in experienced hands and lowering the exposure of the consumer to radioactivity. Additional services of Tracerlab include storage of radioactive material, so that laboratories not equipped to handle large amounts of activity can obtain smaller amounts as needed. Isotope-sharing plans have also been worked out when two or more laboratories are interested in the same isotope but in amounts smaller than the minimum quantities furnished by Oak Ridge. The services offered should prove invaluable for research organizations which prefer no more contact with the radiation emitters than is required in performance of the experiment itself.

Tracerlab does not stock isotopes for resale; it merely acts as the processing agent for the ultimate user, who must obtain them by application to the Isotopes Branch of the United States Atomic Energy Commission at Oak Ridge, Tenn. The company is approved, however, to receive shipments directly from Oak Ridge on behalf of the user, if the latter so requests. If the consumer already has the radioactive material in his possession, he must secure an acknowledgment of transfer from the Isotopes Branch before Tracerlab can process it.

(*Continued on page 16 A*)

NEW LOWER PRICES ON "THFA"
(TETRAHYDROFURFURYL ALCOHOL)

TANK CARS . . . . f.o.b. Echota (Niagara Falls) New York	**$0.36** pound
DRUM-CARLOADS . . . . f.o.b. Waverly, New York 80 drums 475 pounds net	**$0.40** pound
DRUMS L.C.L. . . . . f.o.b. Waverly, New York 475 pounds net	**$0.44** pound
CANS . . . . f.o.b. Cedar Rapids, Iowa or Waverly, New York 8, 40 and 80 pounds net	**$0.47** pound

IN these days of rising costs, a price reduction is often reason enough for consideration of a raw material. But in the case of tetrahydrofurfuryl alcohol (THFA) we suggest that you consider this versatile chemical on the basis of what it can do for you. This new price reduction is an extra dividend and is an indication of what you can continue to expect as the market continues to develop—in this, as in the other furan compounds.

A VERSATILE CHEMICAL INTERMEDIATE

THFA is a useful agent for the preparation of high boiling esters, ethers and other derivatives. Among the compounds which have been prepared are:

Tetrahydrofurfuryl phenyl ether
Tetrahydrofurfuryl acetate
Tetrahydrofurfuryl butyrate
di-Tetrahydrofurfuryl phthalate
Tetrahydrofurfuryl oleate

The unique reactivity of THFA is illustrated by:

1. Ring expansion with formation of dihydropyran.
2. Substitution of nuclear oxygen atom with the formation of pyrrolidines and tetrahydrothiophenes.

PHYSICAL CHARACTERISTICS UNUSUAL IN A PRIMARY ALCOHOL

THFA is probably unique among primary high boiling (170°-180°C) alcohols for it is water soluble. It is virtually water white and has a mild, pleasant odor. THFA is stable under normal storage conditions.

AMPLE SUPPLY

As indicated above, THFA is now readily available in tank cars.

LITERATURE ON REQUEST

Additional physical and chemical properties of THFA and other uses are contained in Quaker Oats Technical Data Sheet 87A, a copy of which will be sent upon request. Our Technical Staff, always exploring the possibilities of the furans, will be glad to assist you in the application of THFA to your requirements.

Don't forget the Symposium on Furan Chemistry, A.C.S. meeting, New York City, week of September 15th.

The Quaker Oats Company CHEMICALS DEPT.

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I&EC reports

The Oak Ridge isotopes, when shipped, are classified into three groups: separated isotopes, fission products, and irradiation units. The first group (examples are C^{14}, I^{131}, P^{32}, and S^{35}) meet ordinary purity specifications but may need further purification for certain investigations, such as therapeutic work. Fission products, usually in the form of mixed isotopes, generally require separation and purification before they can be used. The last category, the irradiation unit, is defined as an aluminum can in which target material has been sealed and irradiated. These are shipped without chemical processing and frequently require purification before use. After purification it is usually necessary to convert the radioactive material to a chemical state most suitable to the eventual use. This may entail the preparation of the desired compound, e.g., potassium cyanide, methyl alcohol or benzene from barium carbonate containing C^{14}, and dilution to a standardized concentration.

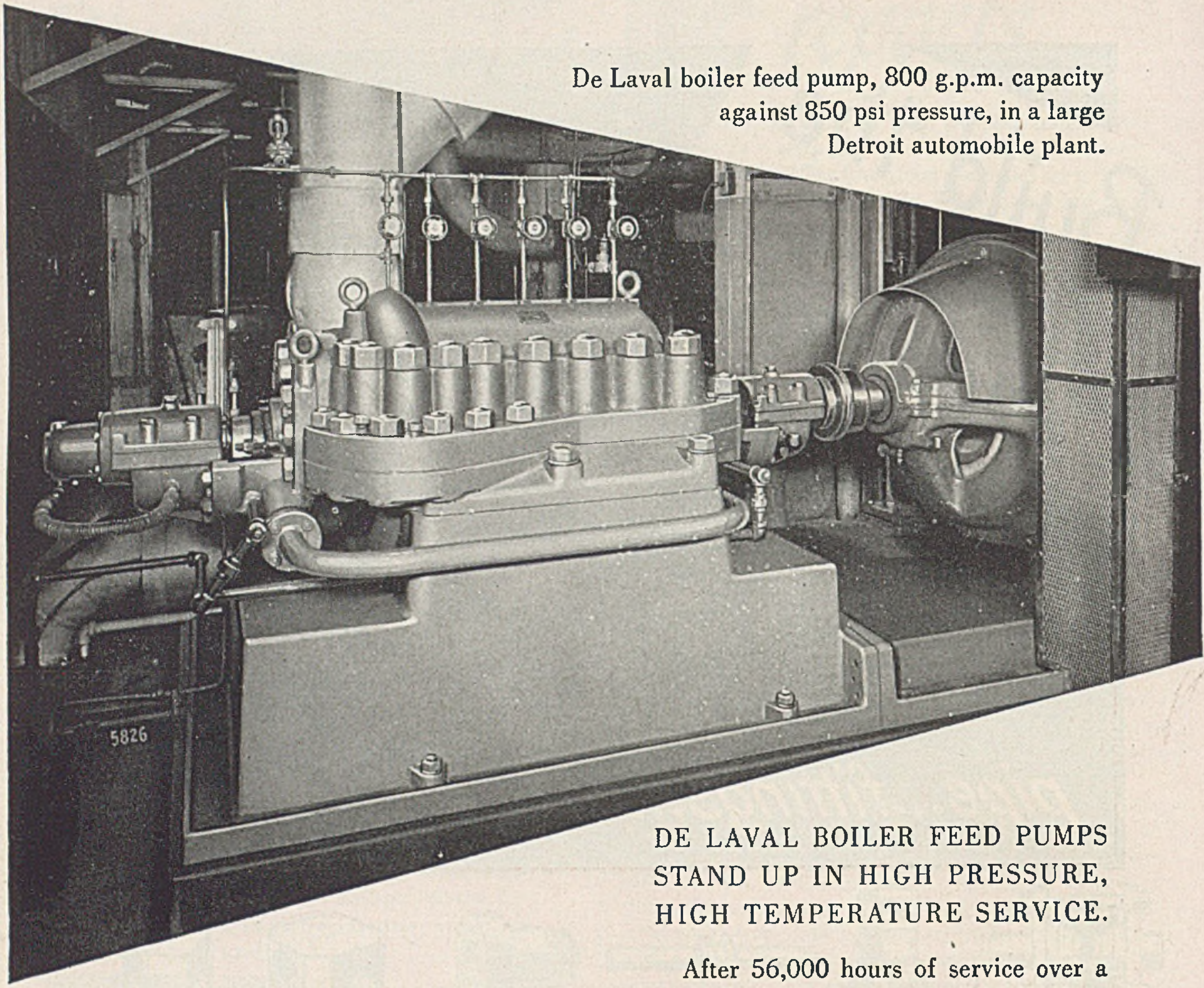
An example of this type of work is found in the preparation of hexaethyltetrapolyphosphate containing radiophosphorus, undertaken by Tracerlab for the Department of Pharmacology at the Harvard Medical School. The compound is one of the newer insecticides, and its mode of action appears to be through inhibition of enzymatic systems at extremely low concentrations. The problem on which the radiophosphorus was used was to determine whether the insecticide combined with enzymes through the phosphate groups.

It was first necessary to devise a synthesis that would permit the inclusion of the radioactive P^{32} in the molecule of insecticide. Radiophosphate ion from Oak Ridge was precipitated as lead phosphate, and the phosphate reduced with silicon dioxide and carbon at 500° C. to elemental phosphorus. After conversion to phosphorus pentoxide, a reaction was run with triethyl phosphate to form the desired hexaethyltetrapolyphosphate. The entire reaction was worked out on a 0.1 millimole scale and by the exclusive use of high vacuum technique gave a better than 95% over-all yield.

The subsequent experimental data obtained when the Harvard group tested the compound on the enzymatic systems showed that an insignificant quantity of phosphorus had become attached to the enzyme. It is now planned to repeat the experiment with carbon 14 in the ethyl groups of the insecticide to determine whether the inhibition is produced through ethylation of the enzyme.

The Atomic Energy Commission reports that business in isotopes has totaled nearly 1100 shipments since August 2, 1946, when this activity was started. About 570 of these orders were for the separated isotopes, 450 for irradiation units, and the remainder for fission products. About 100 isotopes of fifty elements have been supplied, with C^{14}, I^{131}, Na^{14}, and P^{32} most in demand. Most of the orders have been for the minimum amount of material, ranging from 1 to 50 millicuries, depending on the half life of the material, and were requested for basic research in medicine and biology. However, repeat orders account for nearly half of the total, and a number of larger orders have occurred in this category. Requests from industrial laboratories have increased significantly recently; this indicates more use for the radioisotopes in nonbiological tasks. The ingenuity of chemical research workers can be relied upon to find an ever-increasing variety of ways to utilize this powerful new tool, as its potential applications become more widely realized.

R.L.D.



De Laval boiler feed pump, 800 g.p.m. capacity against 850 psi pressure, in a large Detroit automobile plant.

"IN EXCELLENT CONDITION after 56,000 hours"

reports inspector

DE LAVAL BOILER FEED PUMPS STAND UP IN HIGH PRESSURE, HIGH TEMPERATURE SERVICE.

After 56,000 hours of service over a period of nine years, the power plant superintendent of a large Detroit automobile manufacturer asked for an inspection of this pump. The inspection was made and the following report received.

"We completely disassembled the pump and found wheels, diaphragms, shaft, bearings and all other parts in excellent condition. There was no washing of the pump case or any kind of corrosion. The shaft sleeve was highly polished. Balance parts including labyrinth leak off and the leak off bushing over the discharge end of the shaft sleeve hubs had but .005" wear."

In every detail De Laval pumps are designed for long trouble-free service.

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

U.S.I. CHEMICAL NEWS

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

New Dye Method For Testing Cotton Fiber Maturity Is Developed

A differential dyeing procedure which demonstrates the maturity of cotton fibers has been developed in this country, it was announced recently. The method is based on the facts that mature cotton fibers are thick-walled and immature ones thin-walled, and that thick- and thin-walled fibers take the same dyes differently and also take different dyes. The test is said to be made easily on unprocessed cotton lint in laboratory or dyehouse.

A mixture of dyes of contrasting colors, red and green, and of different dyeing properties, is used with a standard method of dyeing. The thick-walled, or mature, fibers dye definitely red, whereas the thin-walled fibers, commonly called immature, dye a distinct green. As a result, differentiation is easy.

The test may be used to test the progress of fiber development on seed, for comparing commercial cottons of different growth varieties, or to indicate to cotton mills certain lots of cotton which require special care.

Copies of Illustrated U.S.I. Booklet Available

An interesting 48-page booklet entitled, "U.S.I. in the World of Chemistry," describing the use of U.S.I. chemicals in modern industry is now available.

Full color pictures and charts show how solvents, alcohols, resins and other chemical building blocks are utilized in the everyday commodities of commerce. Copies may be obtained by writing to the New York office of U.S.I. on your letterhead.

New Method Slashes Moisture Assay Time

A method for the determination of moisture in certain bituminous mixtures which slashes almost three hours from standard analysis time has been developed by a mid-western government bureau.

In this test, samples of a bituminous mixture are shaken with Solox, U.S.I.'s proprietary alcohol-type solvent, which is miscible in water. The resulting effect is manifested by a change in gravity of the Solox-water solution which may be determined by a sensitive hydrometer. Previously prepared curves are consulted to obtain the moisture value of the bituminous mixture. Accuracy is usually plus or minus .1 to .3 per cent when the original material contains 4 per cent moisture or less. Time of analysis is stated to be 20 minutes or less, compared with 2 to 3 hours by conventional methods.

Solox is one of the most versatile and widely used of all solvents. It is finding an ever increasing market as a general solvent for innumerable industrial purposes. It has faster and better solvent power than completely denatured alcohol, has a mild non-residual odor, and is readily available for any manufacturing or other lawful purpose with only minor restrictions.

U.S.I. Boosts Diethyl Oxalate, Diethyl Carbonate Production

Move is Made to Meet Increasing Demands for These Versatile Chemicals in Lacquer Formulations and Organic Syntheses

Requirements for diethyl carbonate and diethyl oxalate, increasing steadily since the end of World War II, have made it necessary for U.S.I. to step up production of these versatile chemicals and to put plans into operation for expanding its manufacturing facilities. Diethyl carbonate is used in special-purpose lacquers and as a raw material for a wide variety of organic syntheses. Diethyl oxalate has found its greatest use in organic syntheses, but it also is employed today to extend and replace nitrocellulose solvents.

Diethyl Carbonate Has Many Applications

Originally used for lacquers which require a pure neutral solvent—lacquer for radio tube cathodes is an example—diethyl carbonate is now employed in many diverse types of organic syntheses. These range from manufacture of comparatively little-known compounds such as ammeline (2-hydroxy-4, 6-diamino-1, 3, 5-triazine), to the preparation of pharmaceutically-important barbiturates.

Diethyl carbonate may be employed in Claisen condensations to react with esters of aliphatic acids, with esters of aryl substituted aliphatic acids, and with ketones and cyanide derivatives. It may also be reacted with a Grignard reagent to give the next higher acid, and with primary and secondary amines to give the corresponding substituted ureas. Among the other products produced with the aid of diethyl carbonate are: sodium ethyl carbonate, urethan, urea and carbohydrazide.

Diethyl carbonate is considered as nearly a neutral solvent as it is possible to make. It is a medium evaporating solvent, characterized by the desirable features of mild odor and

(Continued on next page)

Claims New Process Will Develop Film in 15 Seconds

A high-speed process for developing photographic film that makes it possible to project an image on a screen only 15 seconds after a picture is taken was announced recently.

The exposed film is treated with hot solutions in a special processing cup which restricts the liquids to a small circular area on the film. The process is carried out at approximately 60°C., development requiring only three to four seconds and fixing six. The spent solutions are quickly removed by suction, and the nearly-dry developed and fixed film is fed into the projection system where an air-pressure gate completes the drying, cools the film, and holds it flat while it is being projected.

If it is desired to project a positive rather than a negative, a strong dichromate bleach is used in place of the fixing bath, and reversal processing can be achieved in less than 10 seconds. In a typical machine, the film is drawn through a series of tanks containing developing, rinsing, fixing, and washing solutions at a uniform rate so that a given portion of film remains in each bath about 5 seconds. Drying requires about 15 seconds. Total processing requires about 35 seconds and yields image quality comparable to that obtained in normal motion picture processing machines in 35 or more minutes.

High fidelity video reproduction is made possible by the new-type television camera said to be as sensitive as the human eye. To prevent current leakage, cathodes in the camera tubes are impregnated with a lacquer containing diethyl carbonate.

ADVERTISEMENT—*This entire page is a paid advertisement*

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

Diethyl Carbonate, Diethyl Oxalate

(Continued from page 1)

high stability. It is useful wherever a pure neutral lacquer solvent is required.

Diethyl Oxalate is Nitrocellulose Solvent

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

Diethyl oxalate offers many possibilities in chemical syntheses. Here are a few typical examples: With ethyl acetate in the presence of sodium ethoxide (sodium ethylate) it yields ethyl sodium oxalacetate. With acetone in the presence of sodium ethoxide, it yields xanthochelidonic acid ester (acetone dioxalic ester) from which the ethyl ester of chelidonic acid may be obtained. Gamma-pyrone may in turn be obtained from this latter substance.

With zinc and alkyl iodides, it gives ethyl esters of dialkylglycolic acid. With sodium amalgam, the alcoholate of ethyl glyoxylate, diethyl oxomalonate, ethyl *dl*-tartate, and the ethyl ester of desoxalic acid may be obtained, and by reacting with phenylhydrazine, the phenylhydrazone of ethyl glyoxylate.

Electrolytic reduction gives ethyl glyoxylate. With sodium ethoxide and urea, it gives parabanic acid (oxalylurea). It is used to manufacture phenobarbital. With ortho-nitrotoluene and sodium ethoxide there results ethyl o-nitrophenylpyruvate. By distilling with an alcohol other than ethanol, the oxalic ester of the alcohol may be obtained through alcoholysis.

HEAVIER POULTRY PRODUCED WITH FERMENTATION SOLUBLES IN BROILER FEED

In raising broilers it is essential to produce the maximum quantity of poultry meat at the lowest possible feed cost. Listed below is a ration which has been recommended by a leading university's experimental station. It has been used with success by feed manufacturers and individual farmers.

Ground yellow corn	580
Ground heavy oats	300
Wheat middlings	200
Wheat bran	250
Soybean oil meal	200
Corn gluten meal*	50
Alfalfa leaf meal	100
Meat scraps	100
Fish meal	100
Manganese sulphate	¼
Fermentation solubles (80 micrograms riboflavin per gram)**	25
Dried milk product***	50
Ground limestone or oyster shell	25
Bonemeal or defluorinated rock phosphate	10
Salt	10
Vitamin A and D feeding oil or its equivalent (400 units D per gram)	4

*Corn gluten meal or other vegetable protein meal such as peanut meal. Additional soy bean meal may be substituted when other vegetable protein are not available.

**U.S.I. manufactures Curbay BG, a dried fermentation soluble product which contains 80 micrograms of riboflavin per gram of material.

***This may be omitted if riboflavin or riboflavin substitutes are available. U.S.I. offers two natural riboflavin products in its line: U.S.I. Riboflavin Concentrate No. 85 (85%) and U.S.I. Riboflavin Mixture No. 1 (1 gram per ounce).

New Seed-Disinfectant

A new chemical seed-disinfectant, said to control insects that attack seeds in storage, has been announced.

TECHNICAL DEVELOPMENTS

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

A photosensitive glass, which is said to be capable of receiving permanent colored photographic prints with three-dimensional effects, has been announced. **(No. 224)**

USI

A new-type spark-resistant flooring, used during the war in munition plants and gun-turrets, is said to be static conductive. **(No. 225)**

USI

A new synthetic detergent, can be used on all types of washables in both hard and soft water, according to the manufacturer. **(No. 226)**

USI

To measure moisture in any substance, a direct-reading electronic moisture meter has been placed on the market. It is said to provide the percentage of water automatically in 15 seconds. **(No. 227)**

USI

A new anti-corrosive finish, aimed at protecting metal, wood, and concrete against moisture, acids, and other disintegrating elements, is claimed to dry by evaporation and to be free of paint odors. **(No. 228)**

USI

A true-polyvinyl chloride paste-forming resin, claimed to be the first of its type to be made in this country, is said to eliminate the necessity for heavy and expensive equipment in coating operations. **(No. 229)**

USI

To fray-proof rugs, a new rubber-like compound has been developed, which the makers say is waterproof and can be applied to any type of rug. **(No. 230)**

USI

A polystyrene that withstands boiling for short periods of time and has other improved physical and chemical properties has been developed. It is claimed to have an unlimited color range. **(No. 231)**

USI

A new non-flammable paint remover is rapid, requires no neutralizing after-use, and contains a plastic retarder to keep the remover on upright and overhead surfaces, according to the manufacturer. **(No. 232)**

USI

To improve leather quality, a new coating for chrome- and vegetable-tanned leathers is being marketed. It is said to reduce shrinkage and to provide added smoothness in grain. **(No. 233)**

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

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Ethanol (Ethyl Alcohol)
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- Diethyl Phthalate

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- Ethyl Chloroformate
- Ethyl Formate

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

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

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

ACETONE
- Chemically Pure

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

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. . . if so, assure oil withdrawal in coldest weather with a G-FIN TANK OIL HEATER

Note These Advantages of the G-R G-FIN Tank Oil Heater

GREATEST HEATING EFFECTIVENESS . . . provided by the G-FIN elements which have six to eight times the heating surface of bare tubes

MOST COMPACT UNIT . . . fewer tubes and shorter shell for a given duty

LEAST PRESSURE DROP . . . has maximum free area and straight-through flow of oil

NO STRATIFICATION OR VAPOR BINDING . . . oil outlet at top of shell prevents dead pocket

USES LESS STEAM . . . heats oil only locally at point of withdrawal

FEWER TUBE JOINTS . . . resulting from small number of required heating elements

ACCESSIBILITY . . . easily examined and cleaned throughout entire length and diameter of heating elements

LEAKPROOF JOINTS . . . the conical ends of the heating elements are seated in the tube sheet with accurately machined metal-to-metal joints held tight by lock-nuts

NO TEMPERATURE STRAINS . . . the U-bend elements are free to expand or contract

Many hundreds of installations of the G-R G-FIN Storage Tank Oil Heater have fully demonstrated the speedy action, thorough reliability, low steam consumption, and economical maintenance of these units.

Users report that even in sub-zero temperature, or where oil has partly solidified through long periods of storage, these highly effective heaters assure a steady flow of oil soon after steam has been turned on.

Wherever fuel oil, lubricating oil, crude oil, road oil, tar, asphalt, glycerine, cotton seed oil, molasses or other viscous liquids are stored . . . at process plants or power plants, tank farms or distributing centers, loading wharves or platforms . . . the G-R G-FIN Tank Oil Heater is a necessary insurance against difficulties or delays in oil withdrawal. Available for installation outside of, or partly within the tank.

Write for Bulletin 1641 describing these units in detail.

THE GRISCOM-RUSSELL CO.
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GR-133

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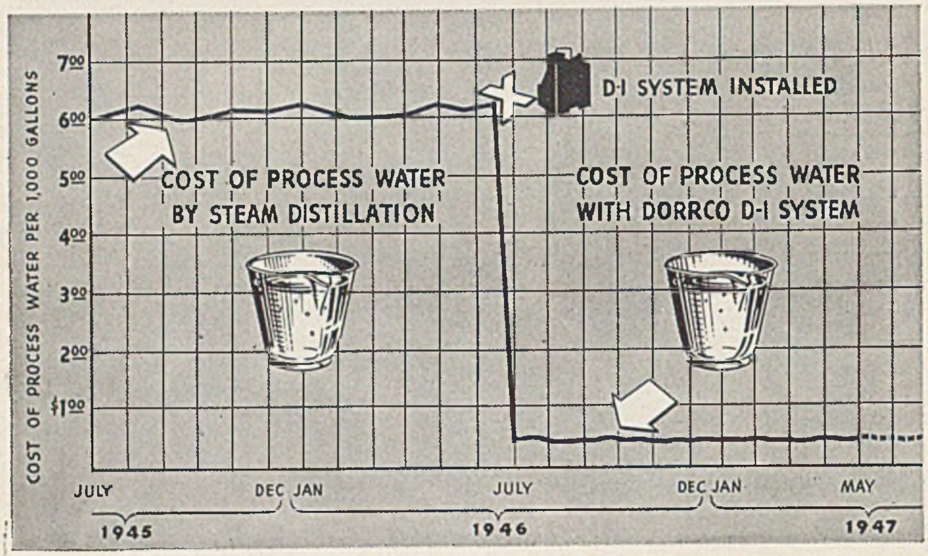
COST OF PROCESS WATER PER 1,000 GALLONS
7.00
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3.00
2.00
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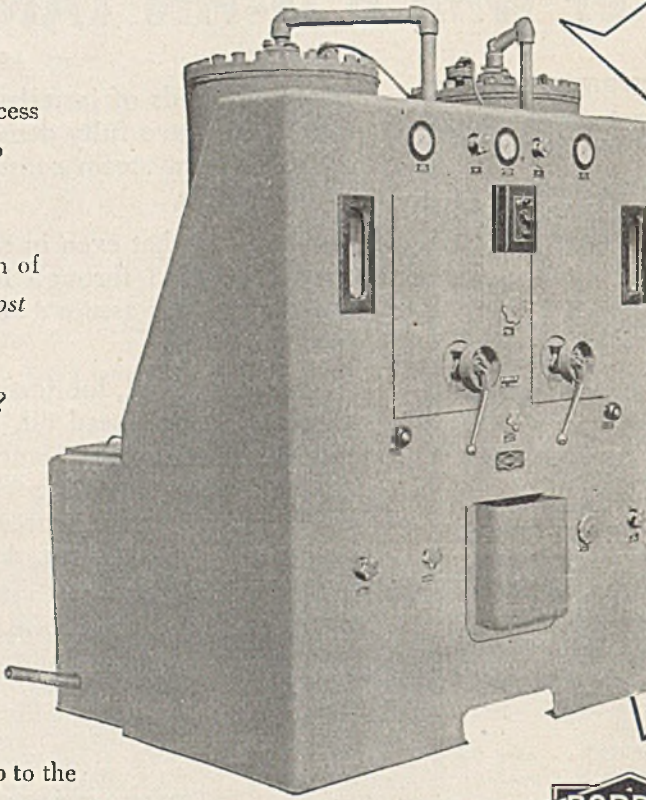
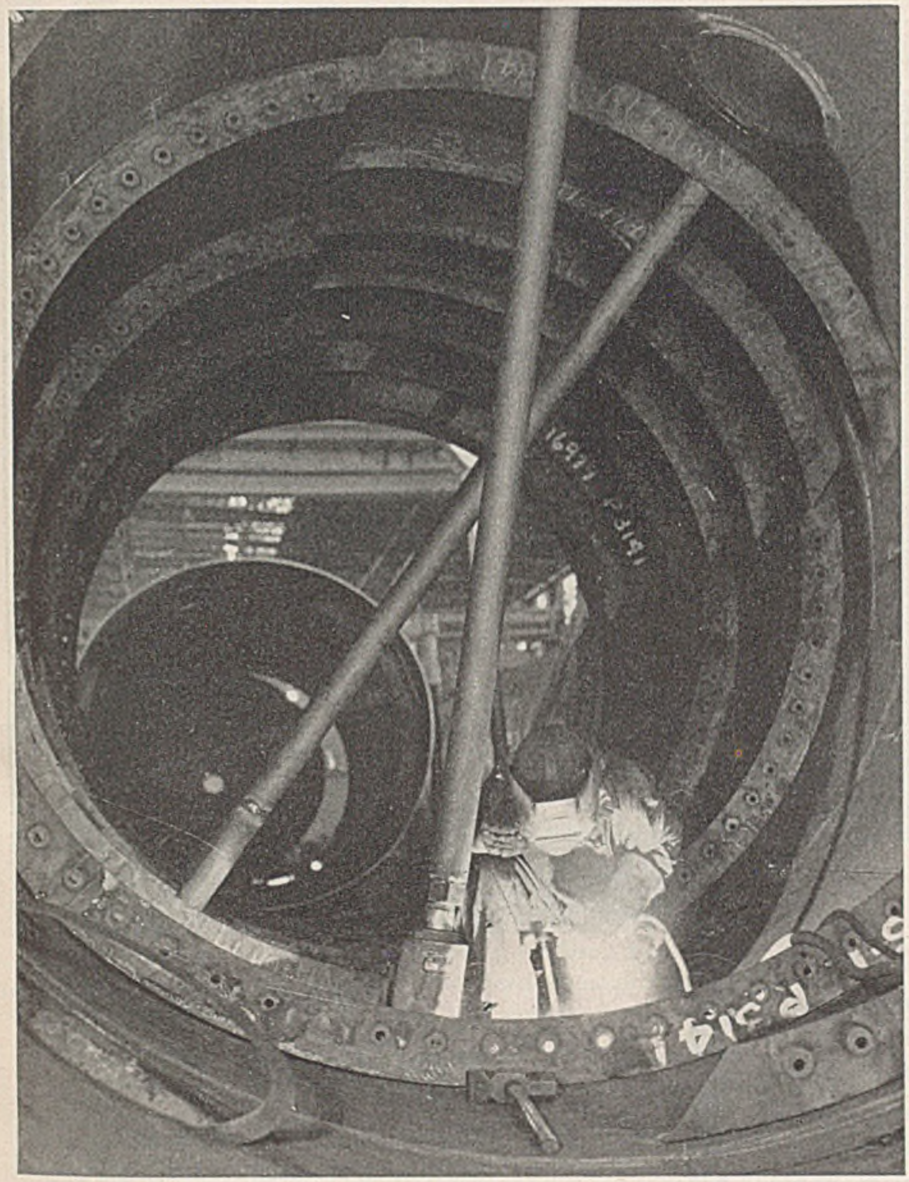
COST OF PROCESS WATER BY STEAM DISTILLATION
COST OF PROCESS WATER WITH DORRCO D-I SYSTEM
JULY
DEC JAN
JULY
DEC JAN
MAY
1945
1946
1947



FOR LOWEST COST CONTROL OF HIGH TEMPERATURE CORROSION IN REFINERY PRESSURE VESSELS

–nothing equals Stainless Steel!



REFINERY experience with many kinds of pressure vessel linings has clearly demonstrated this fact: –From the standpoints of economy, durability and prolonged corrosion resistance none can be compared with Stainless Steel liners applied by welding.

In more than 500 applications, Stainless Steel bubble tower linings have shown an apparently unlimited life in hot end service. Many of them lined in the shop and in the field, ten and more years ago, are still in successful operation. Even when handling sour crudes at 900°F. and higher, U·S·S Stainless Steel linings reduce corrosion to a minimum.

Just how economical such linings are–despite Stainless Steel's higher first cost–is indicated by the experience of a leading oil company. Before setting up a program for standardizing on stainless steel for pressure vessel lining, they made a careful study to determine comparative costs on the basis of life expectancy. Here is what they found by actually lining bubble towers:

- *Arc-welded carbon steel lining* (0.75 in. in heading, 0.5 in. in shell lining) cost $12.62 per sq. ft. Life was estimated at 4.5 years, making cost of lining $2.81 per sq. ft. per year.
- *Sprayed cement coating* cost $3.11 per sq. ft. Life was estimated at 1¼ years–making cost of lining $2.49 per sq. ft. per year.
- *Welded Stainless Steel lining* (0.109 in. thick) cost $4.95 per sq. ft. With life conservatively estimated at 15 years, lining costs $0.33 per sq. ft. per year!
- In other words, savings with Stainless Steel linings as compared with carbon steel linings were given as $2.48 per sq. ft. per year, or 88.3%;–as compared with sprayed coating, $2.16 per sq. ft. per year, or 86.7%.

U·S·S STAINLESS STEEL

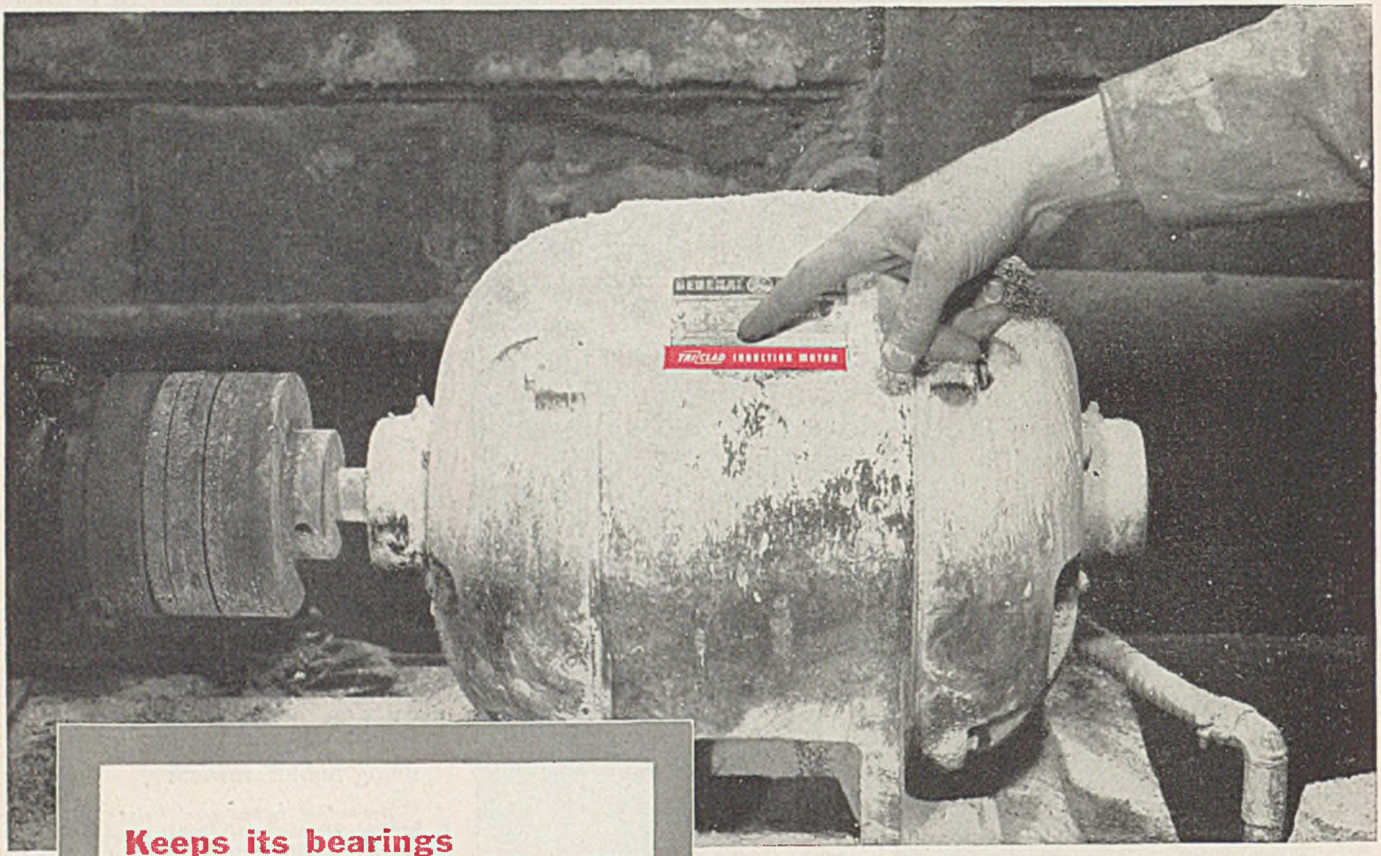
SHEETS · STRIP · PLATES · BARS · BILLETS · PIPE · TUBES · WIRE · SPECIAL SECTIONS

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
7-566

The various grades of U·S·S Stainless Steel available for lining use and a complete description of the most approved methods of field lining are fully detailed in our booklet "U·S·S Stainless and Heat Resisting Steels for the Petroleum Industry." We will be glad to send you a copy and believe you will find it helpful.

UNITED STATES STEEL

ON 1,220,000



Keeps its bearings *in a "dust bowl"*

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

and now—THE TOUGHEST TRI/CLAD YET

REG. U.S. PAT. OFF.

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

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

MOTORS

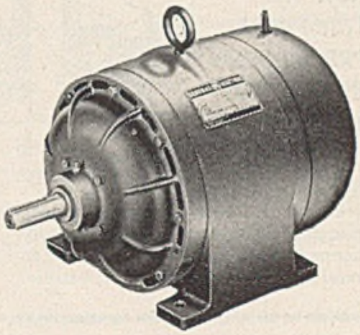
TRI/CLAD

THE SYMBOL OF

EXTRA PROTECTION

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

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



EXTRA PROTECTION... AGAINST PHYSICAL DAMAGE!

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

EXTRA PROTECTION... AGAINST ELECTRICAL BREAKDOWN!

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

EXTRA PROTECTION... AGAINST OPERATING WEAR AND TEAR!

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

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

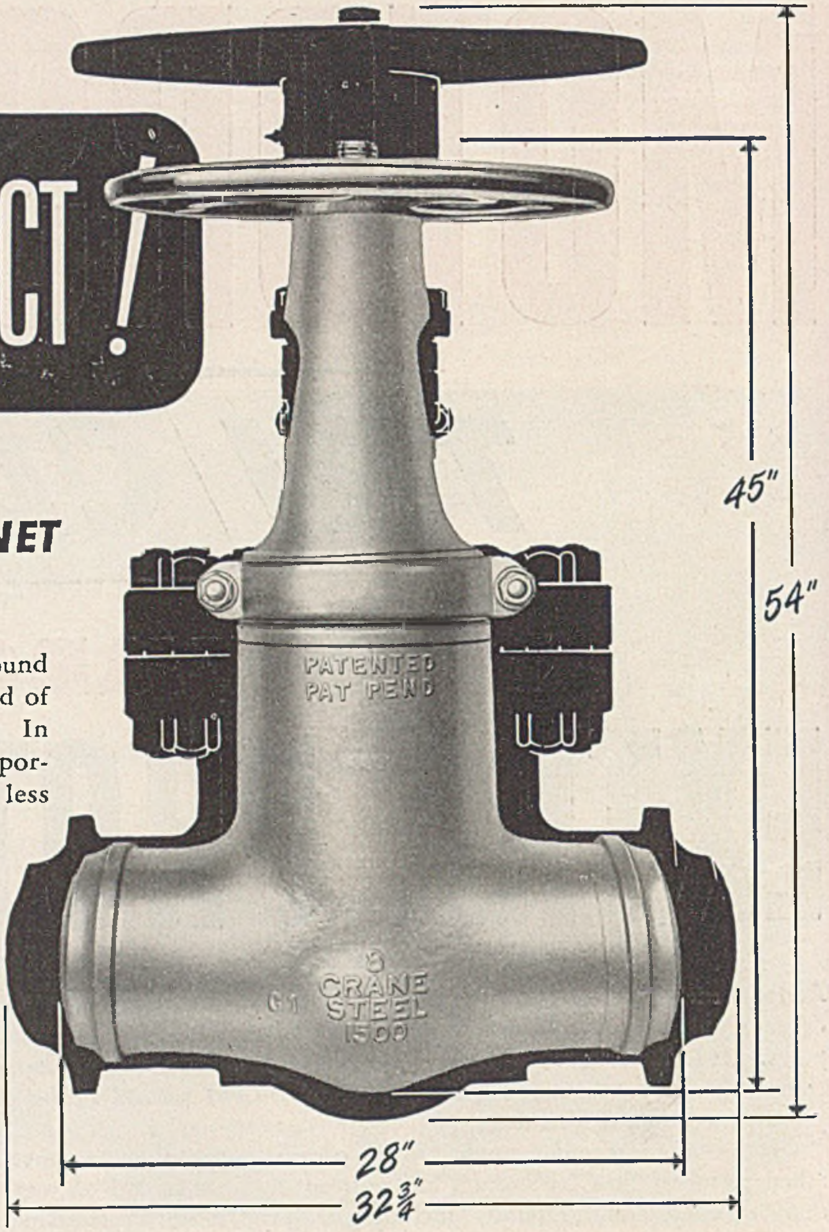
GENERAL ELECTRIC

750—285

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

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

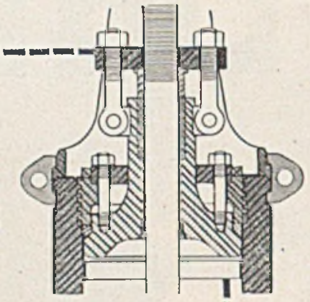
MORE COMPACT!



New CRANE PRESSURE-SEAL BONNET VALVES

Note comparative dimensions of 1500-Pound Crane Pressure-Seal Steel Gate Valve and of conventional design. Both are 8-inch. In every size, these new valves give you important space-saving advantages. Require less head-room to operate.

HOW THE LEAK-PROOF PRESSURE-SEAL BONNET JOINT OPERATES



Bonnet joint is inside the valve . . . sealed with wedge-shaped seal ring. Fluid pressure in valve automatically keeps bonnet joint tight. No bolts to retain pressure. Leakage is impossible.

NEW PERFECTION IN VALVE DESIGN FOR HIGH PRESSURES AND HIGH TEMPERATURES

New streamlined, simplified construction . . . inside and out . . . saves 40 to 60% weight over conventional valves. Inspection is easier . . . insulation is simplified. New disc and seating arrangements assure highly improved operating efficiency. As developed by Crane, the Pressure-Seal principle brings a whole new era in valve engineering and valve performance.

The Crane Pressure-Seal line includes gate, globe, angle, and automatic stop-check patterns with welding ends. Complete information regarding performance and adaptability to your requirements supplied on request. No obligation . . . call your Crane Branch.

1500-Pound Crane Pressure-Seal Bonnet Globe Valve.

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

EVERYTHING FROM . . .

VALVES • FITTINGS
PIPE • PLUMBING
AND HEATING

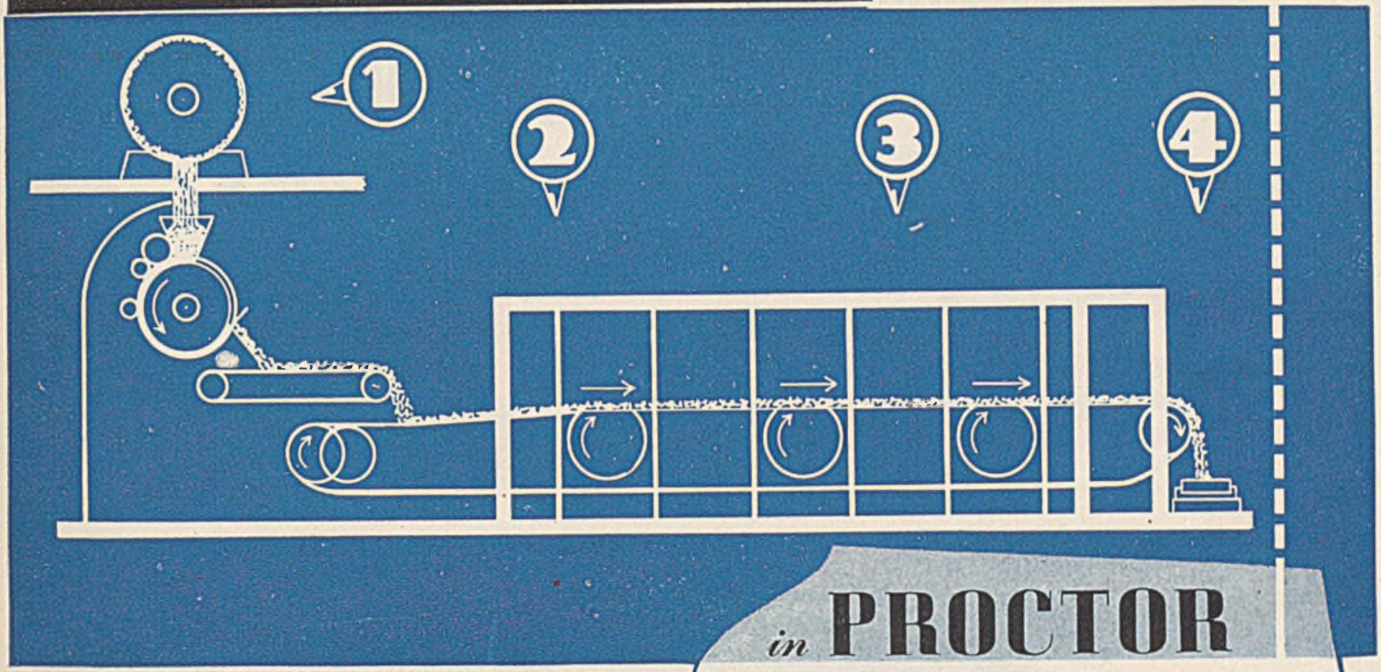
CRANE

FOR EVERY PIPING SYSTEM

LEAD ARSENATE

REDUCED TO 0.5% (B.D.W.B.*)
MOISTURE CONTENT
AT RATE OF
1,000 POUNDS PER HOUR . . .

*Bone Dry Weight Basis



in PROCTOR

Continuous Conveyor System

It is entirely possible to thoroughly dry lead arsenate to a uniform moisture content, and at the same time achieve tonnage production, by means of a Proctor continuous conveyor drying system with a preforming feed. Then, too, this continuous system minimizes dust in the atmosphere of the plant—a major consideration in the handling of this product.

Here is how one typical Proctor continuous system is employed for this purpose: ① The wet lead arsenate is first dewatered by means of a continuous centrifuge. ② From the centrifuge, the material is mechanically distributed into the hopper of the fin drum feed of the dryer. The paste-like substance is pressed into grooves of the internally heated, revolving drum of this feeding device. By means of this feed, the material will be sufficiently "pre-dried" so that it can be discharged to the conveyor of the dryer in the form of small "sticks" about ¼'' square in thickness. ③ Entering the dryer with a moisture content of 58.5% (B.D.W.B.), these "sticks" of lead arsenate lie in a bed on the perforated plate continuous conveyor of the dryer. The reduction of the material to the form of these small sticks makes it possible for heated air, at a temperature of 250° F., to circulate *through* the bed of material—thus promoting rapid diffusion and subsequent speedy, thorough and uniform drying. ④ After 71 minutes of drying time, the "sticks" of lead arsenate are discharged with a moisture content of 0.5% (B.D.W.B.)—uniformly dried at the rate of 1,000 pounds (C.D.W.†) per hour.

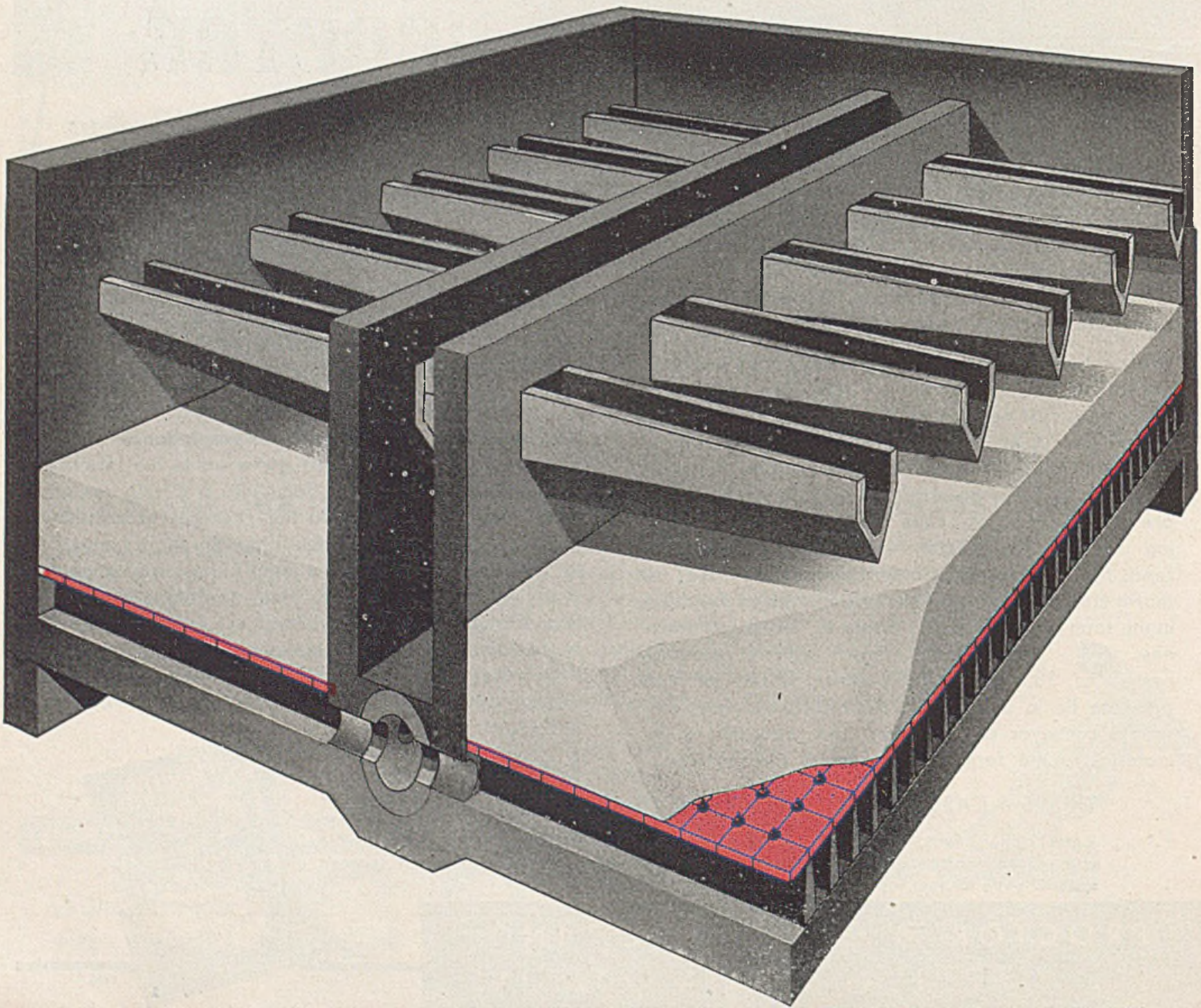
This installation represents one more instance where Proctor engineers took facts gathered in the laboratory and translated those facts into a drying system that is meeting a need in the chemical process industries. Every Proctor system is literally "tailor-made" to meet individual product and plant requirements. If drying is a part of your plant operation, and you feel there is room for improvement in your present method—consult Proctor engineers without obligation. If you contemplate expansion, it will be to your distinct advantage to settle your plans for drying equipment early.

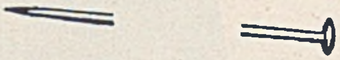
†Commercial Dry Weight

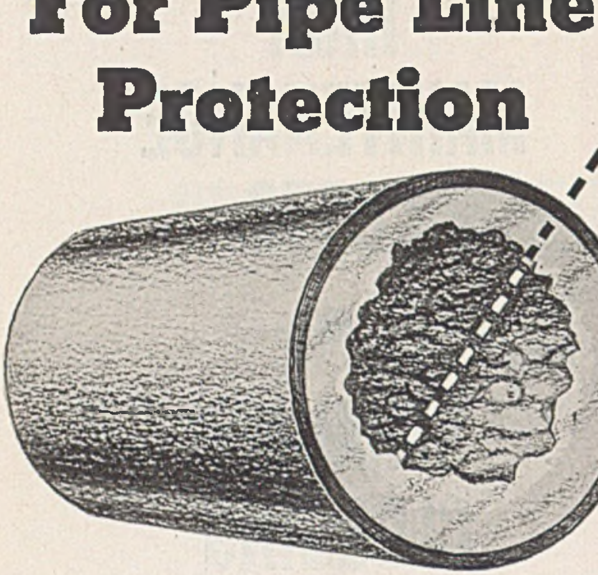
THIS IS A CASE HISTORY TAKEN FROM THIS NEW PROCTOR BOOKLET

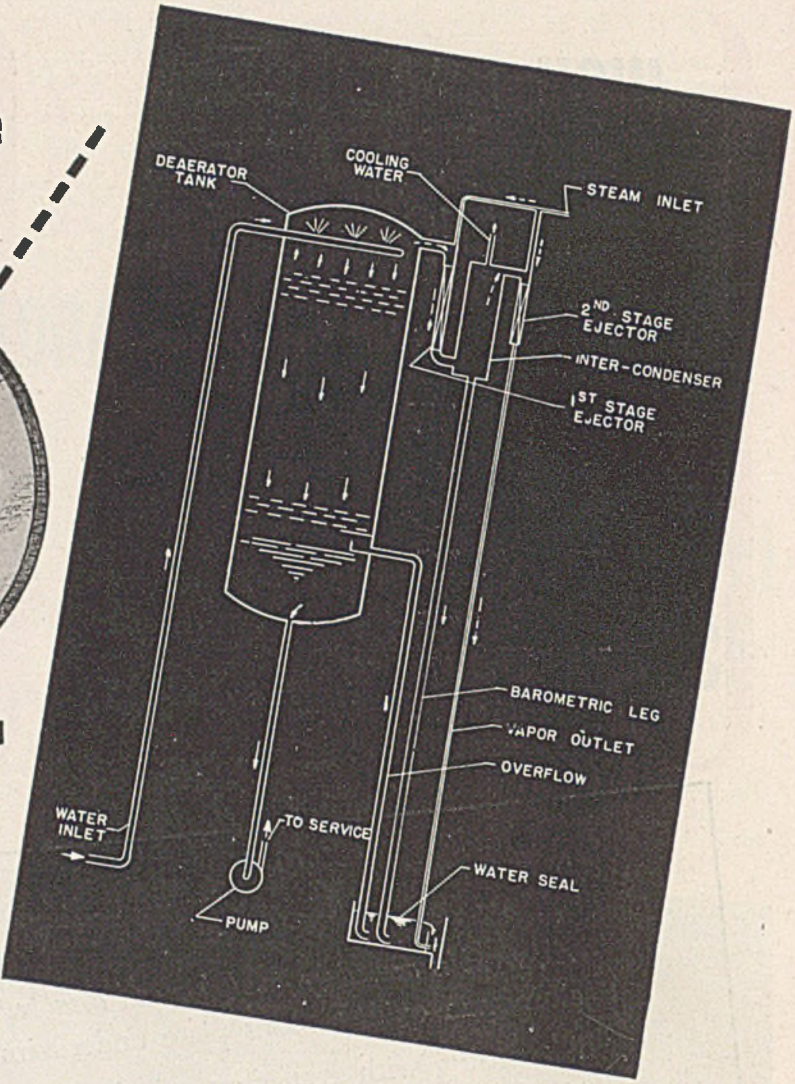
A new 12-page booklet on "Proctor Continuous Drying for the Chemical Process Industries" is available upon request. It contains many case studies showing the application for Proctor individually designed systems. Write for your copy of this informative booklet today.

PROCTOR & SCHWARTZ, INC.
PHILADELPHIA 20, PA.








DEAERATOR TANK
COOLING WATER
STEAM INLET
2ND STAGE EJECTOR
INTER-CONDENSER
1ST STAGE EJECTOR
BAROMETRIC LEG
VAPOR OUTLET
OVERFLOW
WATER INLET
TO SERVICE
WATER SEAL
PUMP

Announcing...

The New Multi-Purpose SIMPSON *Intensive* MIXER

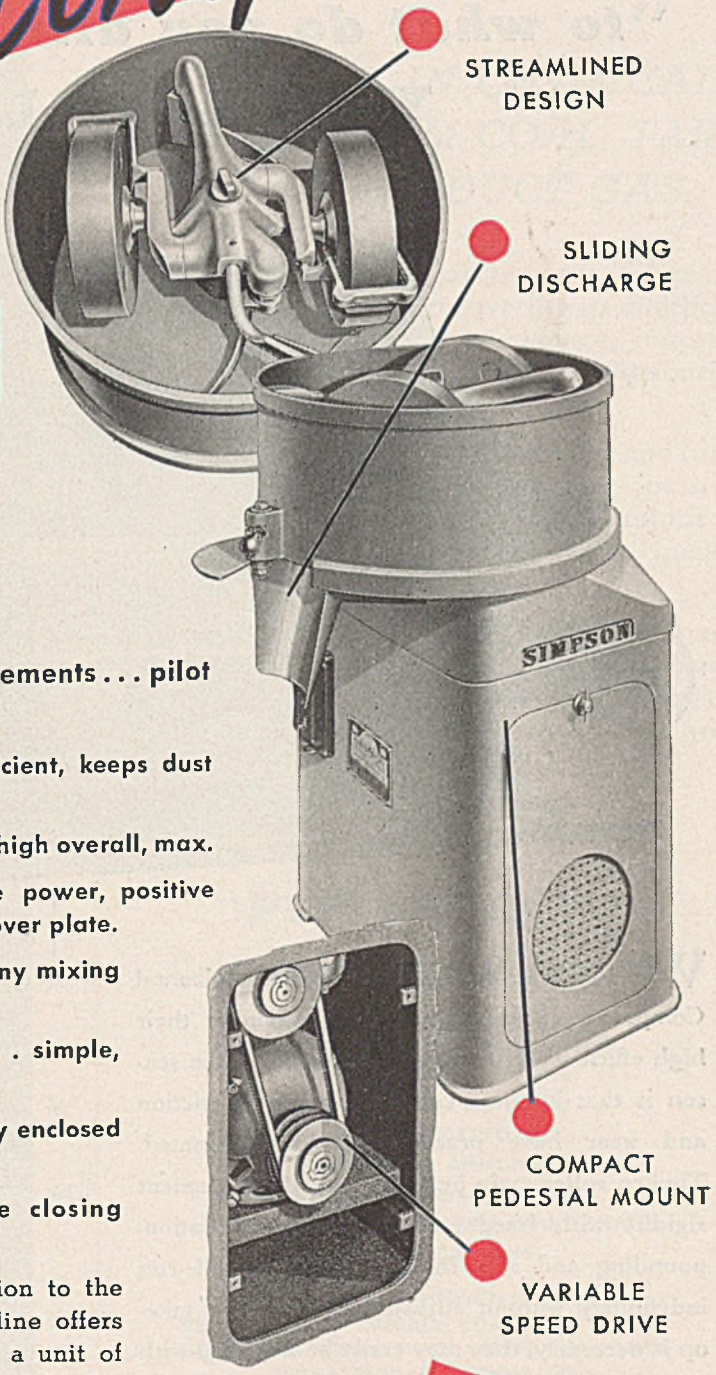
NUMBER 00

Ideal for smaller production requirements . . . pilot plants . . . and for laboratory work.

- **STREAMLINED DESIGN** . . . more efficient, keeps dust out of mix, virtually self-cleaning.
- **LESS FLOOR SPACE** . . . 28" wide x 41" high overall, max.
- **VARIABLE SPEED DRIVE** . . . ample power, positive drive, easily accessible by removing cover plate.
- **VARIABLE MULLER WEIGHTS** . . . for any mixing requirement.
- **ONE-POINT PLOW ADJUSTMENT** . . . simple, sturdy construction.
- **SAFER—EASIER OPERATION** . . . totally enclosed drive, push-button control.
- **SLIDING DISCHARGE** . . . positive closing mechanism.

Yes, the new Number 00, latest addition to the famous SIMPSON Intensive MIXER line offers advantages never before available in a unit of this type. Like all other SIMPSON models, the "Double-O" will do a *better* mixing job *faster,* at *lower cost* . . . on any type of dry, semi-dry or plastic material.

Write for full particulars, or better yet, let a National Engineer analyze your specific mixing requirements . . . no obligation, of course.



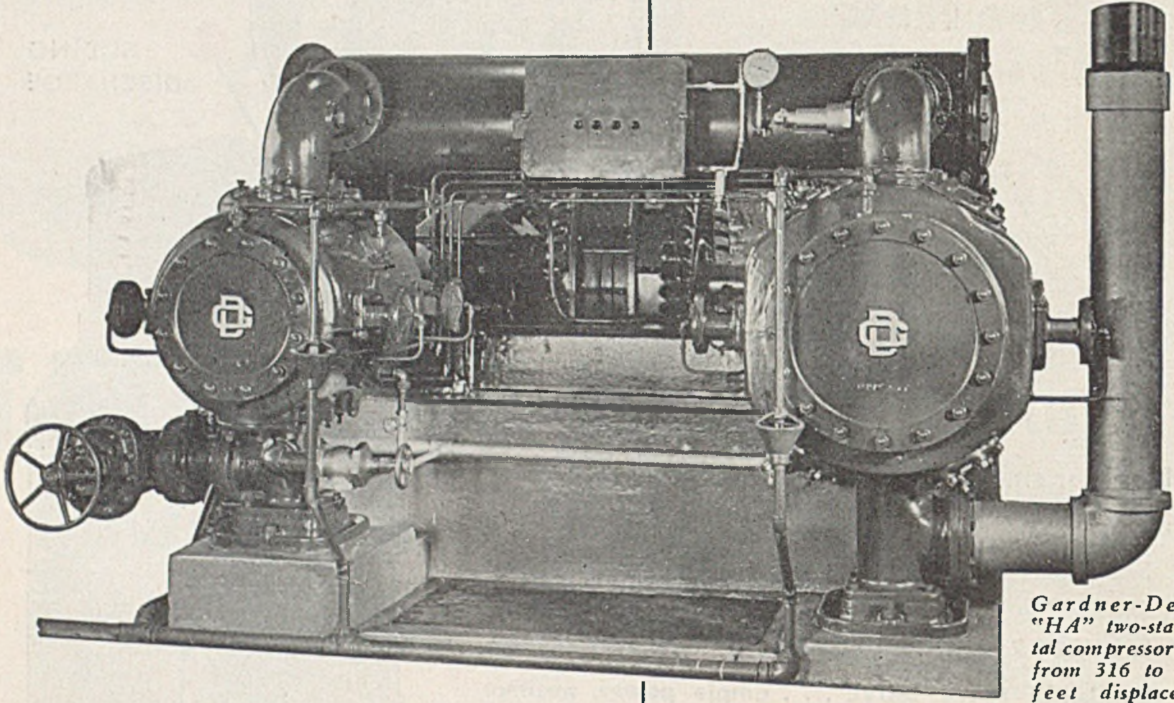
SIMPSON Intensive MIXERS are built in 10 sizes, from 1/5 to 50 cu. ft. capacity . . . available with oil, steam or water jackets, for vacuum mixing, and may be had in corrosion-resistant materials.

SIMPSON *Intensive Mixer*

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

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

"to what do you attribute YOUR LONG LIFE?"



Gardner-Denver Class "HA" two-stage horizontal compressor. Capacities from 316 to 2012 cubic feet displacement per minute.

WHY do Gardner-Denver "HA" Horizontal Compressors last so long — maintaining their high efficiency after years of service? One reason is that in these compressors, shaft friction and wear have practically been eliminated. Timken roller main bearings provide permanent rigidity with freedom from bearing vibration, pounding and side thrust. Bearings will run indefinitely without adjustment, but when take-up is necessary, they may easily be adjusted with assurance that the main shaft will be in line. Here are other reasons why you'll want a Gardner-Denver "HA" in your plant—

✳ *Duo-Plate cushioned valves for high delivery capacity — high compression efficiency and lowest power consumption.*

✳ *Air cylinders designed for highest volumetric efficiency and lowest horsepower requirements.*

✳ *Large water jacket areas for cooler running . . . lower discharge temperatures and lubricating economy.*

✳ *Heavy-duty massive main frames, heavily ribbed and reinforced for maximum strength and rigidity.*

✳ *Five-step capacity control regulates air output to suit your air needs.*

For complete information, write
Gardner-Denver Company, Quincy, Illinois.

USE COMPRESSED AIR FOR SAFETY CONVENIENCE FLEXIBILITY

GARDNER-DENVER
SINCE 1859

"Pittsburgh"

SPECIALISTS IN CHEMICALS DERIVED FROM COAL, TAR AND BY-PRODUCT GAS

Unlocking the chemical treasure house of coal, and extracting and recovering its multifold components for the uses of science, industry and commerce, is the business of Pittsburgh Coke & Chemical Company.

Here modern plant facilities, earnest and foresighted research, favorable shipping location and advantageous sources of supply combine to assure you of dependable, uniform, quality chemicals.

Expanding volume and range of products and increasing capacities make *Pittsburgh* better able to serve you than ever. Our technicians will welcome an opportunity to discuss your needs.

"PITTSBURGH"

Coke and Chemical Products

AROMATIC HYDROCARBONS:
BENZOL, TOLUOL, XYLOL, NAPHTHALENE
TAR ACIDS: PHENOL, CRESOLS
SULPHURIC ACID: ALL GRADES
TAR, PITCH and CREOSOTE
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SODIUM CYANIDE · SODIUM THIOCYANATE
ACTIVATED CARBONS

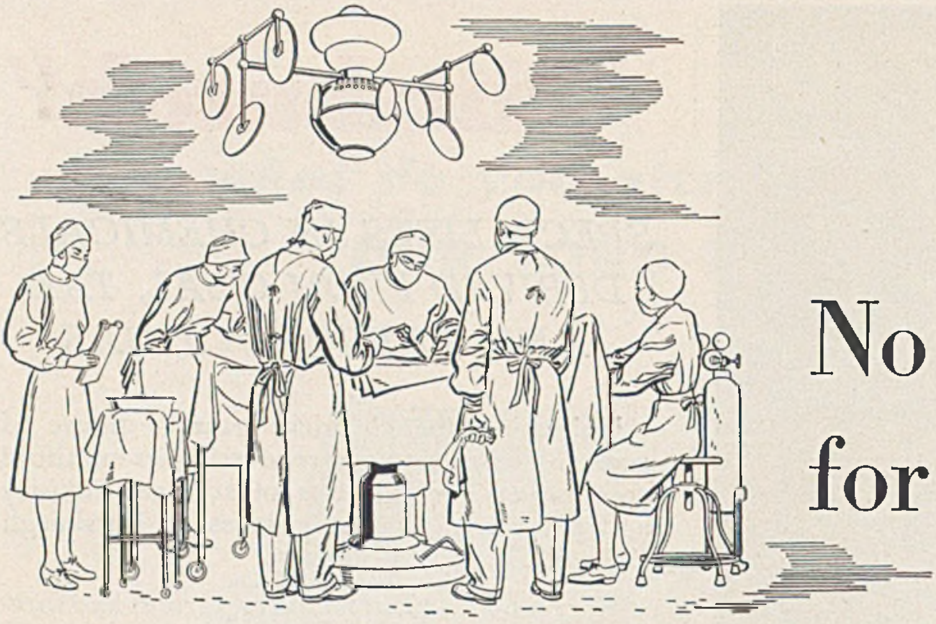
OTHER PRODUCTS:
NEVILLE COKE—EMERALD COAL—PIG IRON—GREEN BAG CEMENTS—CONCRETE PIPE—LIMESTONE PRODUCTS—IRON ORE

INQUIRIES INVITED

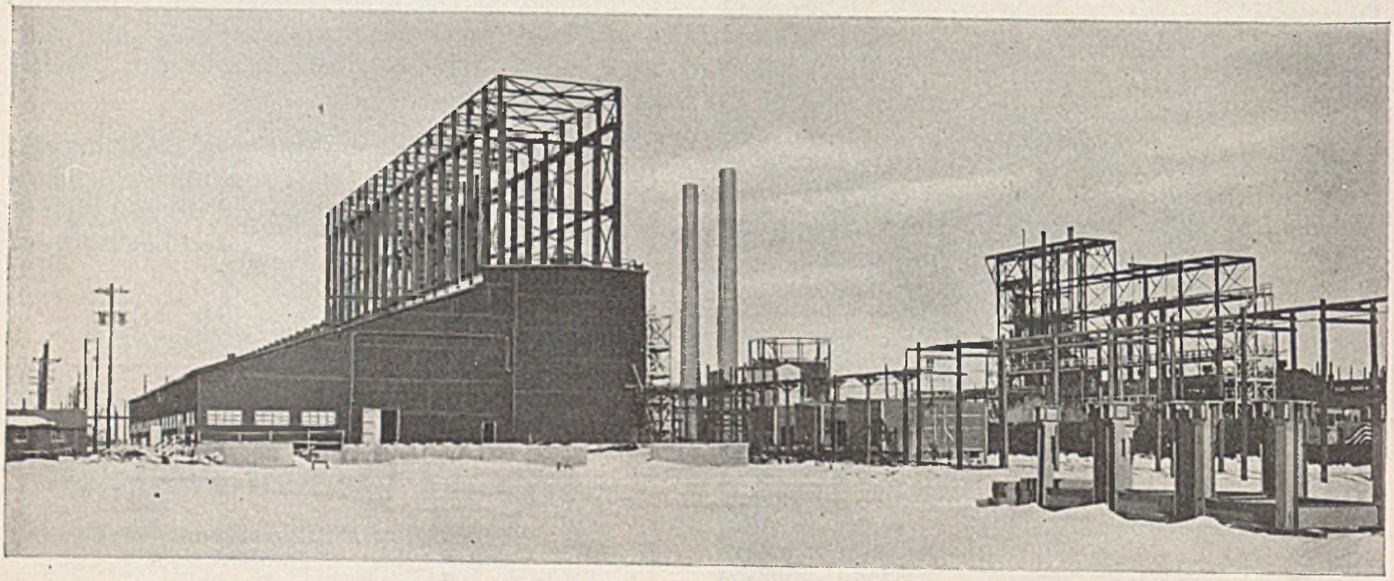
CHEMICAL SALES DIVISION

Pittsburgh Coke & Chemical Company

Grant Building · Pittsburgh 19, Pennsylvania



No job for a novice

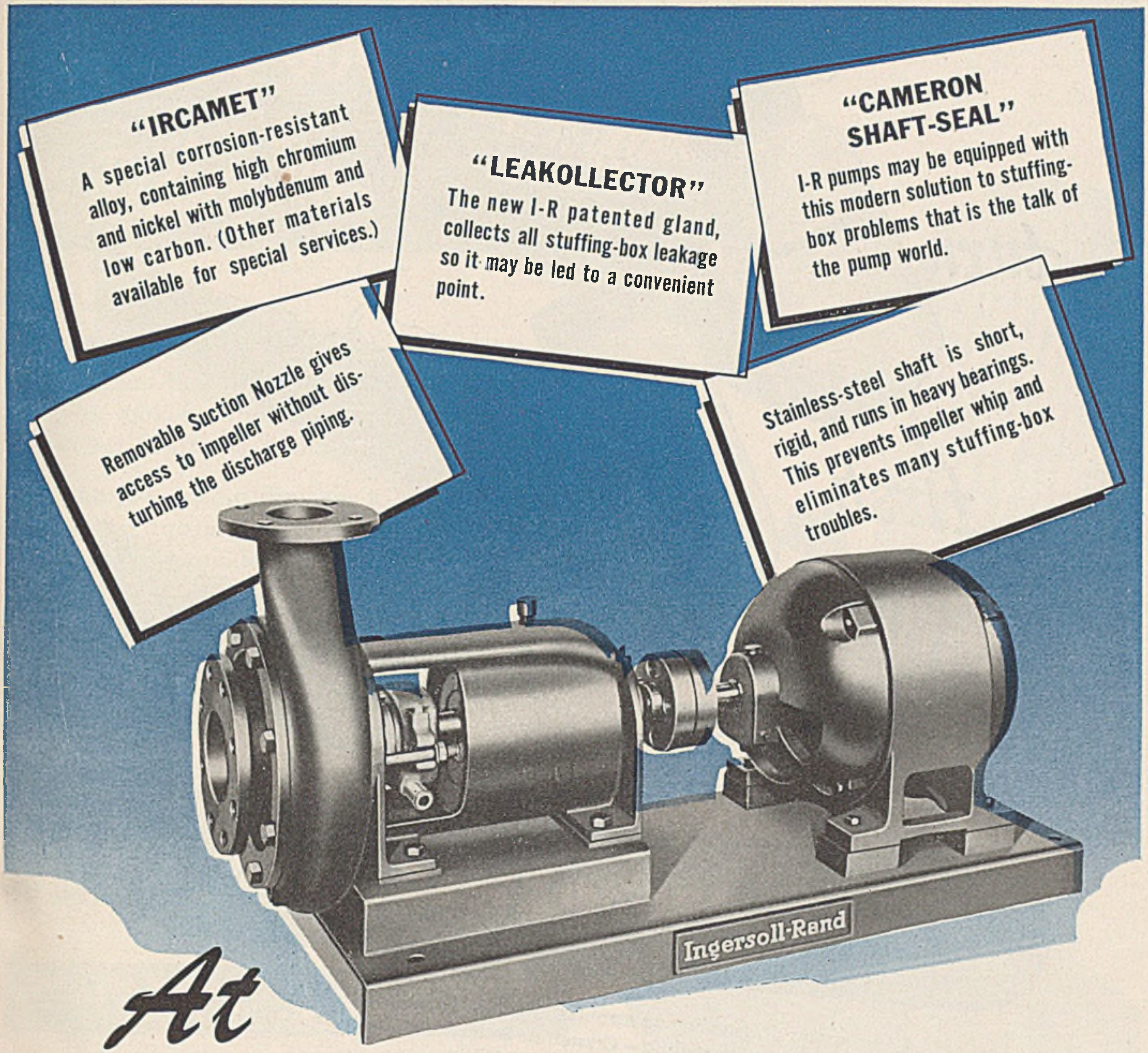


When selecting an organization to design and build a heavy chemical plant, by all means exercise the same discretion as you would in choosing a surgeon . . . trust your dollars as you would your life to *experience* and *skill.* › › Chemico is fully qualified on these counts for Chemico has built over 600 sulfuric acid, synthetic ammonia, synthetic methanol and other heavy chemical plants during the last thirty-three years. Because of this experience Chemico is able to fully guarantee the performance and efficiency of its installations.

CHEMICAL CONSTRUCTION CORPORATION
EMPIRE STATE BLDG., 350 FIFTH AVE., NEW YORK 1, N. Y.
European Technical Representative: Cyanamid Products, Ltd.,
Brettenham House, Lancaster Place, London W. C. 2, England
Cables: Chemiconst, New York

"Chemico plants are profitable investments"

CC-144


Ingersoll-Rand

for BULK PENICILLIN

- In constant demand among manufacturers of pharmaceuticals today are three forms of bulk penicillin – Crystalline Sodium Penicillin "G", Crystalline Potassium Penicillin "G", and Calcium Penicillin.

Chas. Pfizer & Co., Inc. is the first source to which many such manufacturers turn when they need bulk penicillin. Here's one reason: at Pfizer, length of experience in making fine chemicals is combined with what might be called *depth of experience* – gained as the world's largest producer of penicillin.

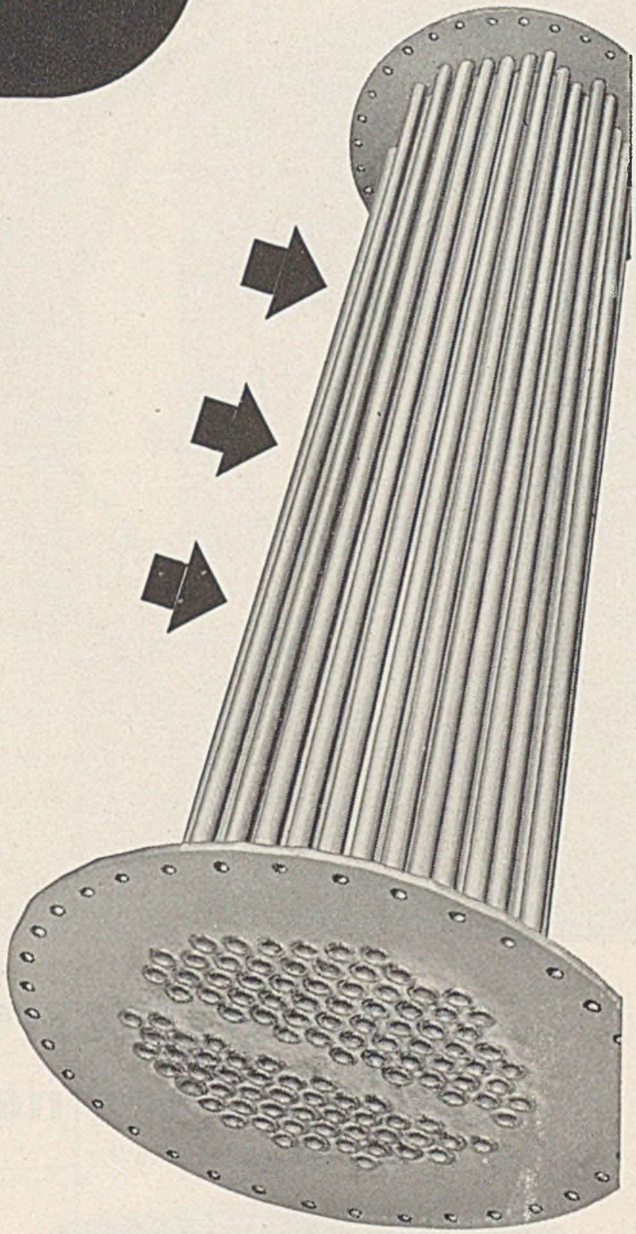
The way in which Pfizer Quality is maintained calls for every necessary scientific precaution carried out by a trained staff of bacteriologists, biologists and other specially trained personnel. As a result, a sterile, non-toxic, pyrogen-free, high potency product is provided – every batch is subjected to a series of bioassays to determine its potency; additional chemical laboratory assays for types of penicillin; tests to determine its solubility, pH, heat stability and other performance characteristics. Chas. Pfizer & Co., Inc., 81 Maiden Lane, New York 7, N. Y.

PFIZER *Manufacturing Chemists Since 1849*

PFIZER QUALITY

5179

HERE'S A GOOD WAY *to Reduce Tube Replacement...*



To guard against the wasted time and labor that tube replacement costs, it pays to look for *more than analysis* when you select Stainless Tubing.

For example, special finishes to provide *extra protection* against corrosion or contamination can often be provided in Carpenter Stainless Tubing. *Uniform wall thickness* is another Carpenter Stainless Tubing advantage that will help you specify lighter gauges . . . and keep equipment on the job with fewer shutdowns for replacement and repair.

To make each of your Stainless Tubing dollars work harder and longer, drop us a line. Carpenter's 20-year experience with Stainless Pipe and Tubing problems is yours for the asking.

OVER 100 PAGES OF USEFUL INFORMATION ABOUT STAINLESS TUBING

To help you make full use of the properties of Stainless Tubing, fabricate it and improve processing, the new Carpenter Stainless Tubing Data Book is available to Engineering and Management executives. A note on your company letterhead will bring a copy to you.

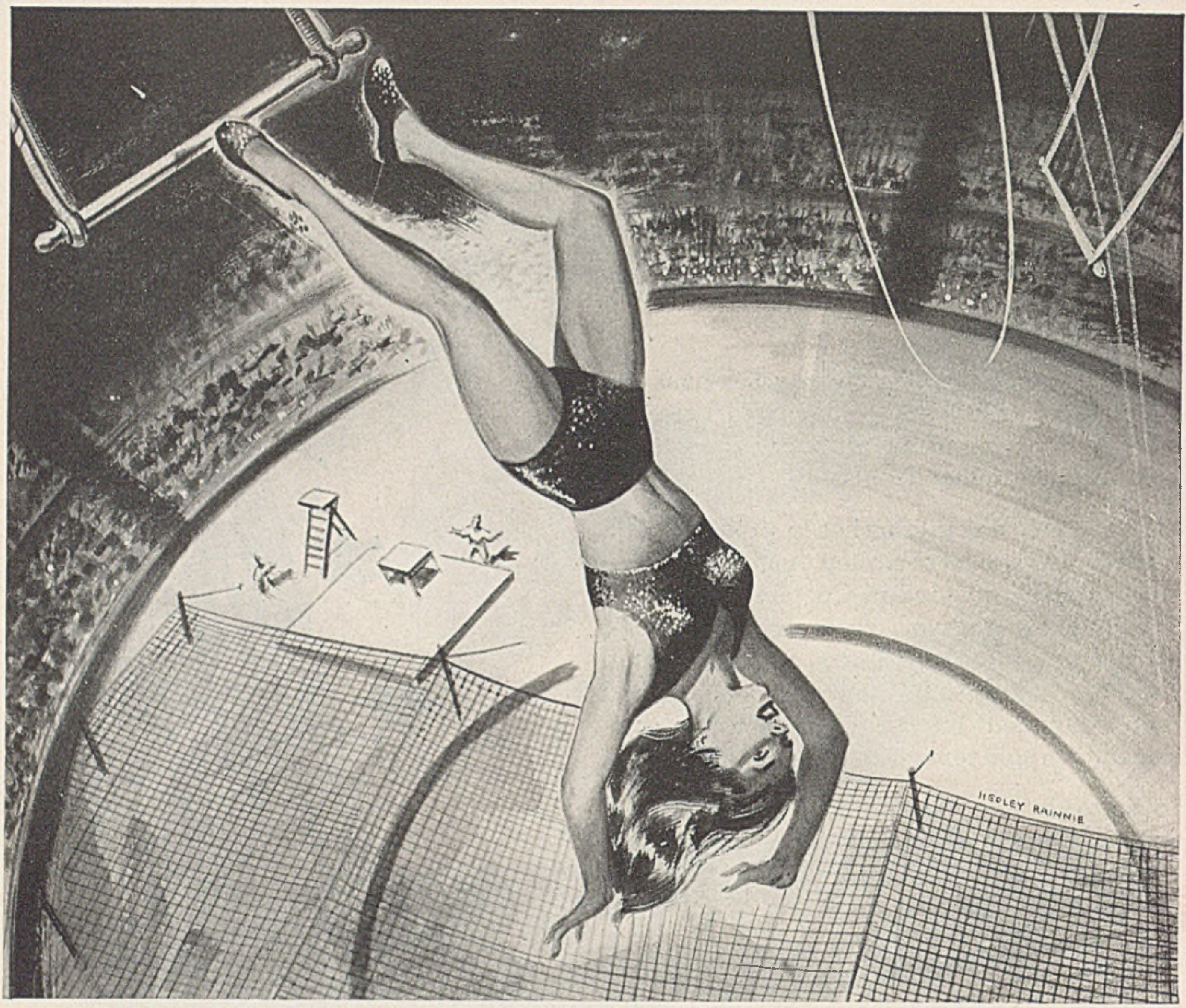
THE CARPENTER STEEL COMPANY

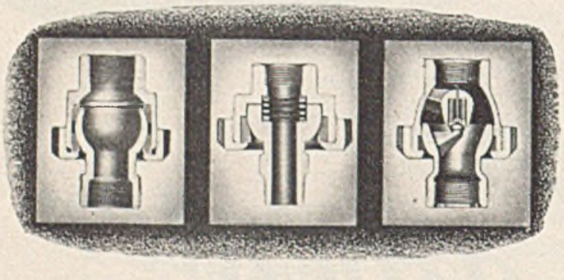
Alloy Tube Division • 111 Springfield Road • Union, N.J.

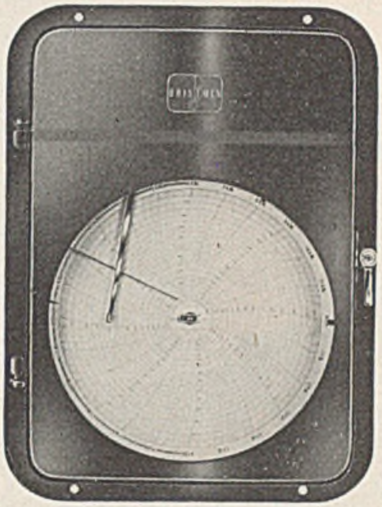
Carpenter

STAINLESS TUBING

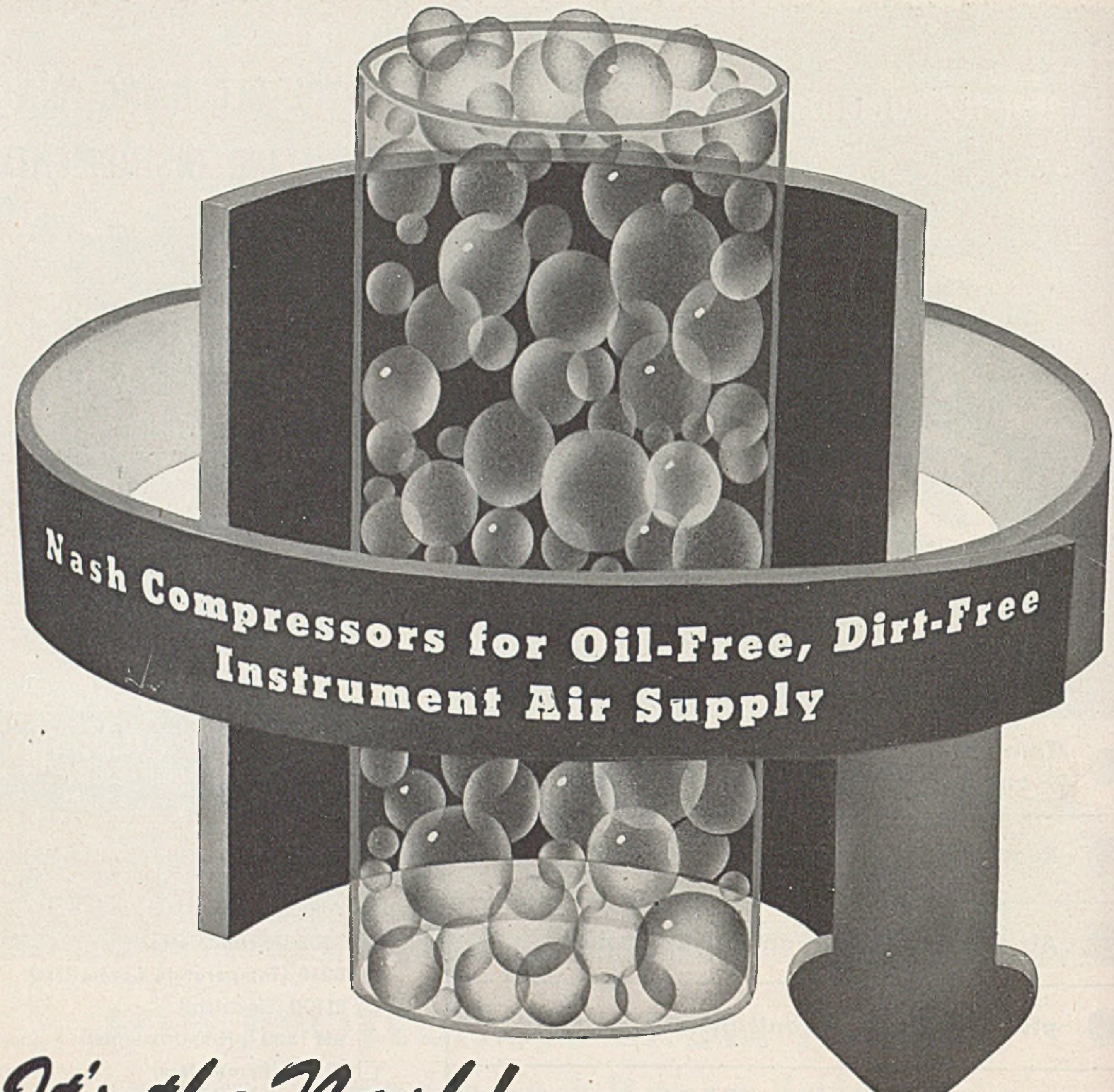
"MORE THAN CORROSION RESISTANCE"


HEDLEY RAINNIE






BRISTOL STOCK INSTRUMENTS
IMMEDIATE DELIVERY


Nash Compressors for Oil-Free, Dirt-Free
Instrument Air Supply

WHEN IS A TANK CAR NOT A TANK CAR?

The answer: *never!* A tank car is *always* a tank car. But even if all tank cars look alike—as all cats look grey in the dark—there are important differences under the tank car's workaday coat of paint.

In the GATX fleet of 37,000 specialized tank cars, there are 207 types. Designed not just for the fun of it—but for the practical purpose of supplying you, the shipper, with the right car for your particular commodity.

Routing cars from one season to another . . . from one commodity to another . . . from one part of the country to another is part of the job General American does for its customers—the railroads and the shippers. A basic service of those hard-working tank cars with the GATX reporting mark.

GENERAL AMERICAN TRANSPORTATION CORPORATION
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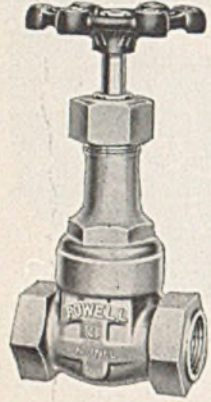
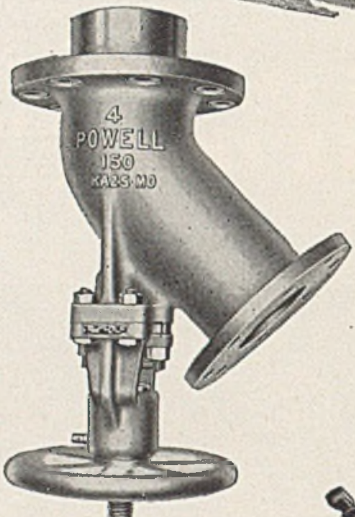
GATX
GENERAL
AMERICAN

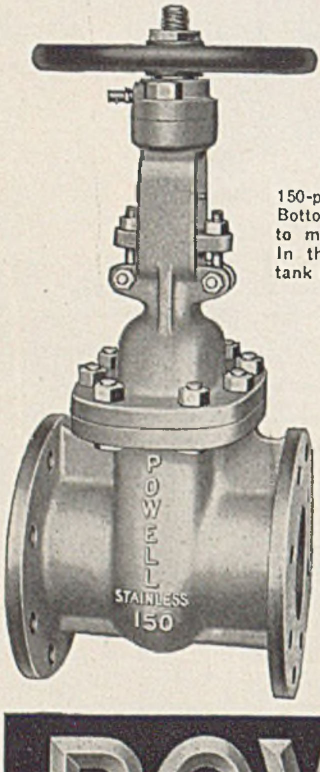
They may look alike, but...
one is a winner..another an "also-ran"



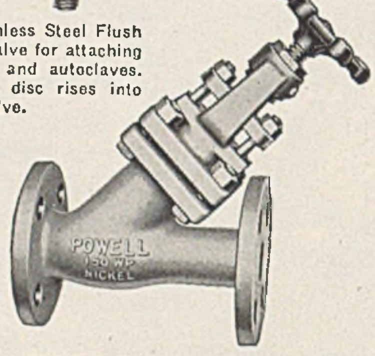
Monel Metal* Gate Valve. 200 pounds W. P. Has screwed ends, screwed-in bonnet and inside screw rising stem.



150-pound Stainless Steel Flush Bottom Tank Valve for attaching to metal tanks and autoclaves. In this design, disc rises into tank to open valve.



New Standard 150-pound Stainless Steel Gate Valve, with outside screw rising stem, bolted flanged yoke bonnet and taper wedge solid disc.



Pure Nickel O. S. & Y. "Y" Valve. 150 pounds W. P. Has flanged ends and bolted flanged bonnet.

Call it "heart", "staying power", or what you will, some thoroughbreds have what it takes to win.

Now let's consider valves!

Compare the outward appearance of any Powell valve with that of other valves of the same type and size. You'll probably see very little difference. *It's the things you don't see that give Powell valves the "staying power" that makes them winners.*

There's nothing mysterious about these things. They're merely the result of the continual progress in design, knowledge of materials, and quality of workmanship that comes from more than a century of making valves—and valves only—for American industry.

For the last 25 years, to meet the ever-growing demands of the Chemical and Process Industries, Powell has been building a complete line of Corrosion-Resistant Valves in many special designs and the widest range of pure metals and alloys ever used in making valves.

The Wm. Powell Company
Cincinnati 22, Ohio
DISTRIBUTORS AND STOCKS IN ALL PRINCIPAL CITIES

*A registered trade name of the International Nickel Company, Inc.

POWELL VALVES

REPUBLIC *Enduro* STAINLESS STEEL

These 500-gallon syrup aging tanks are but one of countless applications for stainless steel in the food, pharmaceutical, textile and other branches of the chemical processing industries.

Improves Employee Relations

Easy to look at . . . easy to work with . . . Republic ENDURO Stainless Steel equipment pays immediate dividends in improved employee relations.

Lustrous ENDURO offers a constant invitation to complete cleanliness, no matter in what branch of the chemical processing industries it is installed. It is so easy to clean—with a minimum of time and effort—that everyone takes pride in keeping it spotless. Thus, ENDURO helps create a bright, cheerful working atmosphere . . . makes work easier . . . gives employees new incentive.

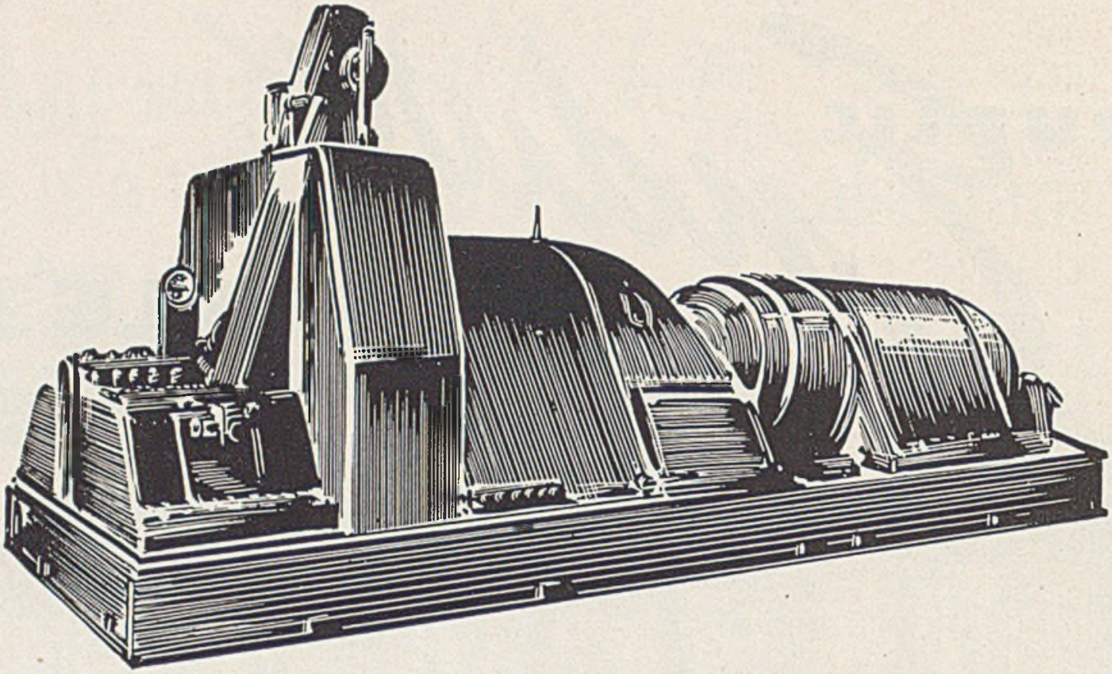
And, ENDURO'S sanitary surface lasts indefinitely. It is solid stainless steel throughout . . . never needs refinishing. It resists rust and corrosion . . . cuts maintenance cost. It resists scaling at high temperatures—has high creep strength. Smooth and pore-free, it never carries over contaminating materials from one batch to another.

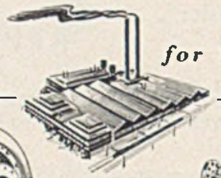
Talk with your equipment manufacturer NOW about putting Republic ENDURO Stainless Steel to work for you, helping to promote better employee relations. For additional information, write to:

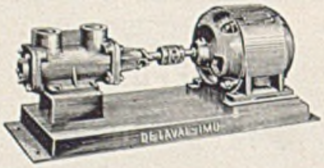
REPUBLIC STEEL CORPORATION
Alloy Steel Division • Massillon, Ohio
GENERAL OFFICES • CLEVELAND 1, OHIO
Export Department: Chrysler Building, New York 17, New York

Republic REPUBLIC STEEL REG. U. S. PAT. OFF.
ENDURO STAINLESS STEEL
REG. U. S. PAT. OFF.

Other Republic Products include Carbon and Alloy Steels—Pipe, Sheets, Bolts and Nuts, Tin Plate, Tubing, Stevens Barrels and Drums







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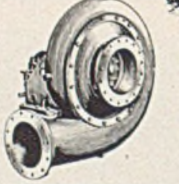
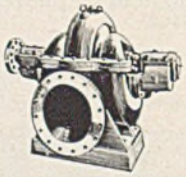
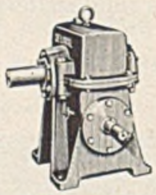






SW

STRUTHERS WELLS

Converters

for Catalytic Processes

STRUTHERS WELLS catalytic converters are used by many leading companies in the chemical industry.

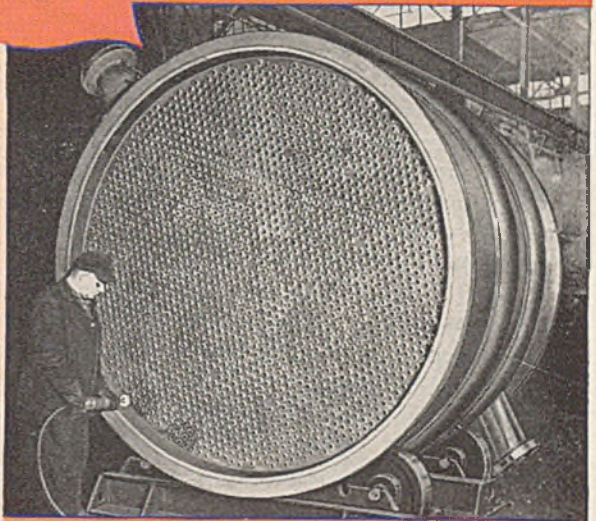
The conversion is accomplished by passing vapors at elevated temperatures through catalyst filled tubes. The catalyst is held in the tubes by screens and supports, which are removable to allow replacement of the catalyst.

The converters are usually heated to the temperatures required by the use of high temperature salt, Dowtherm, flue gases, or electric heating. Close control is required, as the reaction is usually adversely affected by a few degrees variation from the optimum temperature. Thermometer wells are provided for measuring tube temperatures.

Tubes are usually welded to the tube sheets, and expansion joints are provided to take care of differential expansion between shell and tubes.

Converters have been constructed by Struthers Wells for many difficult services, and in sizes as large as can be shipped. Some of the materials of construction used include chrome iron, chrome nickel, nickel alloys and Hastelloy. Many repeat orders testify to the soundness of design and construction.

Electrically heated converter, 60" diameter.



View of phthalic anhydride converter, showing tubes welded to tube sheets.

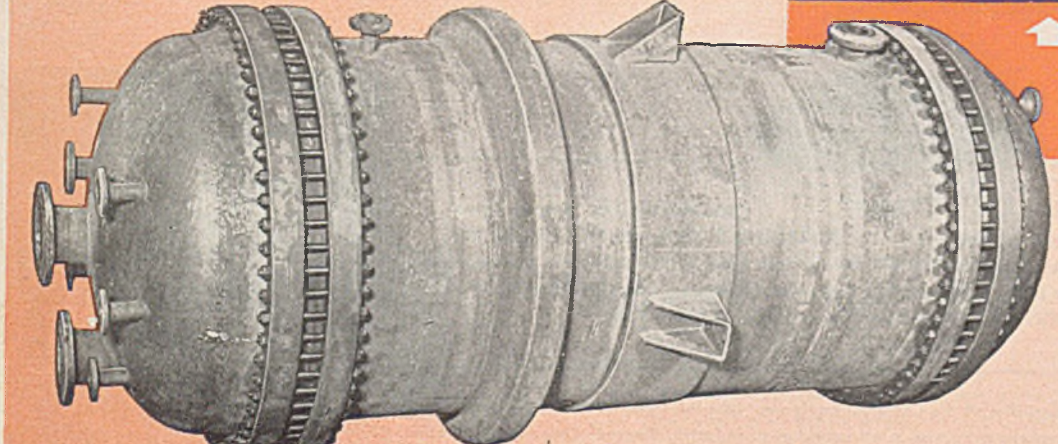
STRUTHERS WELLS CORPORATION

PROCESS EQUIPMENT DIVISION

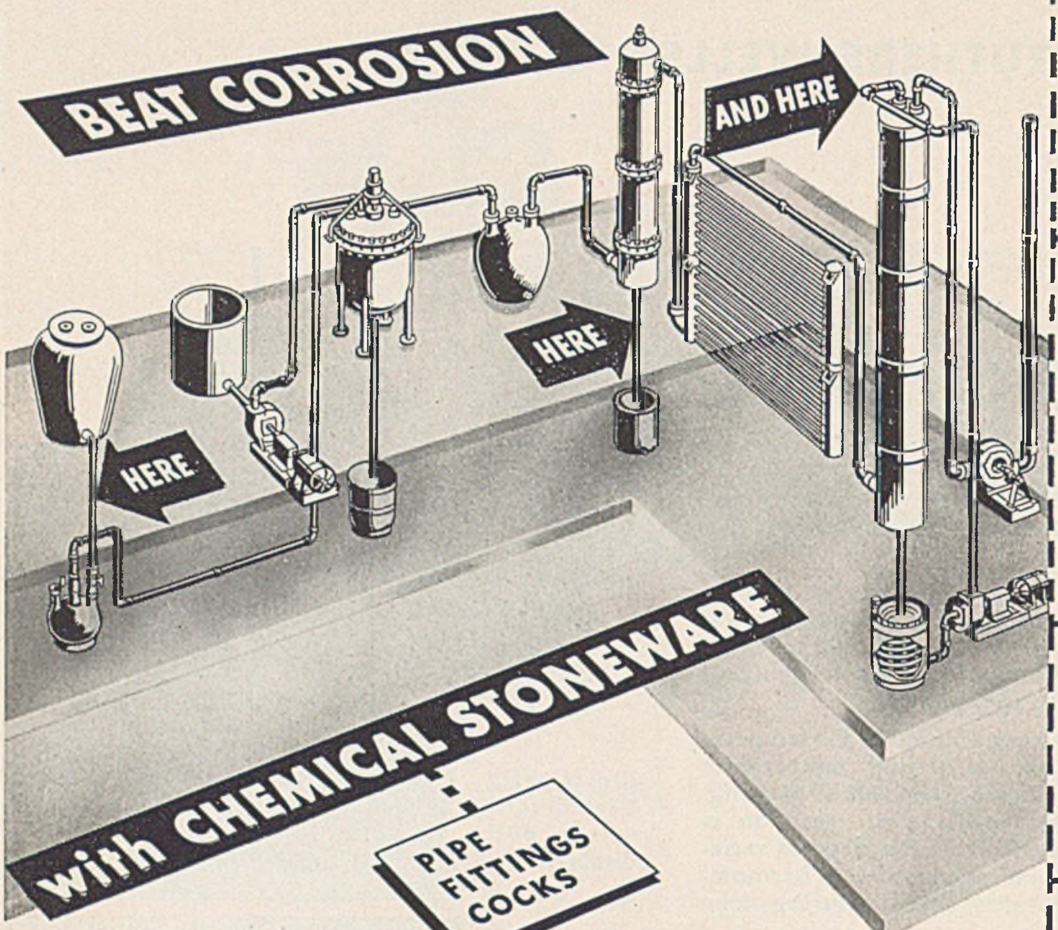
WARREN, PA.

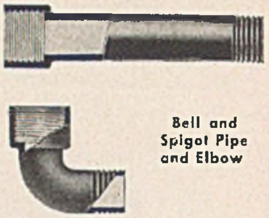
Plants at Titusville and Warren, Pa.

Offices in Principal Cities

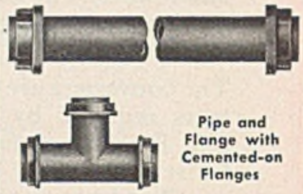


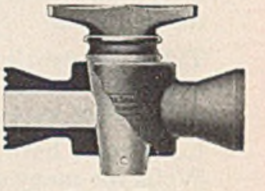
A 60" converter with all internal parts constructed of Hastelloy; the heads are Hastelloy lined and tube sheets faced with Hastelloy.




Bell and Spigot Pipe and Elbow


Conical Flange Pipe and Tee


Pipe and Flange with Cemented-on Flanges


Conical Flange Straightway Cock

In a chemical plant A PIPE LINE IS A LIFE LINE. Modern processes with their stringent requirements of corrosion resistance, thermal shock, and mechanical strength, depend upon high quality piping for low maintenance cost and reliable performance.

General Ceramics chemicals stoneware and chemical porcelain pipe and fittings are manufactured of bodies compounded to give the utmost in corrosion resistance and physical strength. They are designed by chemical engineers with operating experience to provide economical and long-lasting piping installations.

General Ceramics standard line includes Bell & Spigot pipe and fittings, as described in Bulletin 151, for low pressure operation with both liquids and gases. For pressures up to 75 p.s.i.g., flanged pipe is recommended and either the conical flange type, as shown in Bulletin 165, or cemented-on flange pipe, as shown in SD-3 and B-2776, is offered. For special applications, armored stoneware pipe and special fittings can be fabricated to order. Plug cocks for all of these styles of pipe and fittings are shown in Bulletin 131.

To make your PIPE LINE *a reliable* LIFE LINE, send a sketch of your piping layout to our Keasbey office or any of our branch offices for recommendations and a proposal.

GENERAL CERAMICS
AND
STEATITE CORPORATION
CHEMICAL EQUIPMENT

BUFFALO: 610 Jackson Bldg. **CHICAGO:** 20 N. Wacker Drive
LOS ANGELES: 415 So. Central Ave. **PORTLAND 5, ORE.:** 410 New Fliedner Bldg.
SEATTLE: 1411 Fourth Ave. • **SAN FRANCISCO:** 598 Monadnock Bldg. • **TACOMA:** 417 Tacoma Bldg.
MONTREAL: Canada Cement Bldg. • **TORONTO:** Richardson Agencies, Ltd., 454 King St., West
VANCOUVER, B.C.: Willard Equipment Ltd., 860 Beach Ave.

General Ceramics
AND STEATITE CORP.

CHEMICAL EQUIPMENT DIVISION
KEASBEY, NEW JERSEY

In addition to the manufacturing facilities of the Chemical Equipment Division those of the Insulator Division are also available for handling ceramic problems in all branches of industry. General Ceramics & Steatite Corporation is therefore able to offer service covering all industrial applications of ceramic products.

Lithium Salts and Soaps Proving Economically Better Than Traditional Chemicals

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

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

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

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

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

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

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

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

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

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

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MINERAL COMPANY
A Step Ahead in Industrial Ores and Chemicals

Chemicals • Ores • Metals • Alloys

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

Pressure-Vacuum

BS & B VENT VALVES

Here's positive protection against vapor loss when storing benzol, alcohol, gasoline and other products requiring slight pressure for economical storage. Black, Sivalls & Bryson Vent Valves guard against both over-pressure and excessive vacuum. An exclusive, flexible gasket provides a tight seal during normal operations. Over-pressure lifts the hinged cover, breaks the seal, allows vapors to escape until normal pressure is restored. Excessive vacuum causes atmospheric pressure to lift the gasket, permitting in-breathing.

B S & B Vent Valves are available in a full-range of sizes . . . 2 to 24 inches. Standard models have cast iron body and cast aluminum cover; B S & B Vent Valves are also available in bronze, monel, stainless or combinations of these metals. Large Vent Valves also may be used as manhole openings. Many are in use as supplementary relief valves.

Write today for complete information. Address Special Products Division, Black, Sivalls & Bryson, Power and Light Building, Kansas City 6, Missouri.

SPECIFICATIONS

Model Number	Size, Inches	Standard Opening Pressure, Ounces	Maximum Opening Pressure, Ounces	Standard Opening Vacuum, Ounces
2VVH	2	3	16	½
3VVH	3	3	16	½
4VVH	4	2	16	½
6VVH	6	2	16	½
8VVH	8	2	16	½
10VVH	10	2	16	½
12VVH	12	2	10	½
16VVH	16	2	8	½
20VVH	20	2	6	½
24VVH	24	1½	4	½

FOREIGN INQUIRIES INVITED

EFFICIENCY

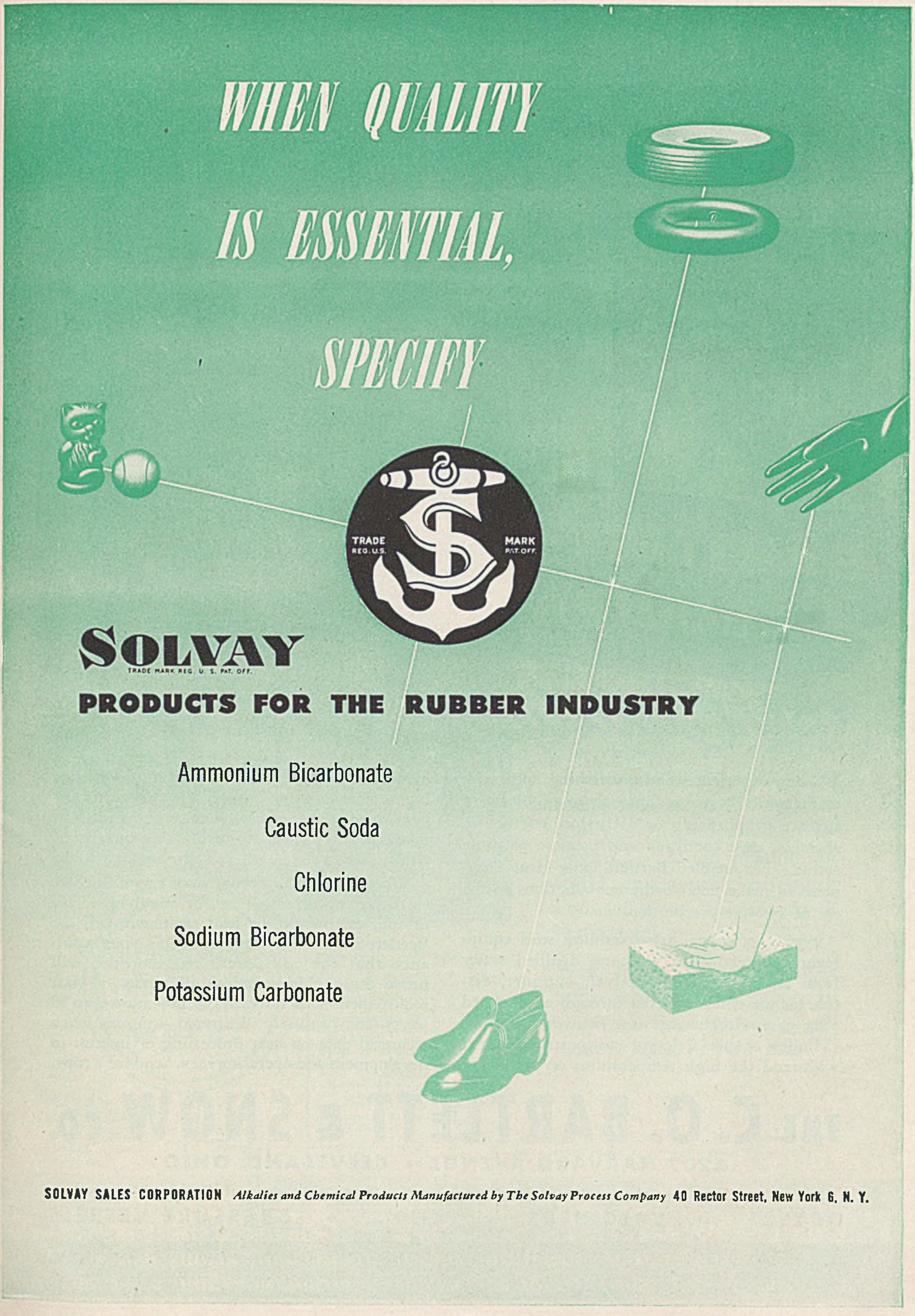
Cable Address: BLACK, KANSAS CITY, U.S.A.

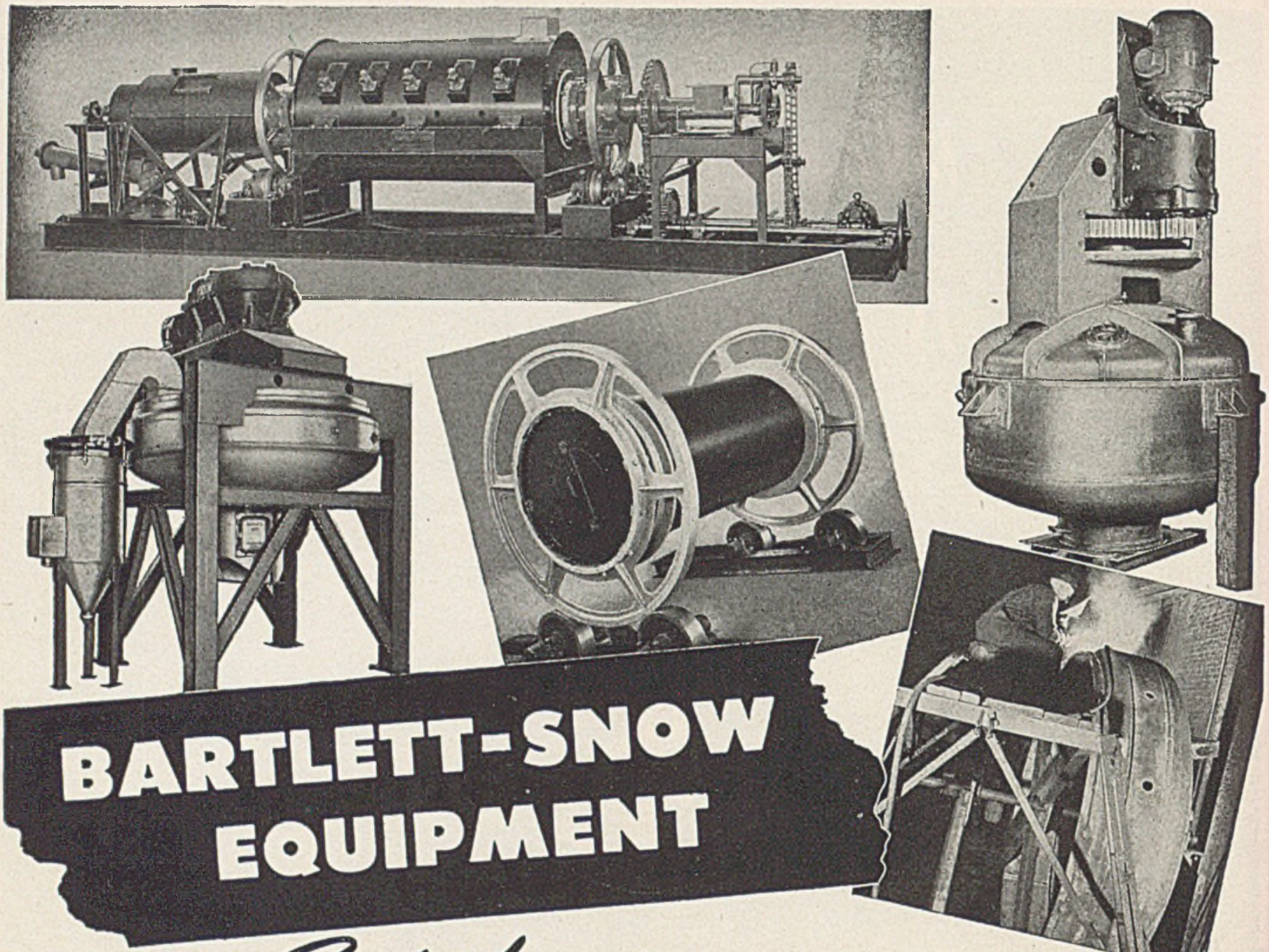
BLACK, SIVALLS & BRYSON, INC.

RELIABILITY

KANSAS CITY, MO.
CASPER, WYO.

OKLAHOMA CITY, OKLA.
CALGARY, ALTA.





BARTLETT-SNOW EQUIPMENT

FOR *Catalyst* PREPARATION

● Long experience, and a searching, technical, mathematically exact approach to problems of surface evaporation or diffusion, corrosion, abrasion, dust condition and possible galvanic action,— has enabled Bartlett-Snow Heat Engineers to make noteworthy contributions to the art of catalyst preparation.

Typical of many, are a stainless steel equipment—jacketed—that separates distilled water from an impregnated catalytic support, discharges the dried material through an enclosed plug gate without any dust loss whatever . . . Cylinders of special design and construction that withstand the high temperatures of producing oxides . . . Equipment for processing in a reducing atmosphere, at 2000°F., that exhausts the hot gases safely, and discharges the processed material, first cooled to normal temperatures, continuously, at the desired rate per hour.

Whether yours is a problem of crystallization, oxidation, or reduction . . . or merely a simple drying, calcination, or heat treatment, call the Bartlett-Snow Heat Engineers,—It's your assurance that the equipment recommended 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.

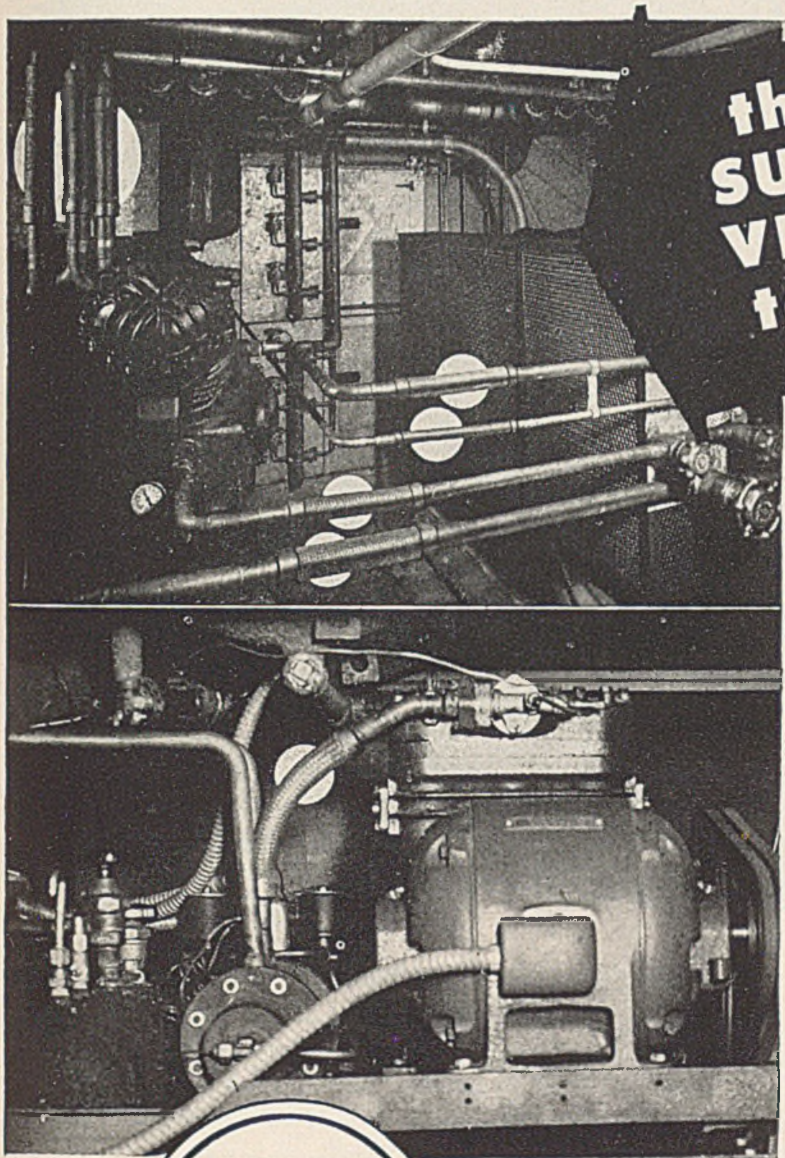
THE C. O. BARTLETT & SNOW CO.

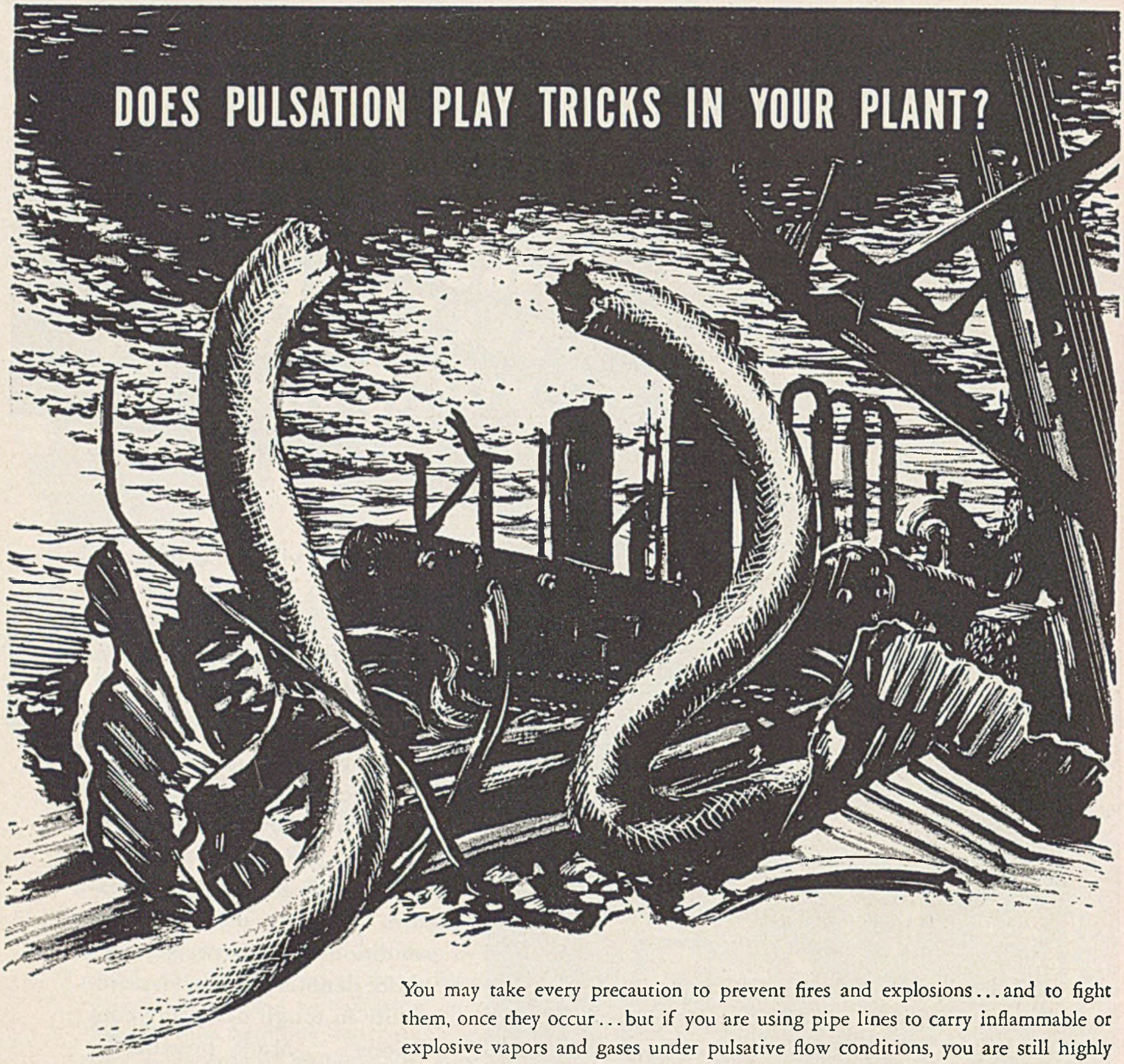
6207 HARVARD AVENUE • CLEVELAND, OHIO

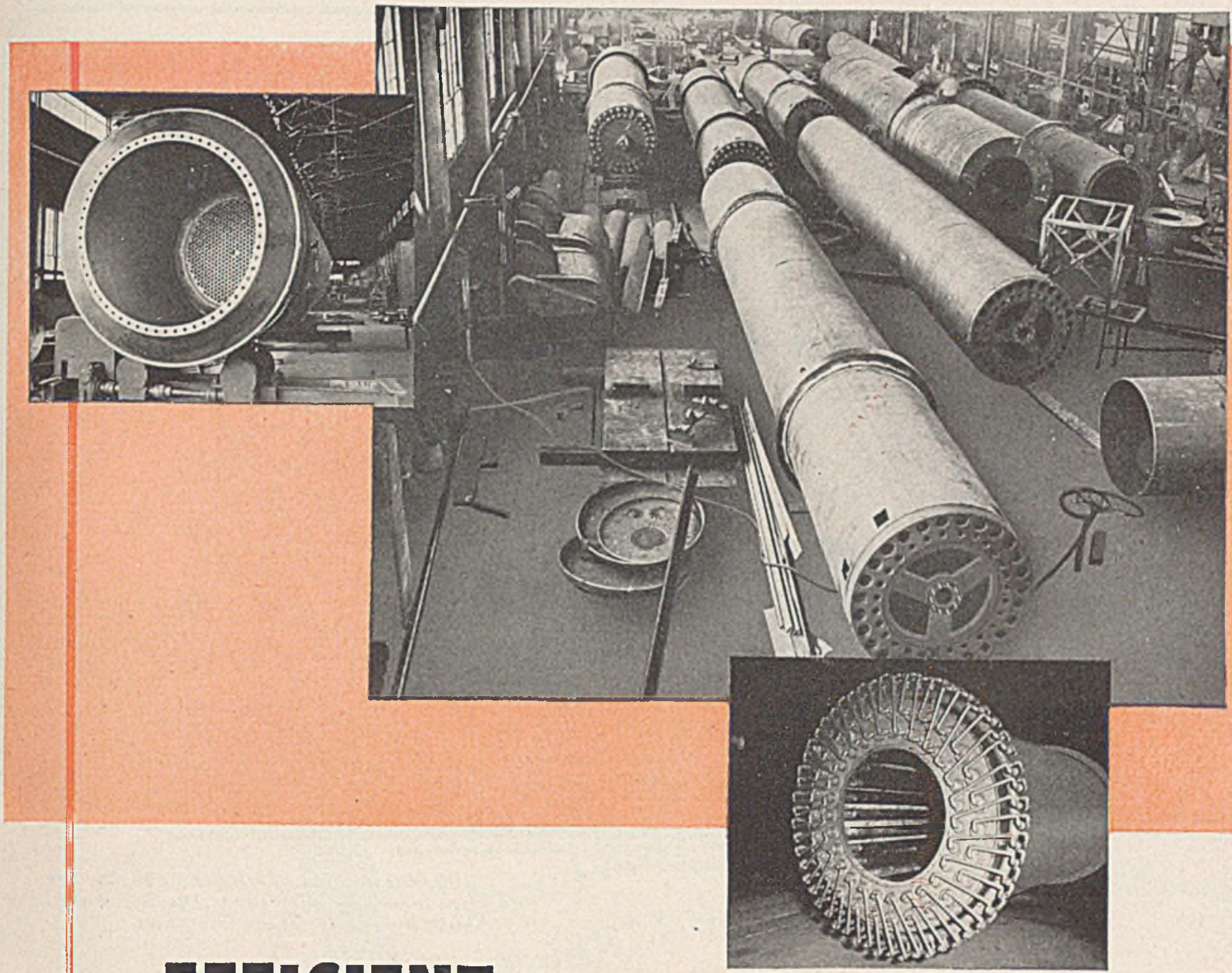
Engineering and Sales Representatives in Principal Cities

DRYERS • CALCINERS • KILNS • PRESSURE VESSELS

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

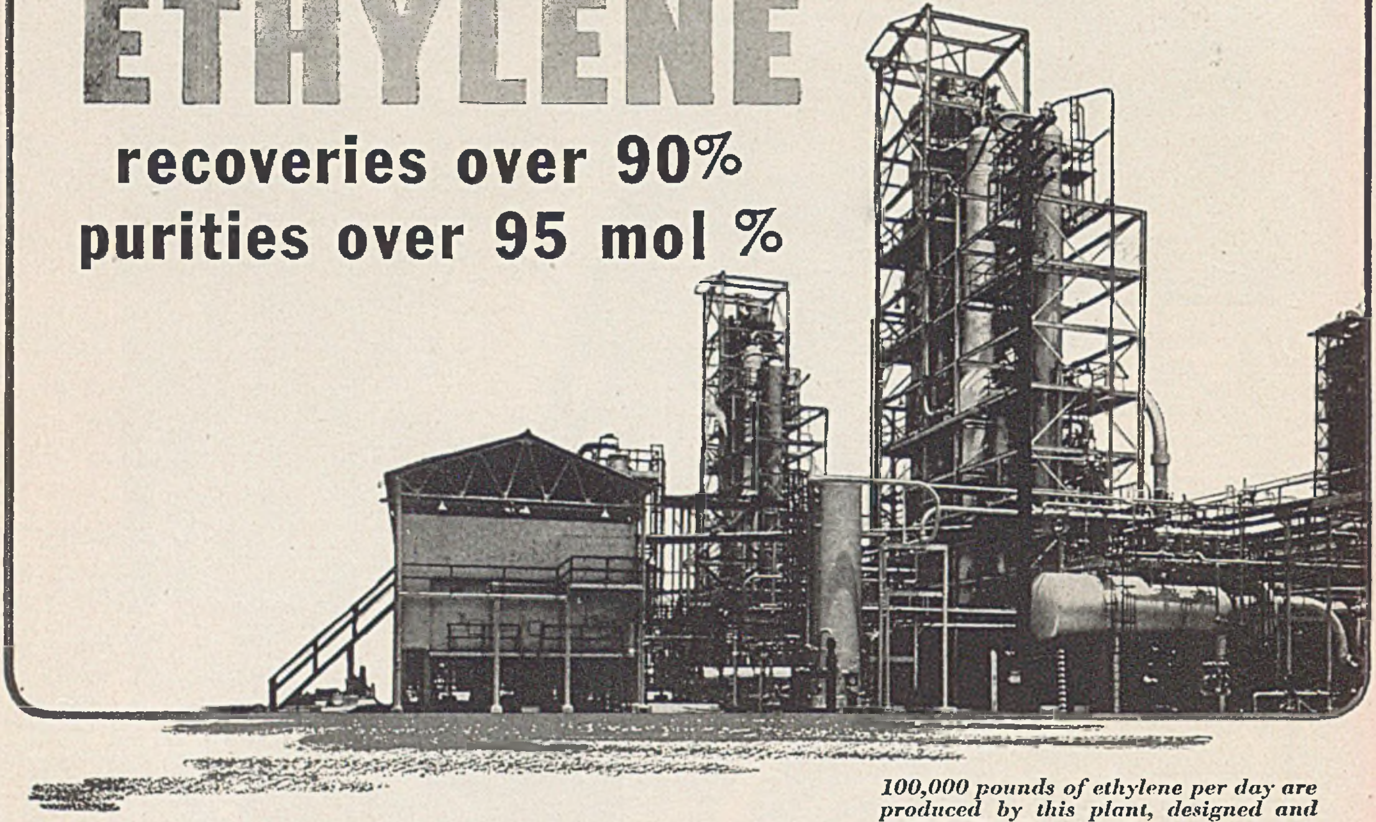



DOES PULSATION PLAY TRICKS IN YOUR PLANT?



ETHYLENE

recoveries over 90%
purities over 95 mol %



100,000 pounds of ethylene per day are produced by this plant, designed and built by The Lummus Company.

. . . without low-temperature refrigeration

In 1943 Lummus completed construction of an ethylene plant for one of the nation's best known chemical companies. With this plant (the first to employ the absorption process for the purification of ethylene) the company has consistently obtained high ethylene recoveries (over 90%) and purities (up to 95 mol %) without use of extreme low-temperature refrigeration.

Among other basic advantages which Lummus incorporated in this plant are flexibility, economical resolution of the charge and furnace effluent gas streams, and ease of control.

Lummus is currently completing construction of two similar ethylene plants with even higher purity—99+mol % ethylene.

With complete research and construction facilities—and with broad experience in petroleum refining and chemical production—Lummus is well prepared to design and build your facilities for the production of ethylene, propylene, phenol, and other chemicals from petroleum.

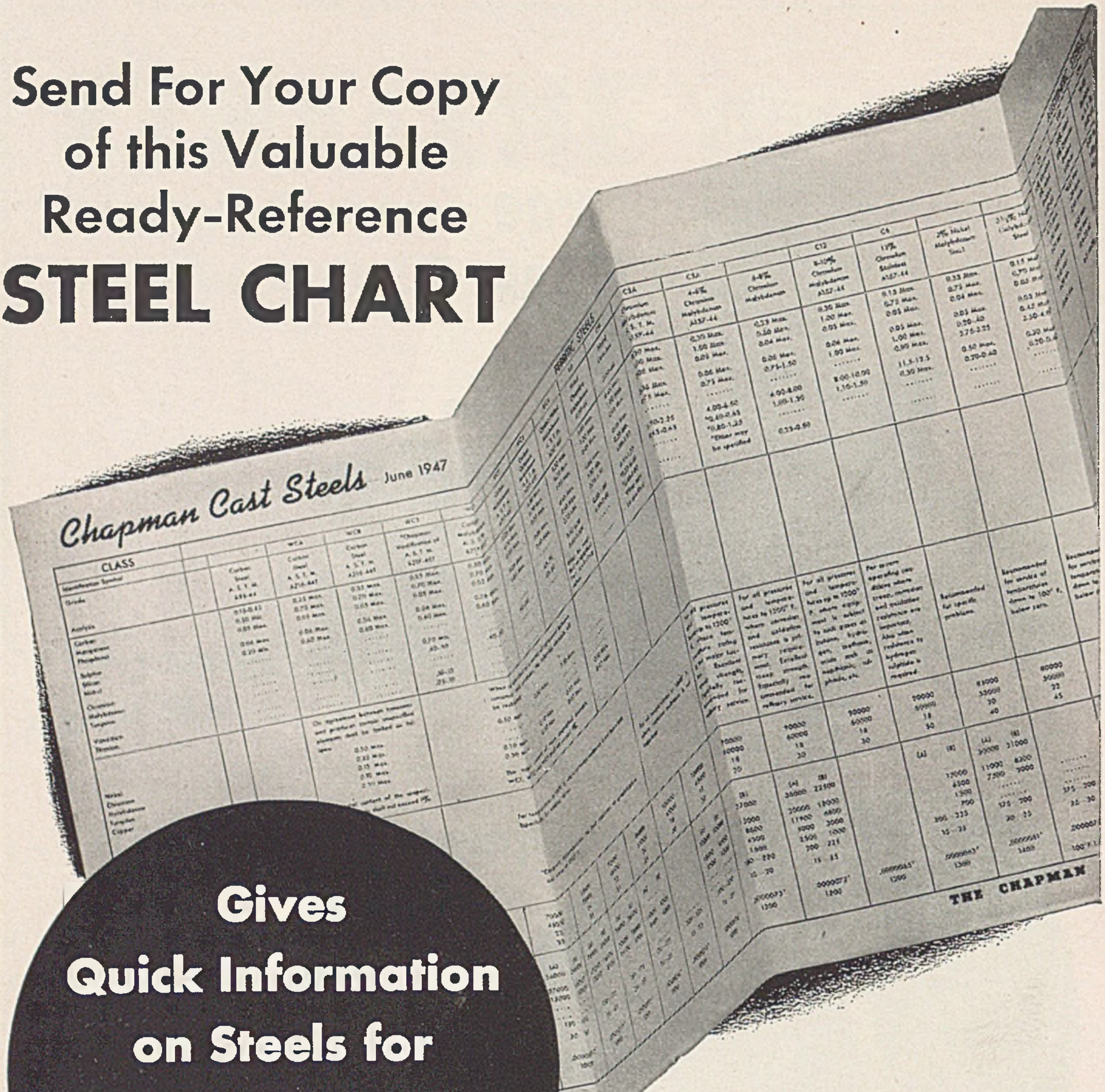
THE LUMMUS COMPANY
420 Lexington Avenue, New York 17, N. Y.

LUMMUS
chemical processes and plants

CHICAGO—600 South Michigan Avenue, Chicago 5, Ill.
HOUSTON—Mellie Esperson Bldg., Houston 2, Texas
LONDON—78 Mount Street, London, W. 1, England


6" STD. TAYLOR FORGE WELDELL PAT. 1926665

Send For Your Copy of this Valuable Ready-Reference STEEL CHART

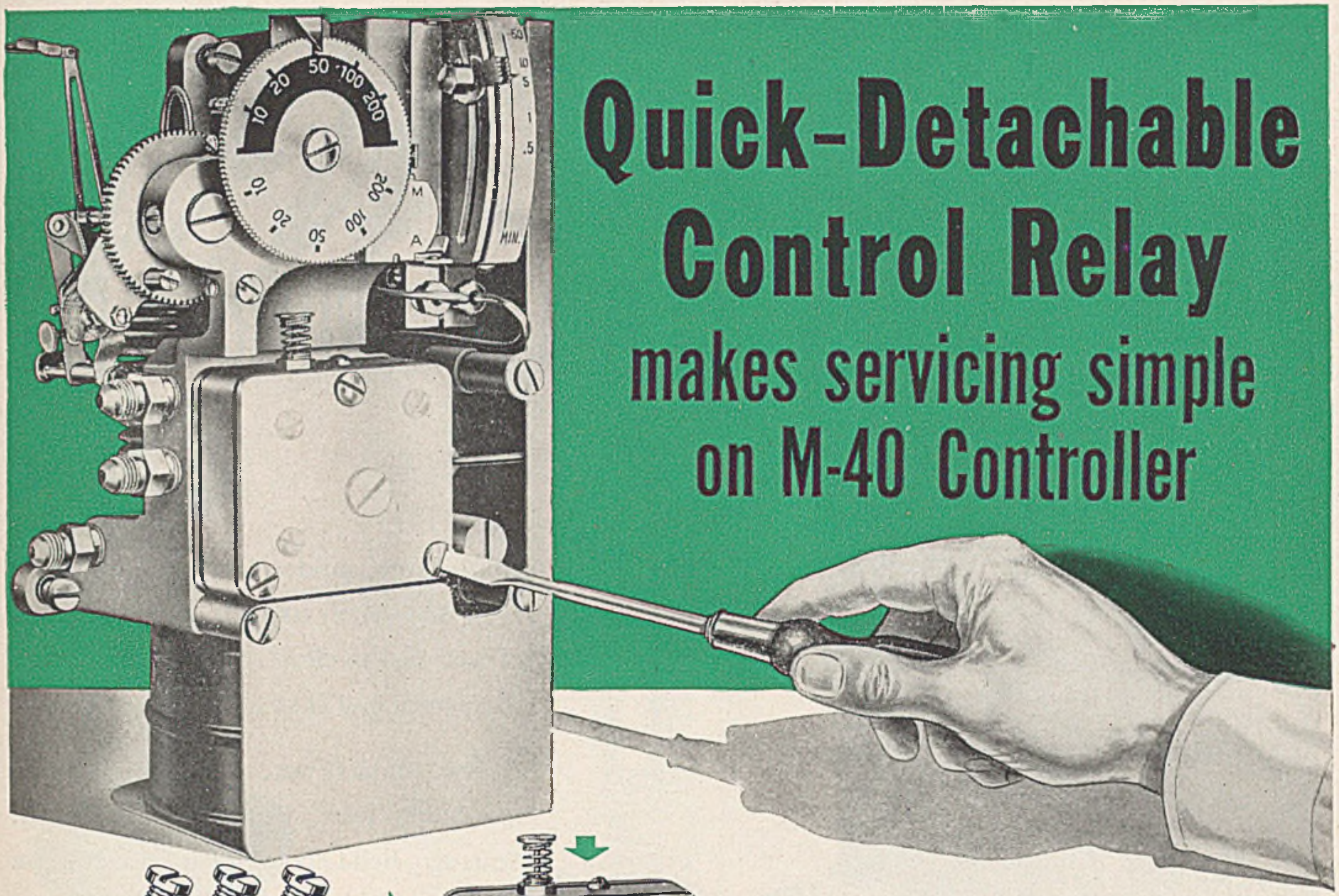


Gives Quick Information on Steels for CHAPMAN Valves

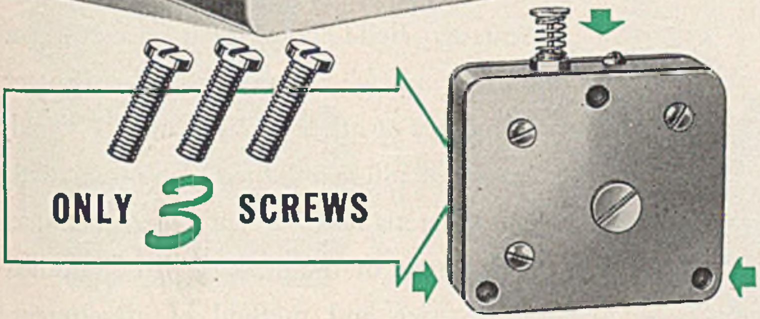
Chapman Steel Valves are available in a wide diversity of compositions to meet every service requirement. The valuable reference chart shown above (reduced in size) tabulates these various types of steels, enumerating the grade, analysis, alloys, applications, and physical properties of each.

Users of steel valves have found this chart to be a handy reference guide. Due to the many requests which Chapman has received for this chart, we have printed a special edition. Chapman now makes the chart available to you. Write today for your copy.

THE CHAPMAN VALVE MANUFACTURING CO.
INDIAN ORCHARD, MASSACHUSETTS



Quick-Detachable Control Relay makes servicing simple on M-40 Controller



Simple to remove . . . and *simple to service!* Taken apart and cleaned in a jiffy, reassembly is no trouble at all: there are *no* adjustments to be made.

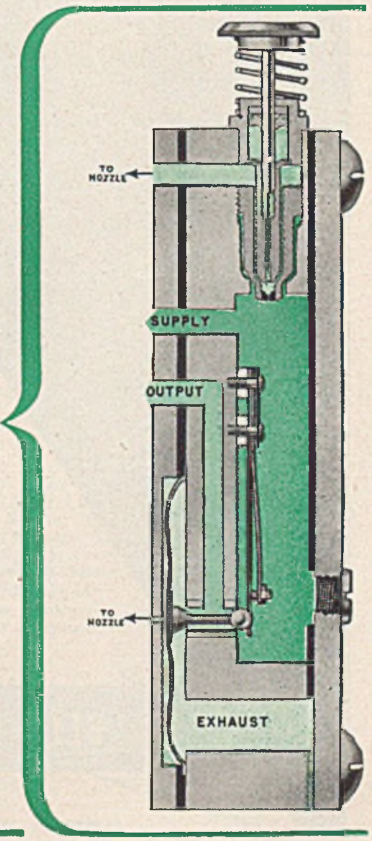
- BY REMOVING THREE SCREWS with an ordinary screw driver, the compact, self-contained control relay can be readily detached from the control unit. Then, with equal ease, it can be stripped down, cleaned and reassembled in a fraction of the time usually required. There are no tight-fitting bushings and no valve to be critically adjusted for exact clearance or travel.

This simple control unit practically eliminates maintenance.

THE ONLY TOTALLY-ENCLOSED CONTROL-UNIT

None of its vital parts are exposed to the elements or to damage by accidental or careless handling. Plugging of the nozzle restriction is made practically impossible by the use of a sapphire jewel passageway (to eliminate corrosion) and a manually operated cleaner button.

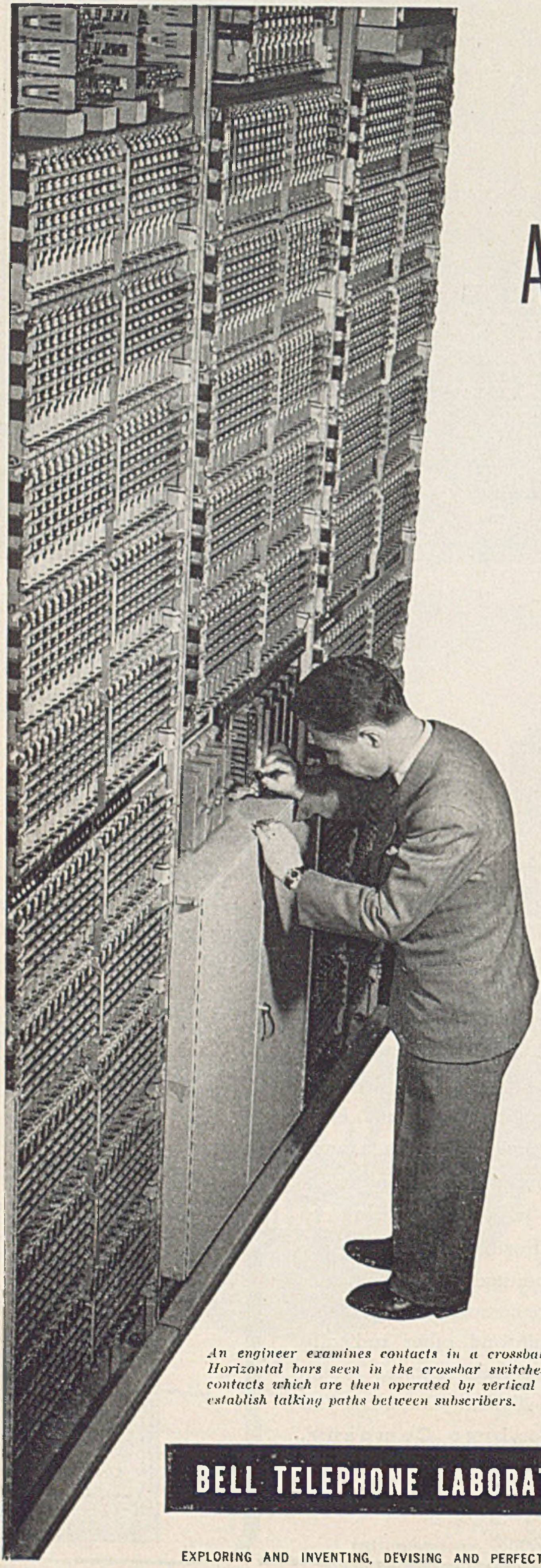
For complete details of this unit and other radically improved features of the M-40 Controller, write The Foxboro Company, 74 Neponset Avenue, Foxboro, Mass., U. S. A.



FOXBORO
REG. U. S. PAT. OFF.

M-40
CONTROLLER

THE ONLY CONTROLLER WITH *Permaligned* CONSTRUCTION

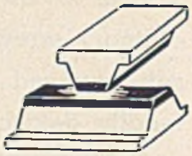


An engineer examines contacts in a crossbar office. Horizontal bars seen in the crossbar switches select contacts which are then operated by vertical bars to establish talking paths between subscribers.

A BILLION ORDERS A DAY

In a large modern telephone office 2,000,000 switch contacts await the orders of your dial to clear a path for your voice. They open and close a billion times a day.

At first, contacts were of platinum—highly resistant to heat and corrosion but costly. Years ago, Bell Laboratories scientists began looking elsewhere, explored the contact properties of other precious metals—gold, silver, palladium and their alloys—and with the Western Electric Company, manufacturing unit of the Bell System, restudied shape, size and method of attachment.



Outcome of this long research is a bar-shaped contact welded to the switch and positioned at right angles to its mate. For most applications, an inexpensive base is capped with precious metal.

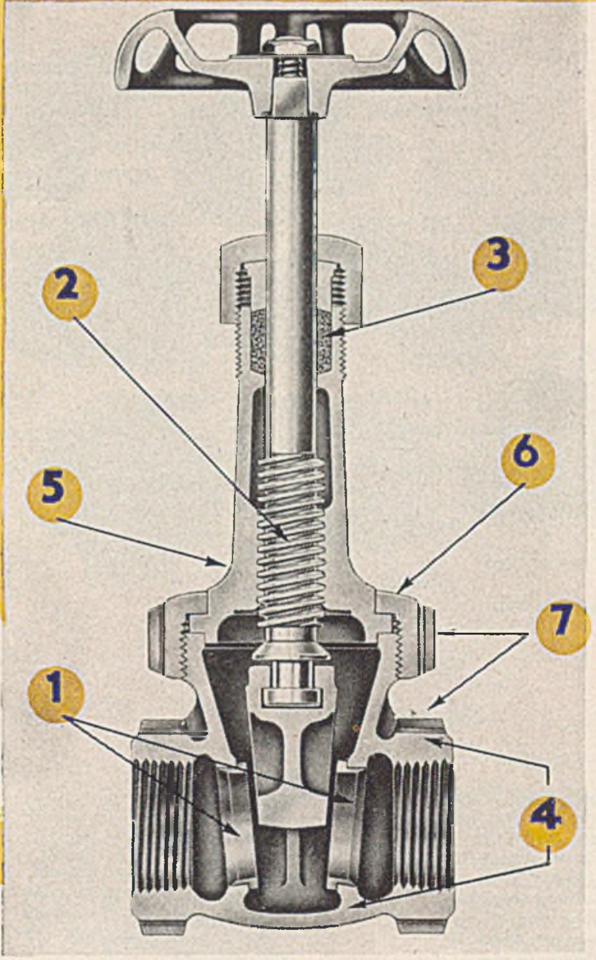
Savings from these contacts help keep down the cost of telephone service. This is but one example of how Bell Laboratories serve the public through your Bell Telephone Company.

BELL TELEPHONE LABORATORIES

EXPLORING AND INVENTING, DEVISING AND PERFECTING, FOR CONTINUED IMPROVEMENTS AND ECONOMIES IN TELEPHONE SERVICE

IT'S NEW . . . IT'S FAR AHEAD — IN DESIGN — IN DURABILITY

JENKINS FIG. 270-U BRONZE GATE VALVE



1. **"MONEL" SEAT RINGS EXPANDED IN BODY** The seat rings, expanded into place in the body, are equivalent to integral faces. The "MONEL" metal used is about 2½ times the hardness of valve body bronze —provides exceptional resistance to erosion and corrosion.
2. **LARGE SPINDLE THREADS LAST LONGER** The threads on the traveling spindle are exceptionally long and large in diameter, which reduces wear to a minimum and insures easy operation. Spindle metal is hard, tough manganese bronze.
3. **DEEP STUFFING BOX—MORE PACKING** Deeper than most 200 lb. gate valves, it holds more packing. Keeps stuffing box tight around spindle with less friction, and packing nut can be turned with less effort.
4. **LIBERAL BODY DIMENSIONS ADD STRENGTH** Made of 35,000 lb. tensile strength cast bronze—has full length of pipe threads and liberal clearance between threaded ends and diaphragm wall. Union assembly reinforces and strengthens body neck.
5. **EXCEPTIONALLY RUGGED BONNET** Projection on bottom assures snug fit into neck of body. Large diameter Acme threads with long bearing, assure improved wear resistance. Machined bevel on underside matches beveled shoulder on spindle for back-seating under pressure and protecting spindle threads when valve is wide open.
6. **HEAVY BONNET RING** Union Bonnet joint withstands exceptionally high hydraulic pressures. Liberal thread engagement assures assembly that can be made tight and kept tight after repeated disassembly.
7. **BODY AND BONNET RING LUGS** Rugged sturdy lugs of novel design on body ends and bonnet ring permit repeated application of conventional wrenches.

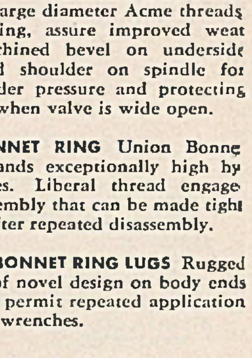
AGAIN JENKINS PRACTICAL ENGINEERING SETS THE STANDARD FOR VALVE ECONOMY

• *IF ANY PART of the seating combination is to eventually need replacement, why not have it the most accessible part—the wedge rather than the seat? It's easier, quicker, cheaper to slip on a new wedge, than to install a new body!*

That's the principle on which Jenkins Engineers designed the new Fig. 270-U Bronze Gate Valve, with a high-quality bronze wedge seating against MONEL seat rings expanded in the body. With this sensible design, the wear affects only the most accessible part—the bronze wedge—which can be replaced by simply slipping it off the stem and slipping on a new one. Prolonged tests, in toughest service, prove it the best seating combination to beat wear, reduce care.

This new, better Fig. 270-U will give you unequalled economy in any service requiring a 200 lb. pressure Bronze Gate, and especially under severe conditions, such as in oil refineries, dye houses, chemical, food, and rubber plants.

Jenkins Bros., 80 White St., New York 13; Bridgeport, Conn.; Atlanta; Boston; Philadelphia; Chicago; San Francisco. Jenkins Bros., Ltd., Montreal.



LOOK FOR THIS DIAMOND MARK

TRADE JENKINS MARK

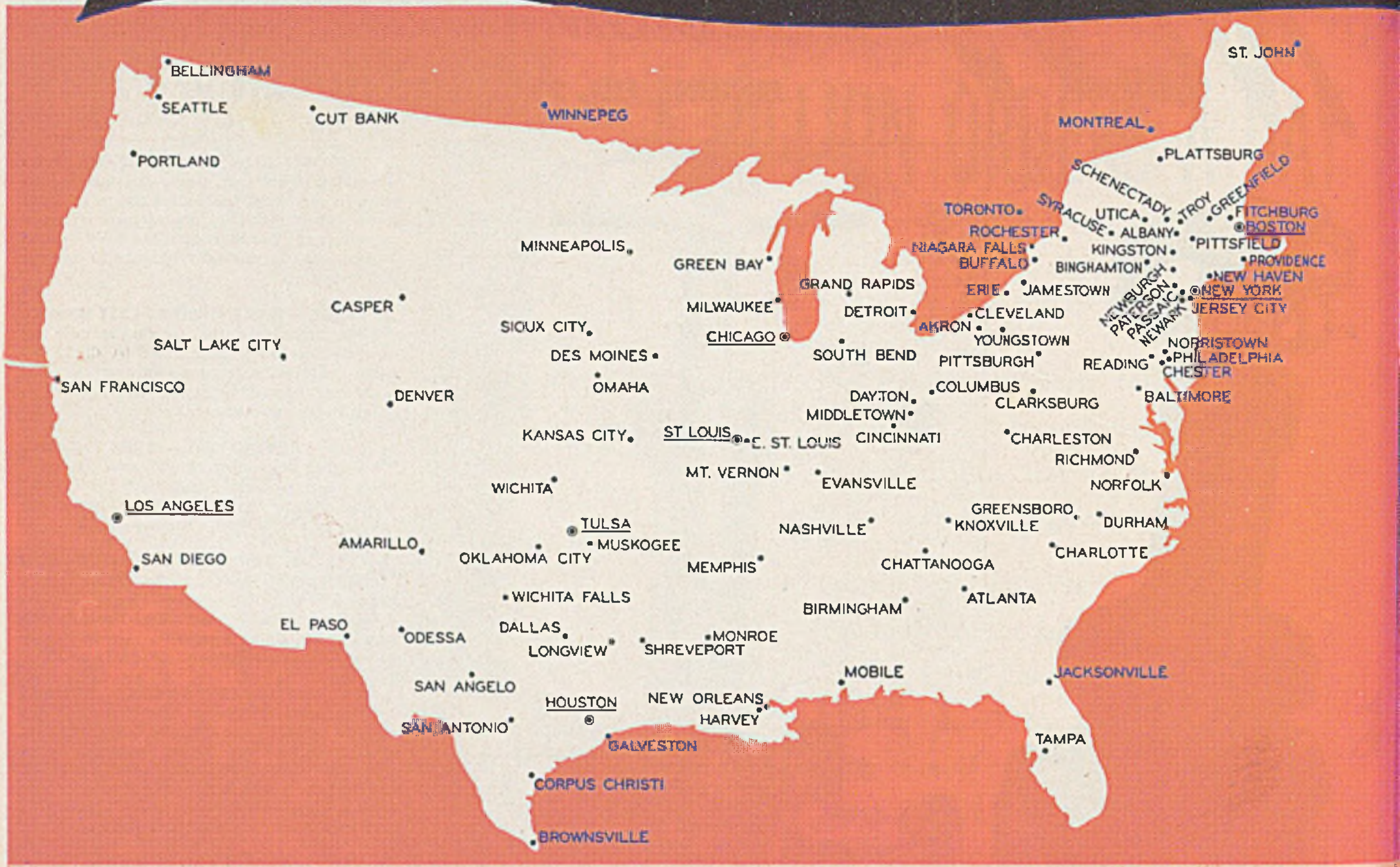
SINCE Jenkins Bros 1864

JENKINS VALVES

Types, Sizes, Pressures, Metals for Every Need

WRITE FOR THIS FOLDER (Form No. 181-A). It describes the Fig. 270-U and many other popular Jenkins Bronze Gate Valves. Or, ask your Jenkins Distributor.

MIDWEST Welding Fittings Distributors



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Universal Valve & Fittings Co.

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Aird-Don Company

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Jones & Laughlin Supply Co.

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Fulton Supply Co.

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Central Metal & Supply Co.
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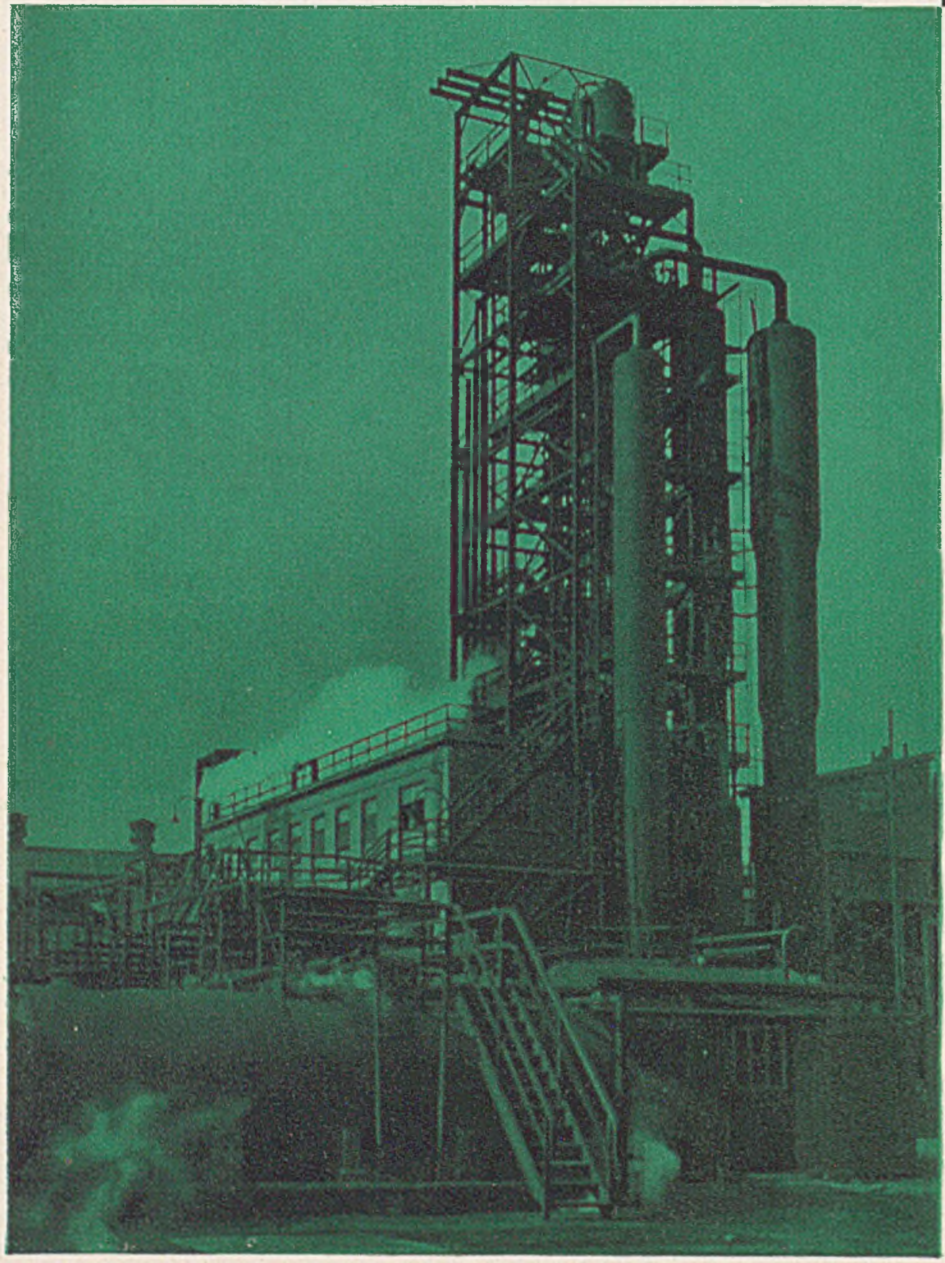

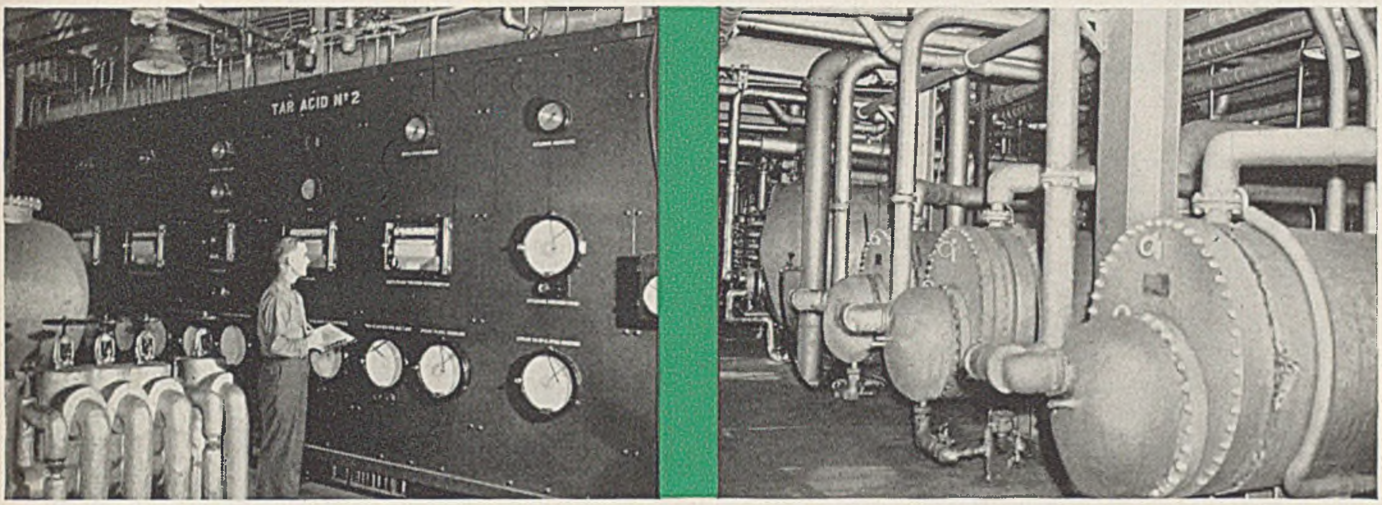

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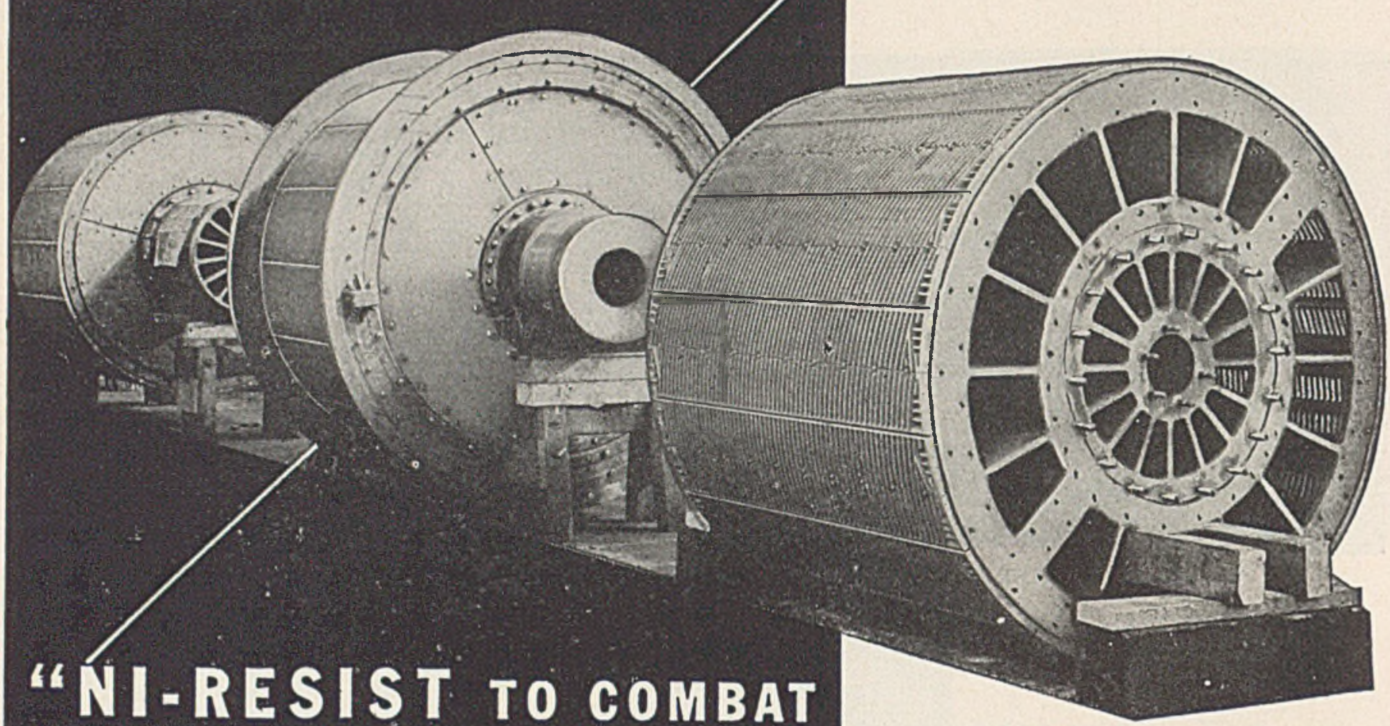

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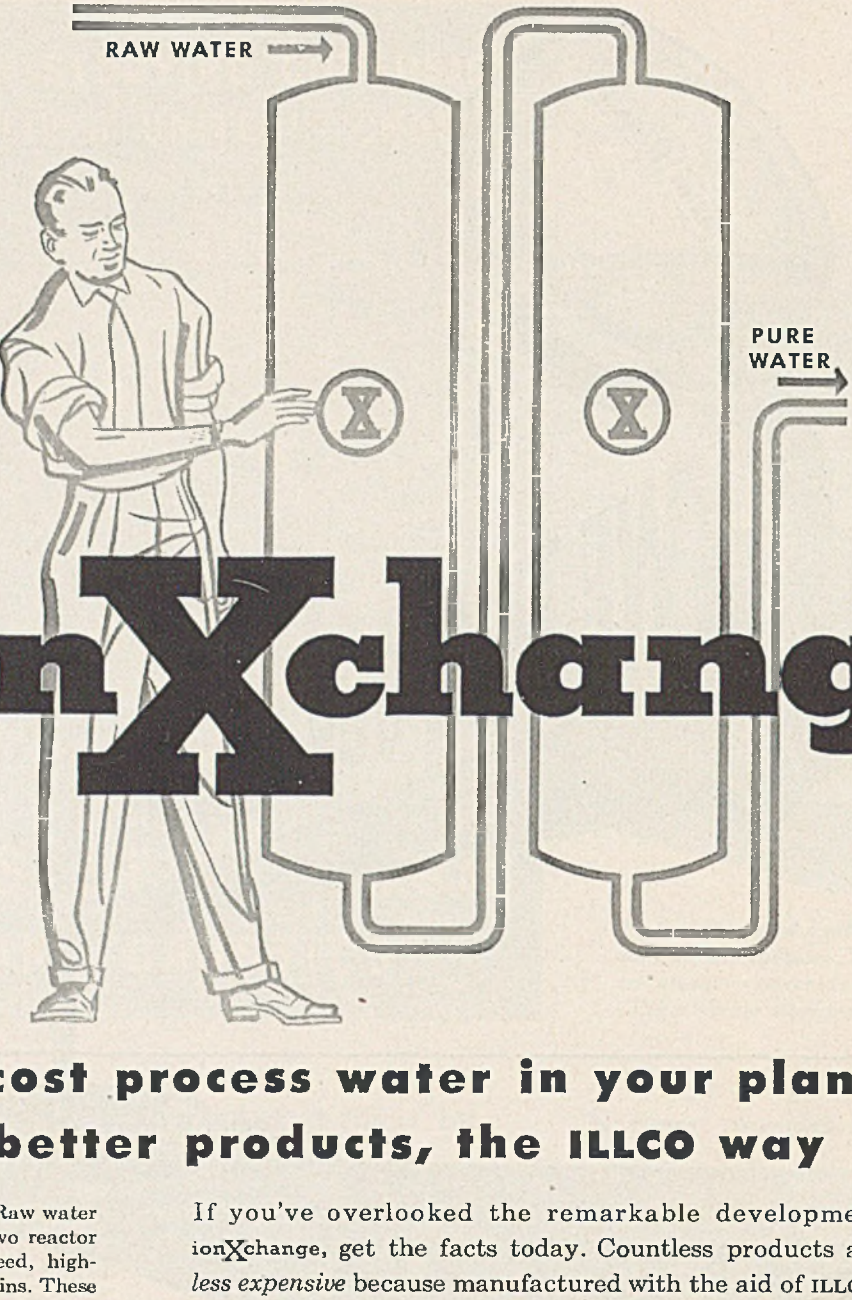
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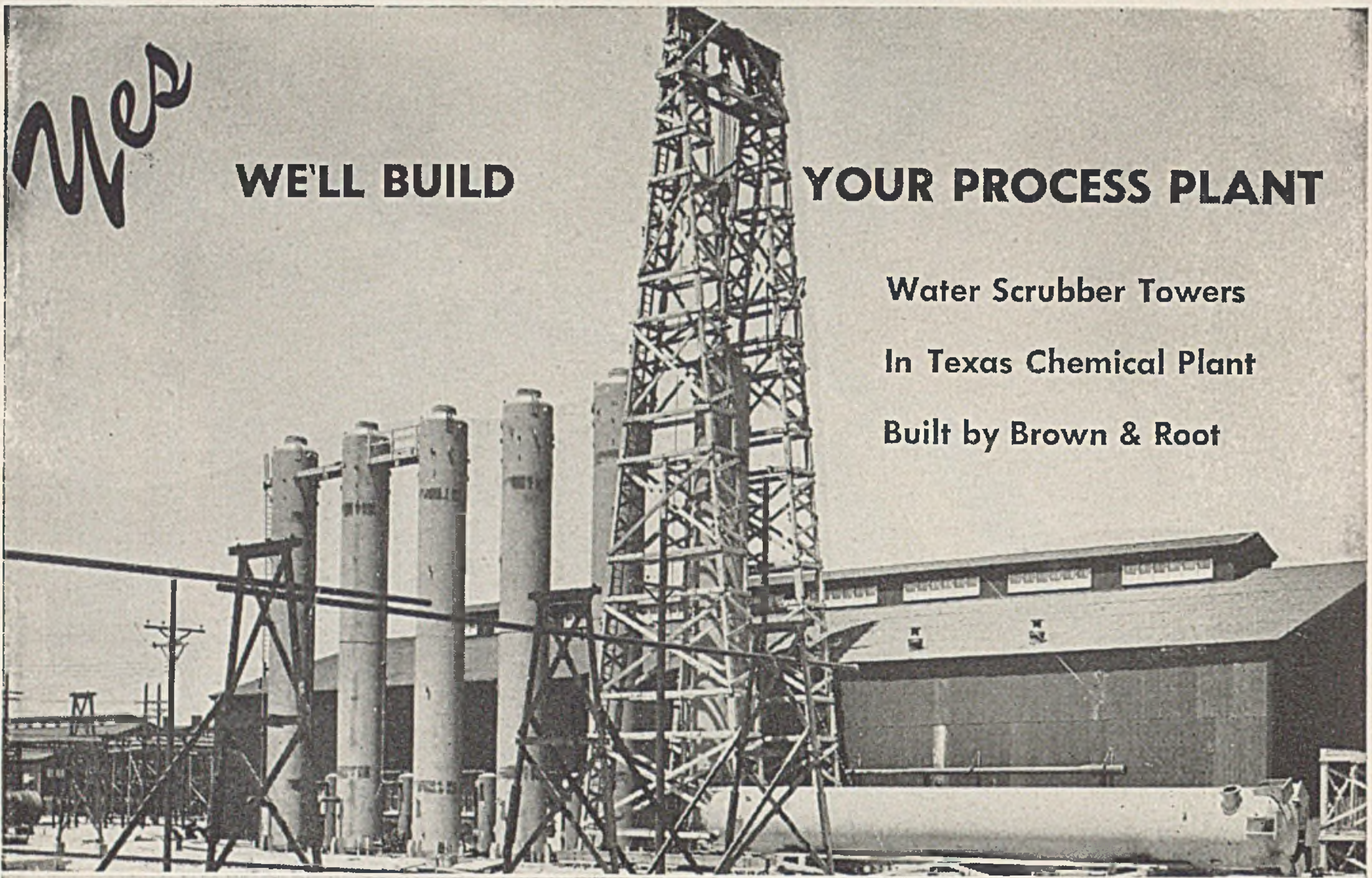

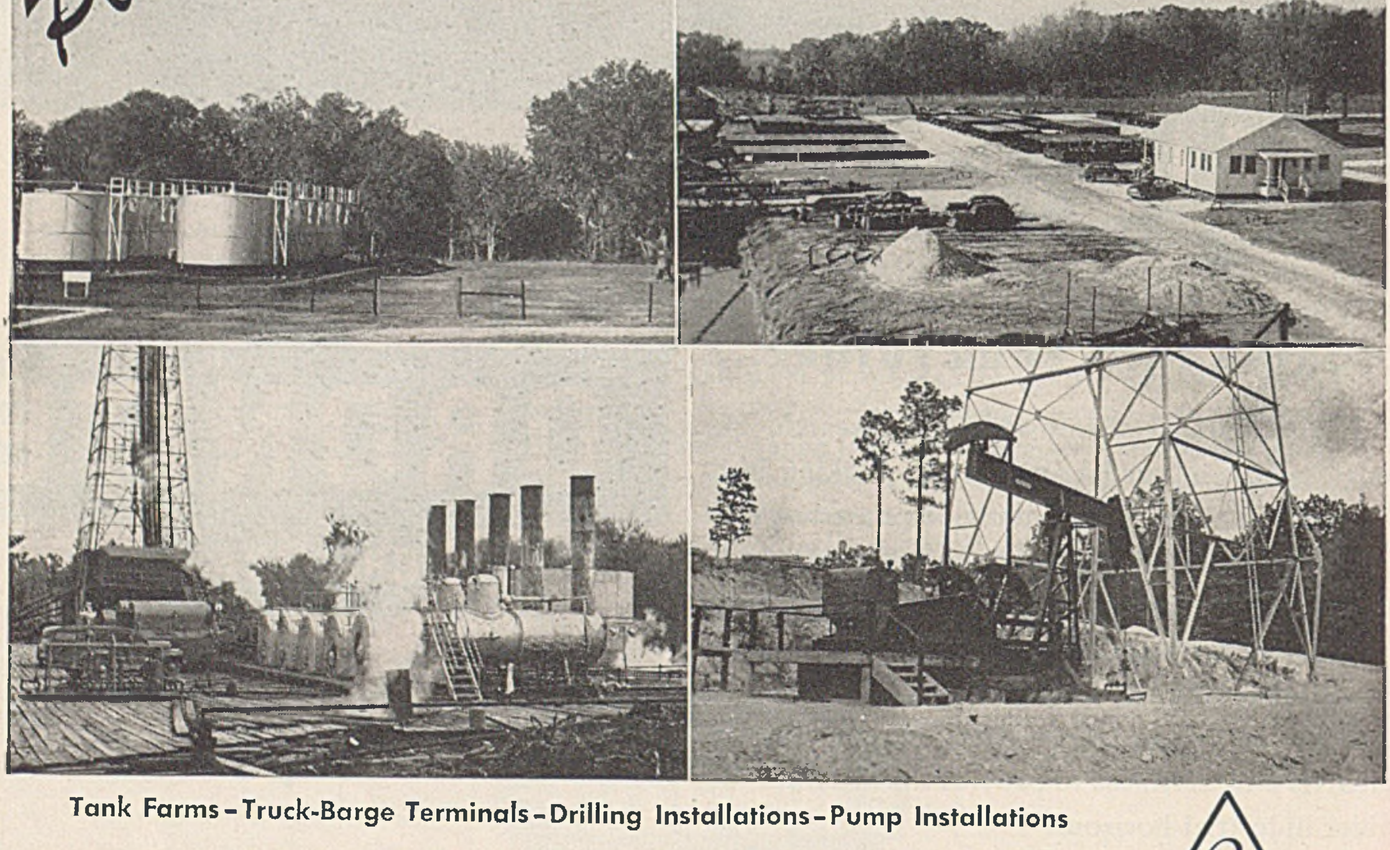

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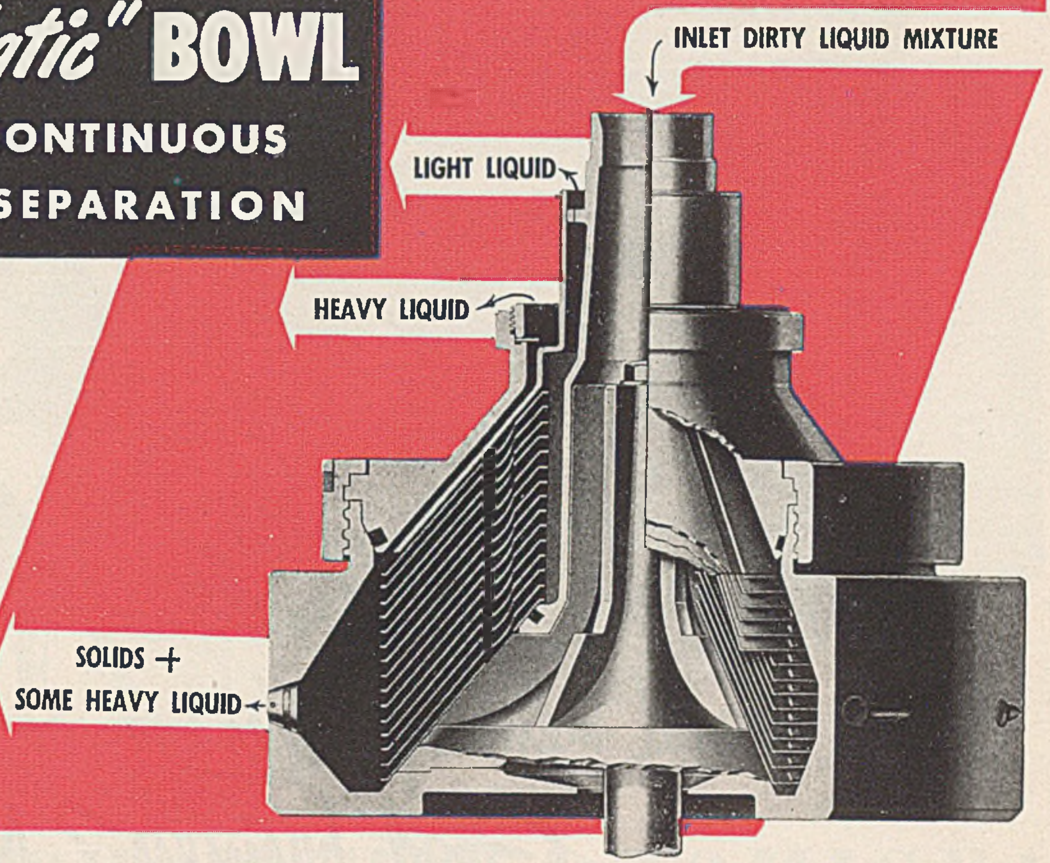

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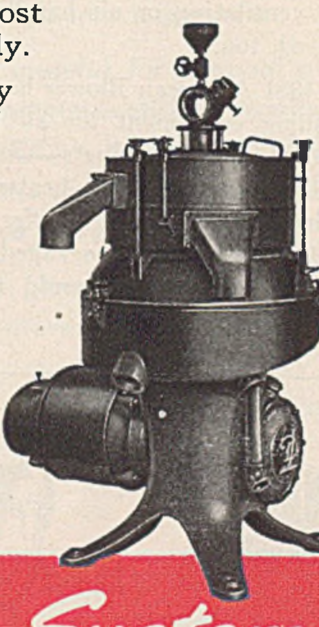

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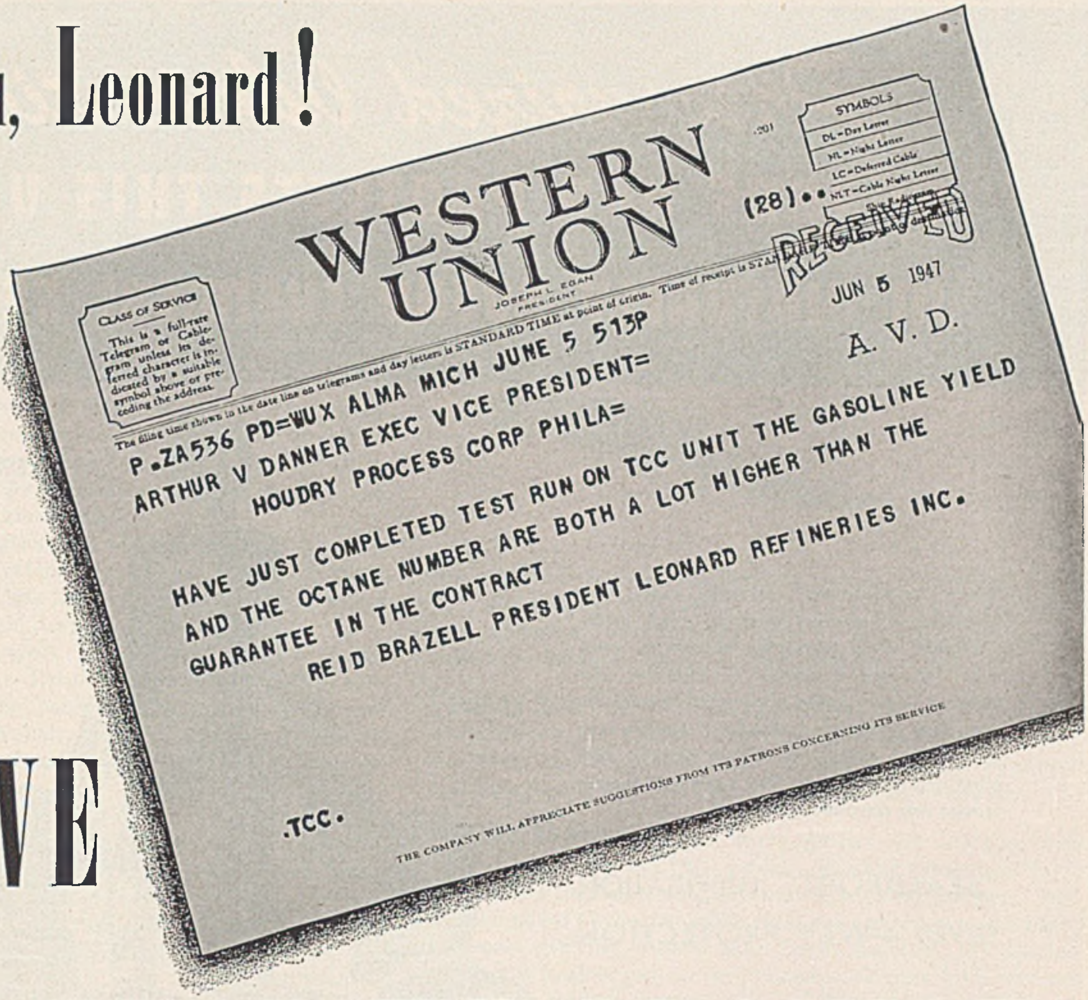

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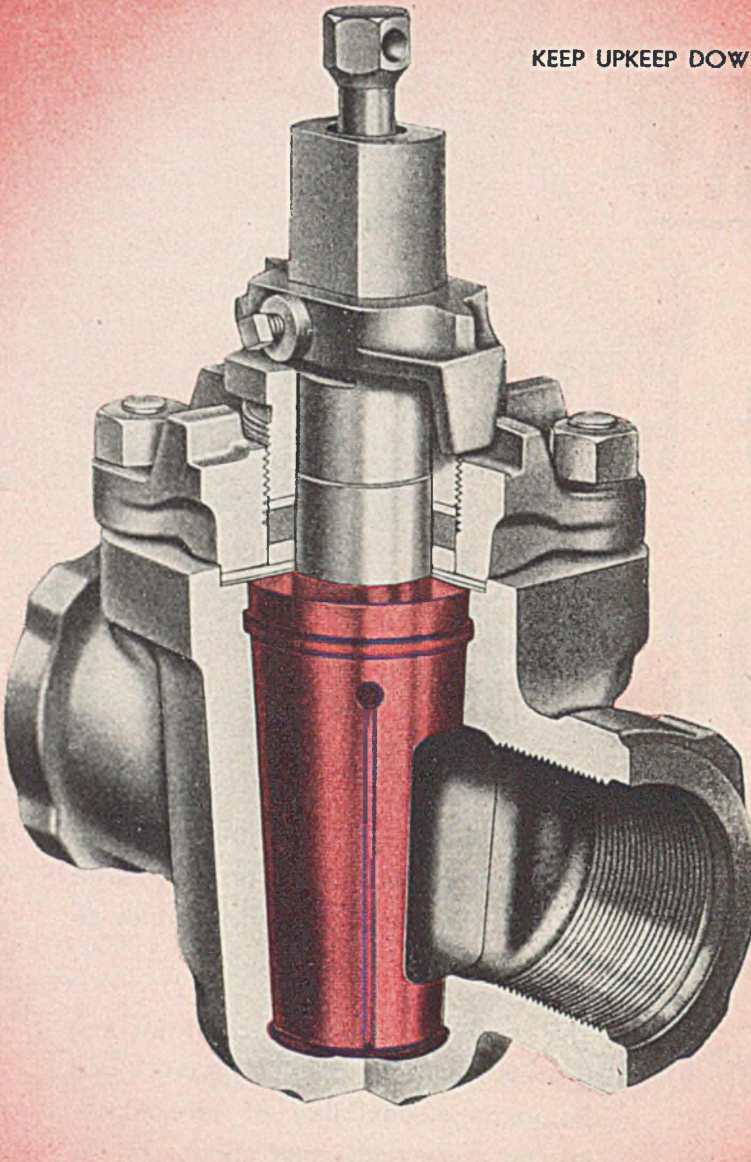

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As We See It . . .

Working under Pressure. Five papers from the symposium on high pressure technology given at the Chicago A.C.S. meeting last September make their appearance this month. Comings starts the ball rolling with a review of recent advances in the use of industrial processes involving high pressures, and includes a reference list of 164 published items of the past five years.

Paden, Martin, and Swain next describe small scale and pilot plant scale studies of guanidine nitrate production from a solution of ammonium nitrate and dicyandiamide in anhydrous ammonia. The process was a war development, the guanidine nitrate being used as an intermediate in the manufacture of nitroguanidine for flashless powder. Diagrams of the laboratory and pilot plant size autoclaves are included.

Colburn, Drew, and Worthington add information concerning heat transfer of ammonia synthesis gas mixture at pressures from 30 to 900 atmospheres. Their investigations cover a region for which no data are reported in the previous literature.

Comings and Nathan report on the thermal conductivity of gases at high pressures. Result of the authors' studies is a method for calculating the conductivity for any given temperature. Required for the calculation are the critical pressure of the gas, its critical temperature, and its thermal conductivity at atmospheric pressure.

Johnson and Nagle conclude with a paper describing use of the sodium nitrite–potassium nitrate mixture known as HTS as a pilot plant heat transfer medium. The particular apparatus involved was not operated at high pressures. The temperature range of 600° to 800° F. is of interest, however, for a number of reactions where high pressures are involved.

Radial Chromatography. A contribution from England tersely discusses chromatography as an industrial tool that already is of proved value and promises to become even more important in the future. Hopf, the author, injects into the existing story some experimental work with radial chromatography, using a device for which he proposes the name "chromatofuge."

Fermentation Accomplishments. In the lead-off paper of the issue, Boruff and Van Lanen review the achievements of the fermentation industry during the war. The list is impressive. A number of production statistics are included.

The paper was originally presented at a session of the 1947 Atlantic City A.C.S. meeting that may become a modest milestone in the Society's history. The occasion was the first technical meeting of the Fermentation Section of the Division of Agricultural and Food Chemistry. The sponsors of the section believe that interest in fermentation processes has now advanced to the point where the A.C.S. could sustain an active divisional program devoted to the subject. This prospect is assured if the record of the first meeting is maintained, at which time thirteen papers relating to fermentation were presented.

Calculated Economy. Harbert uses four pages, starting on page 940, in stripping successful plant operation to its bare mathematical skeleton. Expressed in words, his method becomes the incontestable statement that an additional dollar in outlay should be made only if its brings a return of more than a dollar. Two examples are given in which the method is applied to determination of optimum operating conditions for a natural gasoline absorber and a high temperature gas reactor. In a brief discussion the author "puts in its place" the overhead item, summing up convincingly with the comment: "The reflux to a distillation column is not changed because a vice president's salary is increased." One of our reviewers pointed out that Harbert's method requires quantitative knowledge of plant performance through a general area described by the controllable plant variables. Where such information is available, the method will be very useful. For those less fortunate operations where empirical and unrelatable requirements control, the foundation for the method is deficient, and experiment must be utilized.

Canning Nutrition. Five papers report the effects of canning on nutritive value of foods. Four relate to vitamin content of various fruits and vegetables; the fifth investigates the proximate and mineral content of certain vegetables after blanching.

New Development. The first specimen for our new pilot plant "case history" section (this month's editorial gives more background) is a unit for testing an alumina-from-clay process. During the phase of the war when Nazi submarines wreaked havoc on boats carrying bauxite from South America, the development of a feasible process for producing alumina from clay was given high priority in war research. Hignett's article on page 1052 demonstrates that some of these investigations had matured to a stage where full scale operations could have been undertaken with substantial assurance of technical success.

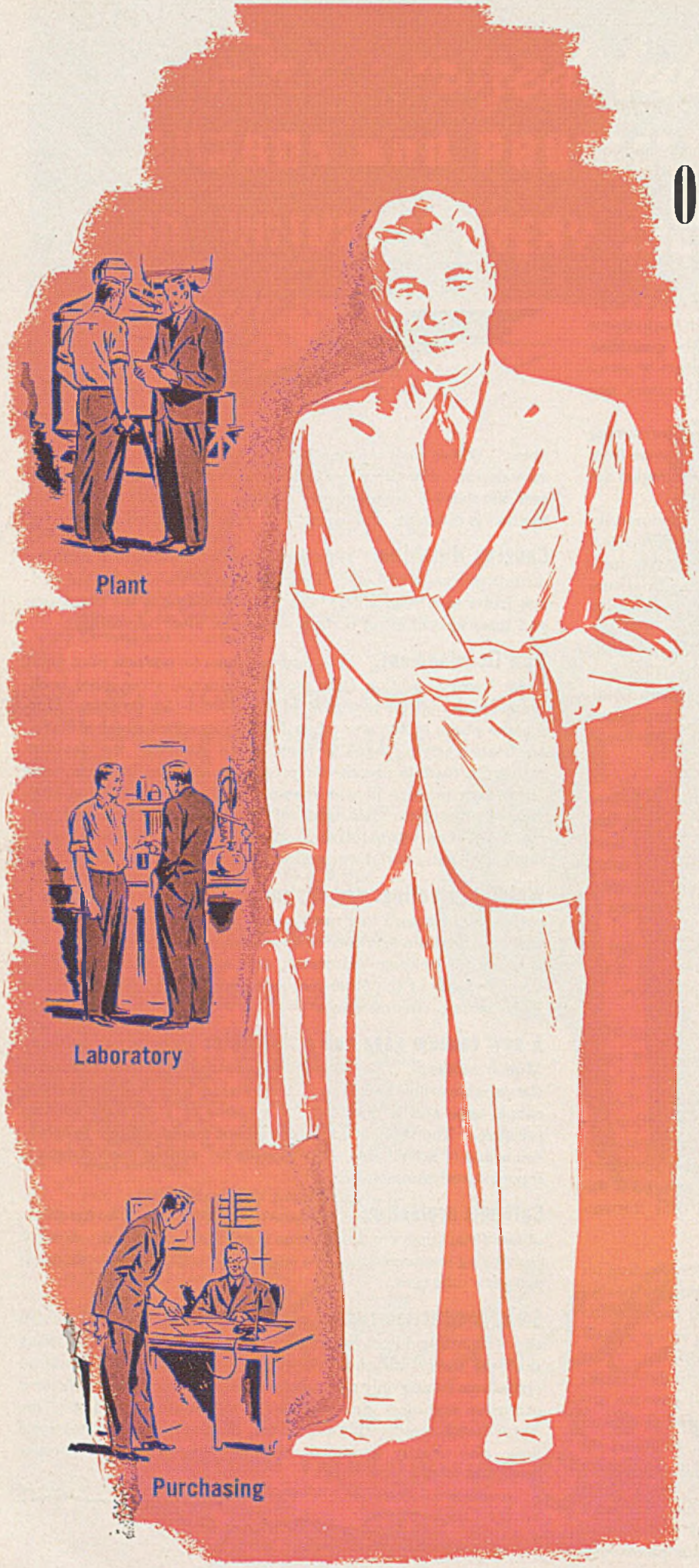
Welding, riveting, and casting as methods for metal fabrication are discussed in Brown's contribution of the month. He betrays an admiration for the extensive variety of work that can be done by welding. However, also cited are examples which show that one of the other methods may be distinctly preferable under certain circumstances.

A new vacuum gage and a flowmeter command attention in Munch's column. The flowmeter is electronically operated and of the variable orifice area type. The vacuum gage is of the thermocouple type and is designed for systems of 1 to 1000 microns pressure. The trend of some instrument manufacturers to establish a line of interchangeable elements for various applications is reported and commended.

Cathodic protection is Fontana's contribution. The functions of sacrificial anodes and impressed current are described. Several convincing instances are given of cathodic protection for chemical process equipment.

Small production runs deserve attention in planning which they frequently do not get, comments von Pechmann. He thinks this is a costly mistake. Substantial savings can be made on operations lasting only a few days or a few weeks if the production executive organizes the project for maximum efficiency. One factor handicapping this procedure, however, is the executive's boss, who usually underestimates the time needed for proper execution of this job.

D. O. Myatt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INDUSTRIAL and ENGINEERING Chemistry

WALTER J. MURPHY, Editor

Pilot Plants

THE rapid growth of the chemical engineering profession has been an outstanding development of the past several decades, coinciding with an equally prominent advance of the chemical process industries. Chemical engineering, offspring of chemistry and mechanical engineering, now contains elements of knowledge available from neither of the other two. We use the term "chemical engineer" and "chemical engineering" advisedly. However, many whose training was strictly chemical, and who now consider themselves industrial chemists, have become highly proficient in the chemical engineering phases of their work. Our comments apply with equal validity to this latter group.

Many facts have been learned about the mechanism of chemical reaction in industrial equipment. These investigations fully justify classification as scientific work. They strike out into a field where phenomena that are of negligible significance in laboratory investigations become of prime importance. Characteristic examples are the dissipation of exothermic heat from large masses of reacting material, time lags in control of process variables, and inherent variation in rate and intimacy of mixing. These variables make the process development problem so complex that data usually are unavailable for a sound theoretical solution.

In such instances the chemical engineer must turn to actual tests for his answers. He takes the infant process from the laboratory and selects the combination of available and custom-designed equipment that he considers the optimum embodiment for volume production. Seldom do equipment characteristics match process specifications well enough to assure immediate success. More often his original choice proves only a "first approximation." Final development is achieved only after many weeks, months, or years of exploring the complex secondary effects introduced by the engineering equipment. In contrast to laboratory research, perfection of achievement in terms of efficiencies and recoveries is unusual. Ordinarily the chemical engineer must make the process work despite basic limitations in equipment and materials. (Perhaps this occupational requirement accounts for the reported high aptitude of the chemical engineer for making a success of marriage!)

The oft-quoted advice to "make your mistakes on a small scale and your money on a large scale" usually is heeded in a chemical engineering investigation. The reaction sequence is tested in equipment too small for industrial feasibility but constructed to reveal the characteristics of the process when on a commercial scale. In some instances the novel elements of a new process are confined to one or two steps, and no integrated study is necessary. Where the unknowns extend throughout the process, a pilot plant is used.

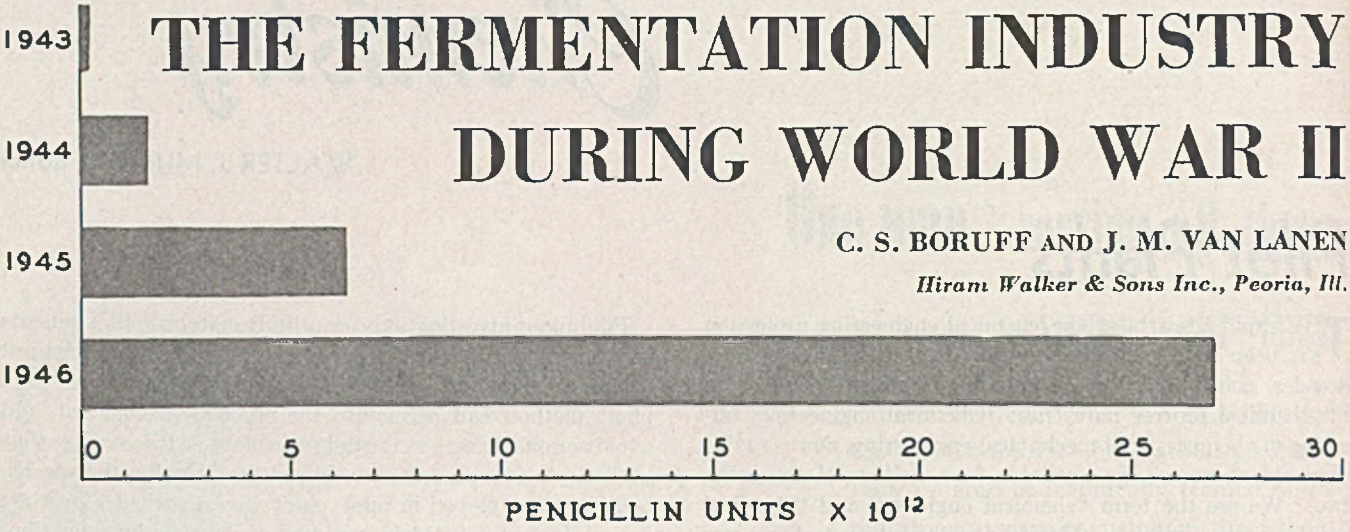
Pilot plant investigations beautifully epitomize the elements in modern chemical technology that call for the chemical engineer's qualifications. Skill in employment of the pilot plant method can accelerate the process development, and avoid serious defects in the full scale plant. It is strange that so little has appeared in technical literature on the specific techniques employed in pilot plant investigations, for they are a popular and widely used tool of chemical investigation. Substantial advantages should result from more extensive accounts of pilot plant work.

INDUSTRIAL AND ENGINEERING CHEMISTRY is introducing a new monthly feature in the present issue that we hope will stimulate more of this desirable discussion. The editors believe that the subject calls for a factual treatment if cumulative advantages are to be obtained. We have chosen, accordingly, the device of the "case history" as a method of presentation. Each month a description of a specific pilot plant study will appear, with the principal emphasis devoted, not to the process, but to the plant as an experimental tool of the process development engineer. Novel solutions to special problems that arose during its operation will be described and the discussion will revolve around the part the pilot plant played in translating the laboratory findings into a technically feasible process. It is intended that the entire series will become a useful reference source for such common problems in pilot plant work as are exemplified by sampling, equipment capacity relations, chemical and operational control, and personnel assignments. We hope you will find it interesting and useful, and welcome your comments.

Inauguration of the new feature is undertaken with the frank intention of enlarging the area commonly accepted as the base for publication of applied chemical knowledge. We invite chemical engineers who have conducted pilot plant investigations and are interested in the feature to submit the account of their work. Our hope is that articles on pilot plant technology soon will become as customary as the chemical research and unit operation papers that have long been established on our pages.

Publication in applied science is successful and equitable only as long as those who benefit from it recognize their moral obligation to support it. The authors who have spent time, thought, and experience in preparing the first articles to appear in the pilot plant feature have demonstrated their faith in its merits. Through their generosity in pioneering the feature, you will have the opportunity to judge from actual examples how this information benefits your own work. In the final analysis, your response will determine whether this new area of technical knowledge is to become a permanent addition to our accepted traditions of scientific publication.

THE FERMENTATION INDUSTRY DURING WORLD WAR II



C. S. BORUFF AND J. M. VAN LANEN

Hiram Walker & Sons Inc., Peoria, Ill.

During the recent war the fermentation industry converted itself to meet increased needs for various chemicals and biologicals. It also participated in the development and commercial production of antibiotics and biological warfare agents. These accomplishments not only have resulted in greater diversification of the industry but also have enhanced interest in the industrial applications of microorganisms.

THE contributions of the fermentation industry to our country's industrial accomplishments during World War II have, for the most part, remained untold. It has seemed appropriate, therefore, to summarize available information on this subject. Prior to World War I the only fermentation product manufactured in appreciable quantities was ethyl alcohol. During World War I the acetone-butanol fermentation was developed to commercial scale and provided much-needed acetone for the manufacture of explosives. Within ten to fifteen years after the war there was a sharp increase in the production of organic acids by fermentation. During the period 1941 to 1946, which is reviewed here, the all-time peak of volume production of conventional fermentation products was reached. Over and above this production the industry contributed much to the outstanding developments in the field of antibiotics, germ warfare, etc. As a result of this progress, interest in the industrial utilization of microorganisms has been greatly enhanced.

ETHYL ALCOHOL

Ethyl alcohol, one of our oldest and most versatile organic chemicals, still ranks first in tonnage production in the fermentation industry. During the five years prior to 1941, an average of 123,000,000 wine gallons of industrial alcohol was made (all figures at 190° proof); about 72% came from the fermentation of molasses, 20% by synthesis from ethylene, and the remaining 8% by fermentation of grains and other carbohydrate materials. With the advent of the war, the need for industrial alcohol was increased tremendously, largely for the manufacture of both butadiene and styrene in the synthetic rubber program, but also for a variety of other essential processing and synthetic operations.

Early in the war the main source of fermentable raw material (molasses) was largely cut off, and the industry was obliged to turn to grain. Production problems were further complicated by the necessity of maintaining an adequate carry-over of corn, the grain most commonly utilized in grain alcohol distilleries. This forced the industry to turn to sorghum grains and to wheat and wheat products since they were more readily available. Not only were distillers unfamiliar with the processing of wheat and granular wheat flour, but relatively few had the preferred facilities for adequately processing the grain and for completely recovering the much needed by-product feeds.

To avoid losses of valuable grain and alcohol and to assure the rubber program of its alcohol requirements, the War Production Board appointed a Wheat-Alcohol Research Committee to solve the problems associated with the fermentation of wheat. With the Northern Regional Research Laboratory of the United States Department of Agriculture as the coordinating agency, a program of collaborative research was formulated. The first wheat alcohol conference was held in Peoria in November 1942. This was followed by another in February 1943 to discuss the information which had been accumulated from the various research projects. From reports presented, it was evident that many distillers had solved the problems involved in processing wheat and were obtaining efficiencies and plant capacities nearly equal to those obtained from corn. However, by this time there was a serious shortage of high protein feeds, and further work was required to improve the recovery of fermentation residues to fill this need. This portion of the problem was satisfactorily covered in a third conference held in September 1943. In all, some seventeen companies, three private research groups, seven educational institutions, and seven government agencies participated in the wheat-alcohol program. The group submitted and discussed over sixty research reports (*9*). From late 1942 to July 1945 nearly 700,000,000 gallons of alcohol were produced from wheat and wheat products, an excellent example of the accomplishment of cooperative effort.

Figure 1 summarizes the role played by the fermentation industry in the wartime production of industrial alcohol (*12*); it shows the quantities of alcohol made from grain, molasses, and ethylene from 1940 through 1946. In 1943 and succeeding years, grain contributed the bulk of the alcohol, while that from ethylene increased slightly and that from molasses decreased slightly. Not indicated in Figure 1 are minor sources of alcohol such as fruit wastes, whey, sulfite liquor, and potatoes. Although these materials accounted for only 0.5% of the total in 1945, they contributed about 2% in 1946, largely as a result of processing surplus potatoes and wood pulping wastes. Government-sponsored plants were erected at Bellingham, Wash., to utilize sulfite liquor, and at Springfield, Ore., to saccharify and ferment wood waste. The combined output of these two plants was estimated to be 6,000,000 gallons of industrial alcohol annually (*7*). Provided alcohol can be made competitively from these materials, considerable quantities of wood waste and sulfite liquor could be put to use in this manner.

That industrial alcohol filled a wide variety of wartime needs is apparent from Table I, which shows the disposition of industrial alcohol from January 1, 1942, to June 30, 1945 (*10*). Over this period synthetic rubber required 611,000,000 gallons, or nearly 40% of the total alcohol consumed. In 1943 and 1944 approximately two thirds of the butadiene and a large part of the styrene were made from alcohol. Allocations for indirect military and civilian needs, which included that utilized in the synthesis of other chemicals, required over 500,000,000 gallons. The remaining alcohol, about 30% of the total, went to Lend-Lease, antifreeze, and direct military uses.

The story of the original government estimates as to wartime alcohol demands and their abrupt change due to the rubber situation, the installation and expansion of high-proof alcohol production facilities in beverage plants, the conversion of eastern seaboard molasses to grain, the construction of three largely government-sponsored and -financed grain alcohol plants in the Midwest, and the problems of the various industry committees and government agencies relative to grain allocation, production, storage, and transportation of alcohol would make interesting reading, but would not be appropriate for this discussion.

The war also brought about the development and adoption of rectifying columns packed with fiber glass (*5*).

Many have asked why the War Production Board and other agencies saw fit to proceed with an expanding grain alcohol program in view of the grain shortage situation. The answer is readily apparent when it is realized that large quantities of expensive, acid-resistant equipment are essential for the conversion of ethylene, with the result that construction costs are nearly three times as high for synthetic alcohol as for grain plants, including complete feed recovery facilities. The cost of a complete grain alcohol plant averaged $275,000 per annual million gallons of alcohol as compared to $800,000 per annual million gallons from ethylene. The total construction time required and the critical materials used are also much less for grain plants.

BY-PRODUCTS

By-products recoverable during the production of grain alcohol are distillers' grains and solubles, carbon dioxide, and fusel oil. Actually these represent approximately two thirds by weight of the grain entering the distillery. Each played an important role in filling wartime requirements.

The recovery of total feed, both grains and solubles, reached an all-time high figure in 1945 of 633,000 tons as compared with a prewar production of about 175,000 tons (*2*). This high figure reflects not only the peak of grain utilization but also the influence of the installation of additional equipment for distillers' feed recovery. Whereas in 1943 only about 10% of the distilleries had complete recovery equipment, present facilities are capable of recovering 92% of the residues from grain alcohol fermentation (*3*).

The annual production of solid carbon dioxide in the United States during World War II ranged from 429,000,000 pounds in 1941 to 659,000,000 in 1945. The quantity of liquid and gaseous carbon dioxide produced during the same period ranged from 247,000,000 pounds in 1941 to 332,000,000 in 1944 (*1*). A substantial portion of this carbon dioxide was recovered from fermentation gases, that from ethyl alcohol fermentations being especially desirable because of its relatively high purity.

Table I. Consumption of Industrial Ethyl Alcohol from January 1, 1942, through June 30, 1945

Use	Total[a]	Per Cent	Jan. 1–Dec. 31, 1942[a]	Jan. 1–Dec. 31, 1943[a]	Jan. 1–Dec. 31, 1944[a]	Jan. 1–June 30 1945[a]
Total Consumption	1,543,500	100	226,000	428,500	605,800	283,200
Direct military	134,200	8.7	52,000	39,900	27,200	15,100
Lend-Lease	167,900	10.9	25,000	63,000	56,900	23,000
Synthetic rubber	611,200	39.6	. . .	126,900	329,600	154,700
Antifreeze	121,100	7.8	29,000	50,800	31,800	9,500
Indirect military and civilian	509,100	33.0	120,000	147,900	160,300	80,900

[a] In thousands of gallons at 190° proof.

The gas from alcoholic fermentation is about 99.8% carbon dioxide.

Besides its application as a refrigerant, carbon dioxide was utilized as a gas in soda ash manufacture and as a liquid in fire extinguishers. One war-born use was that of protecting planes against engine fires in the air as well as on the ground. Dry ice found a variety of new uses and interesting applications, including the cooling and hardening of aluminum rivets and the shrinking of rivets in the manufacture of airplanes.

Fusel oil is a mixture of alcohols derived from the action of yeast upon amino acids and related compounds; consequently its composition varies from one substrate to another. The major portion is composed of propyl, butyl, and amyl alcohols. Fusel oil is produced in alcoholic fermentations at the rate of 20 to 30 pounds per 1000 gallons of 190° proof alcohol. In 1945, 11,000,000 pounds were recovered or just under 20 pounds per 1000 gallons of alcohol. This by-product is fractionated to meet specific needs, one of which—the use of the amyl fraction as a source of amyl acetate—was vital in the recovery of penicillin.

BUTYLENE GLYCOL

Much research and development was done in the United States and Canada on the butylene glycol fermentation. A research program similar to that for industrial alcohol production was set up and functioned during most of the war period. From this collaborative research effort, the production, recovery, and conversion of butylene glycol to butadiene were successfully carried

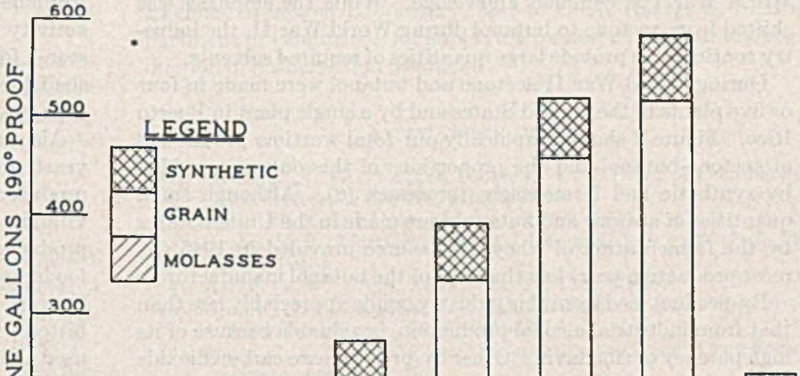


Figure 1. Annual Production of Industrial Alcohol (Year Ending June 30)

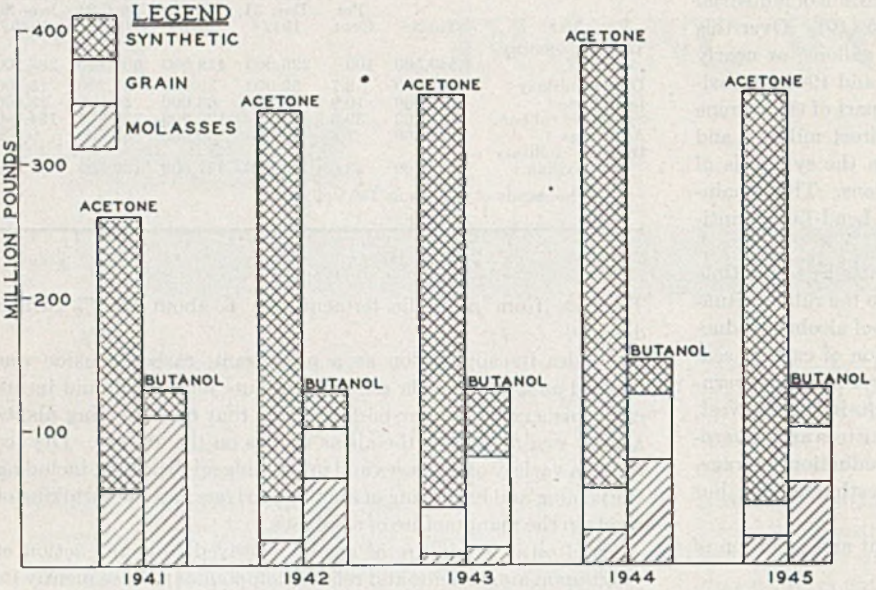


Figure 2. Annual Production of Acetone-Butanol (Year Ending June 30)

out on a large pilot plant scale. Most important contributions were made in the development of methods for the continuous acid saccharification of grains to fermentable sugar, the efficient recovery of butylene glycol from fermented mashes, and the esterification and pyrolysis of butylene glycol to butadiene. It was found late in the war period that 13 to 14 pounds of butylene glycol, convertible to 6.3–6.8 pounds of butadiene, could be produced from a bushel of grain at a cost about equivalent to that for butadiene from alcohol (*3*).

ACETONE-BUTANOL

The production of acetone-butanol by fermentation is, in order of volume, exceeded only by the industrial alcohol industry. The history of this industry and its role in supplying acetone during World War I is common knowledge. While the emphasis was shifted from acetone to butanol during World War II, the industry continued to provide large quantities of required solvents.

During World War II acetone and butanol were made in four or five plants in the United States and by a single plant in Puerto Rico. Figure 2 shows graphically our total wartime production of acetone-butanol and the proportions of this output provided by synthetic and fermentative processes (*6*). Although small quantities of acetone and butanol were made in the United States by the fermentation of whey, this source provided in 1945 (its most productive year) less than 1% of the butanol manufactured.

By-product feed from this industry, while appreciably less than that from industrial alcohol production, is valuable because of its high potency of riboflavin. Other by-products are carbon dioxide and hydrogen, fermentation gases being comprised of approximately 60% CO_2 and 40% H_2. These have been used for the synthesis of methanol. The ethyl alcohol produced by this industry was included under the previous discussion on industrial alcohol.

ORGANIC ACIDS

Lactic Acid. This acid is produced by fermenting sugars, starches, and whey. Three grades are made—technical, fine edible, and medicinal. In 1940 five firms reported production of technical grade, five the edible grade, and two the medicinal grade. Lactic acid production has expanded considerably during the past ten years with the result that little, if any, lactic acid has been imported since 1937. Figure 3 shows production from 1940 through 1946 (*6*).

Vinegar and Acetic Acid. As Table II shows, not only was there an appreciable increase in vinegar production during the war years, but also a substantial amount of vinegar was further refined to acetic acid (*6*).

Citric Acid. No production data are available beyond those given for 1942. Production figures for fermentation citric acid, which represents more than 80% of the total, for 1941 and 1942 are listed as 22,533,000 and 23,638,000 pounds, respectively (*6*). It is estimated that the total production during the years following was in the neighborhood of 26,000,000 pounds annually. About two thirds of the total wartime output was utilized in pharmaceutical preparations, most of the remainder being consumed in foods and beverages.

Gluconic Acid Salts. Production information on gluconic acid and the remaining organic acids is fragmentary. Some 871,000 pounds of gluconic acid salts were manufactured in 1945 (*6*). Most of this was in the form of the calcium salt for use in pharmaceuticals.

YEAST

While the production of all yeast items was greatly increased during the war, the development of active dry bakers' yeast and the expanded use of yeast products in pharmaceutical preparations were outstanding. The reported quantities (*6*) of active dry yeast produced during the war years follow: 1940, 3,000,000 pounds; 1943, 7,000,000; 1945 (11 months only), 13,295,000; 1946, 4,000,000.

Active dry yeast was developed for and utilized almost exclusively by the armed forces. It is produced in a manner similar to conventional bakers' yeast but is dried in specially designed equipment to about 8% moisture. In this operation viability and activity are retained, with the result that the product can be stored for long periods in tropical climates. Because of its longer shelf life, active dry yeast seems destined to supplant the old type bakers' yeast.

Also manufactured in increased amounts during the war were yeast products rich in vitamins. Yeast rich in ergosterol was produced and irradiated to supplement our reduced supplies of vitamin D which normally comes from marine sources. Yeast products fortified with B vitamins were employed extensively in foods and pharmaceuticals. Some 12 to 14 million pounds of brewers' yeast were recovered annually, a third of which was debittered for the pharmaceutical trade and the remainder dried and used as an ingredient of livestock feeds.

One other huge potential source of yeast, probably fodder yeast, is the sulfite waste liquor from the pulp industries. This

Table II. Production of Vinegar and Acetic Acid by Fermentation of Specially Denatured Ethyl Alcohol (*6*)

Fiscal Year Ending June 30	Wine Gallons of 190° Proof Alcohol Converted to		
	Total	Vinegar	Acetic acid
1940	7,718,558[a]	......	....
1941	7,876,631[a]	......	....
1942	8,655,531[a]	......	....
1943	13,751,221	6,926,489	6,824,732
1944	19,341,007	7,592,501	11,748,506
1945	16,426,668	7,174,609	9,252,059

[a] No breakdown is given; presumably this is largely vinegar.

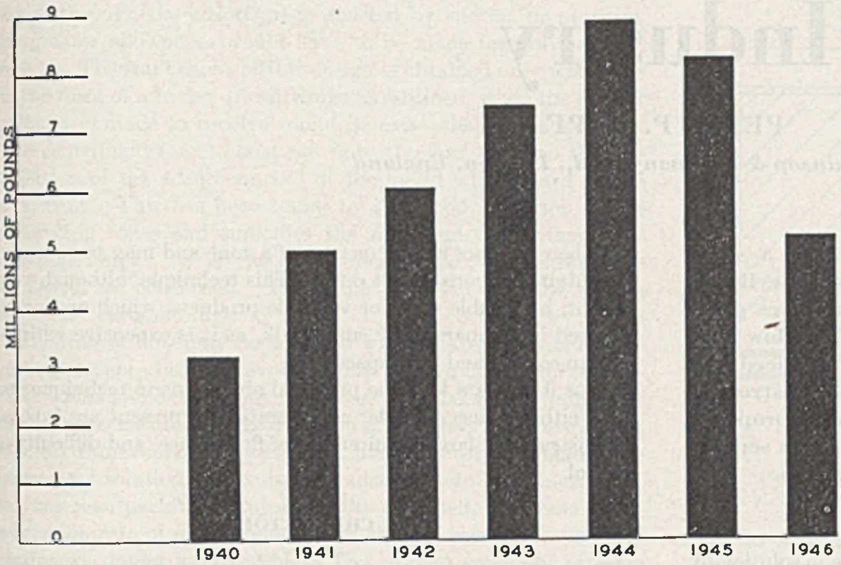


Figure 3. Annual Production of 100% Lactic Acid (All Grades)

source alone, it is estimated, could supply about 270,000 tons of dry yeast annually if fully developed (*13*). Fermentative utilization of sulfite liquor to manufacture lactic acid, ethyl alcohol, acetone-butanol, etc., was given additional study and seems to be entirely feasible.

FUNGAL ENZYMES

Enzymes from microorganisms found many new and extended applications during the war, and their increased commercial production in the future is indicated. Mold enzymes of the mold bran type were manufactured for the first time on a large scale as a substitute for barley malt in grain alcohol fermentations. Later, similar preparations were employed successfully as malt adjuncts in making food sirups. The Eagle Grove, Iowa, plant of the Mold Bran Company has a daily output of about 10 tons of enzymatically active material (*8*).

Bacterial enzyme preparations rich in amylase were also manufactured. These have the property of retaining amylolytic action at relatively high temperatures and for this reason are especially suitable in preliquefying grain mashes and in the textile industry.

ANTIBIOTICS

In December 1941 the supply of penicillin was not sufficient to treat a single patient, whereas today we export a considerable surplus. The increase in production from 1943 through 1946 (*11*) is shown by the graph on page 934. The huge increase during this period coincided not only with the construction of plants utilizing deep tank methods but also with the development of improved strains and with the refinement of culture and recovery techniques.

In 1944 the wholesale value of the 1.6 trillion units of penicillin was given as $35,000,000 (*11*). Estimated at $0.35 per vial of 100,000 units, the 1946 production had a wholesale value of approximately $100,000,000. The penicillin industry is indeed one of our most important commercial fermentations.

The search for other useful antibiotics has received intensive study, especially with a view toward the treatment of diseases caused by acid-fast and Gram-negative organisms. Foremost among the newly developed antibiotics of this type is streptomycin, the discovery and development of which is attributed wholly to American scientists. It is particularly effective against tularemia and shows promise when combined with conventional treatment in tuberculosis. In September 1945 some 3000 grams of streptomycin were produced. By March 1946 this had been increased to 27 kg. and by December 1946, to about 35 kg. a month. Several plants are now in production and the figures given are certain to increase tremendously.

In addition to these two antibiotics, considerable tyrothricin has been made and marketed for specific uses, such as for surface applications, and numerous other antibiotics such as subtilin and bacitracin have received laboratory study and development.

BIOLOGICAL WARFARE

Biological warfare, as defined in the Merck report (*4*), involves the use of germs against human, plant, and animal life, and includes the use of synthetic agents to destroy or distort plant life. During the war an extensive research and development program was carried out in this field in collaboration with Great Britain and Canada. A vast amount of knowledge was gained with regard to the production, properties, and application of biologically active agents.

While not actually employed during the war, the program on biological warfare aptly fulfilled its prime and immediate purpose by precluding the use of similar agents by the enemy. Through the furthering of our understanding of human and animal diseases and in laying the groundwork for the chemical control of plant life processes, this research may be of even greater peacetime significance.

ACKNOWLEDGMENT

The authors are especially indebted to P. B. Jacobs, Northern Regional Research Laboratory, and to C. A. Rager, U. S. Department of Commerce, for supplying numerous data on the production of fermentation products.

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Radial Chromatography in Industry

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Chromatographic adsorption can be effected if a solution is allowed to flow radially through a disk or cylinder from the axis to the perimeter. Adsorption takes place in much the same fashion as in a column. The flow may be assisted by centrifugal forces to give greater speed and clearer zone definition. An apparatus was constructed for this purpose, and the term "chromatofuge" is proposed for this type of plant. It allows some large scale separations with a saving of time, labor, and floor space.

THE separation and purification of substances in solution by chromatographic adsorption have been an object of research for some time. The technique most commonly employed makes use of a column fitted at the bottom with a fritted glass disk and connected to a suction pump. The original Tswett column has been modified from time to time. This column is packed with an adsorbent, and the solution passed through with the aid of suction or by gravity alone. A vast number of substances have thus been isolated or purified from other constituents. Pure materials are thus obtained in a solvent which may be evaporated.

This technique has lately been adapted for industrial purposes, and plants have been erected on a pilot as well as a full commercial scale with substitution of the column by adsorption towers. The cost of this plant and its operation is, however, too high to allow cheaper products to be isolated or purified in this fashion. Various improvements and techniques have been evolved to this end, notably in the production of penicillin. The adaption of existing plants and the recognition of the principles involved in known techniques have been of considerable help in this advance.

LARGE SCALE ADSORPTION

The practice of decolorizing solutions or organic liquids by passage through a filter press packed with an adsorbent, usually animal charcoal, has been in use for a long time. Similarly sand filters packed with adsorbents, usually coal ashes or silica gel, have served the same purpose. In several examined cases analysis of the adsorbent along the direction of flow has shown that the impurities are adsorbed within more or less clearly defined zones, the exact position of which is dependent on the rate of flow, the nature of the adsorbent, and the total amount of impurities present. In the case of a filter press the first plate invariably contains the colloidal impurities, such as carbon and resinous matter. As these have to be regarded as filtered off rather than adsorbed, they have to be ignored in this consideration. The remainder of the impurities, however, will be found to be adsorbed singly in zones and to be in chromatographic series.

A method of chromatographic adsorption used in industry, but hitherto for very special purposes only, is the chromatographic disk, the action of which is analogous to that of a single plate or chamber in a filter press. This has so far been used only for the separation of single substances, such as penicillin. A solution containing several constituents, the isolation of which is desired, might conceivably pass through a succession of such disks, each mounted separately on a suction filter. Every single disk then becomes a zone or part of a zone and may be arranged to contain one constituent only. This technique, although very elegant, is suitable only for valuable products, which are manufactured in comparatively small bulk, as it is expensive with regard to control and floor space.

Thus it appears that the principal objections to technique and plant either in use or under consideration at present are expense of construction, large requirement of floor space, and difficulty of control.

THE CHROMATOFUGE

A new type of construction proposed to facilitate the use of chromatography on industrial scales and for bulk products employs radial rather than longitudinal adsorption. The plant (Figure 1) is capable of being modified to suit any particular purpose. It consists in essence of a cylindrical drum into which the liquid is fed from the axis and passes to the outer perimeter. The cylindrical container (or series of containers) of convenient diameter and height has a perforated outer wall and is lined inside with filter cloth. The axis is in the form of a hollow tube; its wall is also perforated and laid out with filter cloth. This central tube serves as feed pipe. The whole is enclosed in a suitable vessel fitted with an outlet near the bottom. The bottom of the feed pipe may be sealed or open, when a continuous return flow may be arranged.

For the purpose of this investigation a laboratory scale apparatus and a works scale plant were built. The first was made of copper, the perforated walls being substituted by 6-mm. brass wire netting. The lines of design laid down in the sketch were followed. The diameter of the feed pipe was 2.5 cm., and the radius of adsorbent container *A*, 30 cm. Outer container *B* was a copper bowl of 70-cm. diameter, and the height of adsorbent disk *C* was 10 cm. All joints were brazed. The apparatus was driven by a 1-horsepower motor; because it was not sufficiently sparkproof, it was well removed from the apparatus and protected by a tin screen through which the belt was passed to allow the smallest aperture permissible.

The larger scale plant was adapted from an available hydro or works centrifuge such as is commonly used for the drying of crystals. The outer bowl was made of cast iron with direct drainage into a glass-lined sump. The inner container was of galvanized iron with perforated walls to which a lid of the same material was fitted. The feed pipe, which was welded onto this lid, was also made of galvanized iron, and its lower part perforated. The upper part was funnel-shaped. The flow of solution was regulated by adjusting the tap of a drum placed directly over the funnel. This construction was also belt-driven by a gear affixed to the bottom of the construction, the motor being some distance away, and completely nonsparking and vaporproof. These precautions are necessary since, in several cases, solutions containing ether were used, and nonaqueous flammable solvents are common in chromatography. The outer case was also fitted with a lid of galvanized iron, consisted of two well fitting halves, and was fixed to the outer container by means of hinges. To make this lid as tight fitting as possible and to avoid frictional sparking, the feed pipe was fitted with a gland packed with graphite and asbestos at *D*. The diameter of the feed pipe was 15 cm.; the radius of adsorbent container *A* was 125 cm., and its height *C*, 80 cm.

Although a stationary design is possible, where the passage of liquid through the adsorbent is assisted by suction or pressure, far greater allowances would have to be made for gravitational forces. The full benefit of this design is obtained only when it is in the form of a hydro or centrifuge as outlined, when the disk or cylinder is made to revolve round its axis—that is, its feedpipe. The centrifugal forces assist not only the flow but also the distribution of the adsorbent and of the liquid with regard to the adsorbent. This has been found to give good definition of the adsorption zones and embodies the maximum advantage over existing designs, as far as speed, floor space, and adsorptive efficiency are concerned. The name proposed here for such a device is "chromatofuge."

The rate of flow may be adjusted within narrow limits by adjusting the speed of the revolving disk to give maximum separation. This speed must not, however, drop below the minimum necessary to ensure even distribution of pressure. If the cylinder is packed unevenly with adsorbent material, rotation before the passage of solution will cause the adsorbent to rearrange itself, and an even packing is automatically obtained. In some cases, where the rate of adsorption is very slow, it was found that the stationary design is preferable. This applies generally to cases where no great affinity exists between the adsorbent and the adsorbed substance—that is, where the rate of reaction of the adsorption process is less than the rate of flow of the solution under rotation.

In order to adapt the plant to stationary use, the liquid is fed as before under convenient pressure. The bottom of the feed pipe is not sealed off but contains a bean valve which keeps the desired pressure constant and allows for the liquors to be returned through the top.

POSSIBLE USES

If the chromatofuge is used for separation by chemical reaction—that is, by a change in the chemical composition of the constituent which react with the adsorbent—the process is not, strictly speaking, one of chromatographic adsorption. Such reactions, however, may take place at different levels, and the zones are then to be regarded as static rather than fluid. In these cases the centrifugal adaptation is preferable to any other design. The disk is packed with a basic material in the case of acids and with an acid in the case of bases. In all examined cases of separation by chemical reaction, the solution could be passed at maximum speed, and clearly defined, circular, static zones were obtained for each constituent. The zones thus formed cannot be eluted and do not travel on addition of solvent.

Such a design is remarkably adaptable to a variety of problems and may lead to a wide range of new separations and purifications being attempted on an industrial scale. The low cost of construction and the high working speed permit cheaper bulk products to be manufactured in this way. As the sectional area through which the solution is to pass varies directly with the square of the distance from the center clear zones, more even distribution over the disk may be obtained by making the prevalent constituents stay in the outer parts of the disk. This will be possible in many instances either by connection of two chromatofuges in series or careful previous adjustment of the solution.

Collection of more data than have so far been obtained may lead to a theoretical foundation which would correlate adsorption affinity and rate of flow and thus allow the position of each zone to be calculated in advance. It is safe to say that, as the zones approach the perimeter, the rate of flow is slowest; to some extent this counterbalances the fact that constituents with the smallest affinity for the adsorbent will be found there. Gravitational forces would also come into play and would have to be allowed for. It was hoped that a clearer understanding of the theory as well as a balancing of the gravitational and centrifugal forces would be derived by replacing the cylindrical adsorbent container with one of the shape of an inverted cone. This might have given clearer zones and, in the case of fluid chromatograms, might have allowed these zones to be continuously removed along the sloping perforated side at various distances from the center. Experiments so far, however, have not shown any advantage in such a design.

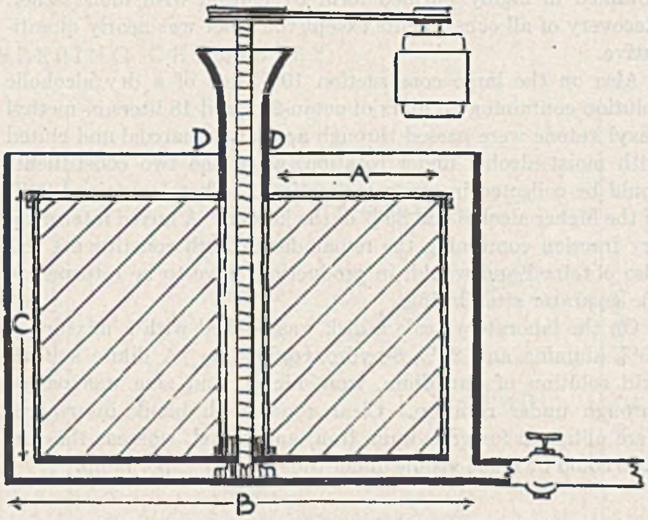

Figure 1. Chromatofuge

ELUTION

The final separation of the single pure constituents has to follow known practice. Usually this will be done by elution with a suitable solvent, which may be the original solvent adulterated with water or a lower aliphatic alcohol. If the top of the adsorbent container is removed, however, the single zones may be dug out by hand or with an adjustable stencil. For industrial products the only feasible method available at present is elution. The eluent will be passed through the chromatofuge in the same manner as is the solution—that is, under centrifuging—or statically—that is, under pressure while the apparatus remains stationary.

PRACTICAL APPLICATION

A variety of separations known and described in the literature were carried out on the constructions outlined, and it was found in each case that separations which have been carried out on a column gave exactly analogous results on the chromatofuge, the single zones being much clearer in definition. The sequence of these zones was identical with that found in columns, and, in the case of inorganic solutions, the chromatographic series remained unaltered.

The procedure in each case involved lining of the outer and inner walls with filter cloth and close packing of the container with adsorbent. The container was then allowed to revolve at maximum speed, after which more adsorbent had to be added to fill the available space. It was then spun dry for a few more minutes before the solution was passed through the feed pipe and the effluent collected.

In this manner on the smaller construction a solution of 100 grams of quinidine and 50 grams of quinine in 2 liters of ether gave two concentric zones with a blank space between them. These zones were eluted without rotation by passing the solvent under pressure and collected individually. This operation was carried out with 2.5 liters of ether containing 5% methanol. The adsorbent used was activated alumina.

On the large construction, packed with barium carbonate, a mixture of 25 liters of oleic acid and 60 liters of ricinoleic acid in 20 liters of ether were similarly separated, both compounds being obtained in highly purified form by elution with moist ether. Recovery of all constituents except the ether was nearly quantitative.

Also on the large construction 100 liters of a dry alcoholic solution containing 25 liters of octan-2-ol and 18 liters of methyl hexyl ketone were passed through activated charcoal and eluted with moist alcohol under rotation, when the two constituents could be collected in separate fractions. These contained 90% of the higher alcohol and 85% of the ketone. A mixed intermediary fraction containing the remainder of both constituents was also obtained and would, in production, have to be returned to the separator after drying.

On the laboratory scale a disk was packed with a mixture of 75% alumina and 25% 8-hydroxyquinoline. A dilute sulfuric acid solution of vanadium, iron, nickel, and zinc was passed through under rotation. Clear zones with blank interspaces were obtained for vanadium, iron, and nickel, whereas the zinc zone could be made visible under the mercury vapor lamp.

A packing of activated alumina was used for the purification of castor oil on the works scale. A dark oil (82% glycerol triricinoleate) containing ricinoleic acid, dihydroxystearic acid, and colloidal impurities was thoroughly dried and passed through the chromatofuge at a rate of 500 liters in 1.5 hours. A little dry ether was added to reduce the viscosity and assist passage. The effluent was found to consist of ether and pure, colorless, neutral castor oil in what could be regarded as quantitative yield. On examining the opened container under ultraviolet light, and by taking analytical samples along a given diameter, clear zones for each constituent were identified. The colloidal impurities were adsorbed or, more likely, filtered off in a small zone round the central tube, the other constituents being separated by blank zones of clear definition. Castor oil was found loosely adsorbed in the outermost zone bordering on the perimeter. Elution with ether containing 5% methanol under rotation allowed the zones to be collected individually.

It is hoped that these experiments and their publication will widen the scope and application in industry of chromatography, and provide a means for using the wealth of experimental results of research workers in this field in works practice.

ECONOMIC PROCESS OPERATION

Method for Determination of Optimum Operating Conditions

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A mathematical method is presented for the positive determination of the process conditions that give maximum profit for a plant operation. The complete interrelations of the process variables and the costs of additional units of each of the variables are necessary for the calculation. Two illustrative examples are given, and the special requirements of the method are discussed.

ONE of the most important and, at the same time, most difficult problems of a process engineer is the determination of the optimum operating conditions of a plant. The decisions as to what temperatures, pressures, flows, etc., lead to maximum plant monetary return can easily mean the difference between profit and loss for an entire organization. The operating conditions chosen are usually based on the engineer's judgment of the economic and engineering relations involved and ordinarily have little or no mathematical background.

In the present article a mathematical system is developed for organizing engineering and economic data to make possible a complete, positive solution for the optimum operating conditions of a plant on the single basis of maximum monetary return. The mathematics of the method is exact, and the results obtained can be made as accurate as the data used.

MATHEMATICS OF METHOD

A simple and familiar example of economic design is the calculation of the optimum thickness of insulation or lagging for a steam line. Figure 1 gives a typical set of data for averaged weather conditions. The cost of the steam lost, the cost of the lagging, and the total cost, all in dollars per year, are plotted against the thickness of lagging in inches. The steam loss in M pounds is designated as a, and the thickness of lagging in inches is designated as b. Also the cost of an additional M pounds of steam is A, and the cost per year of an additional inch of lagging is B. The total cost per year of maintaining the steam flow is T. With these definitions B is the slope of the cost-of-lagging curve of Figure 1. Also da/db is the change in the steam loss with change in thickness of lagging. Then $A(da/db)$ is the change in the cost of the steam loss with change in thickness of lagging—that is, $A(da/db)$ is the slope of the cost-of-steam-loss curve of the figure. Plots of these slopes, B and $-A(da/db)$, are given by the broken curves of Figure 1.

At the optimum design the total cost curve goes through a minimum cost point. But an additional property of the optimum is that the slopes of the cost lines, $A(da/db)$ and B, are equal and opposite in sign. This is shown graphically in Figure 1 where the broken line plots of $-A(da/db)$ and B cross at the minimum cost point. This same property can be stated algebraically as follows: The slope of the total cost curve, dT/db, is the sum of the slopes of the cost-of-steam loss and cost-of-lagging curves, and at the minimum cost point the slope of the total cost curve, dT/db, is zero. Then the equation

$$A(da/db) + B = dT/ab = 0 \qquad (1)$$

is true at the minimum cost point. This equation can also be written as $A\ da + B\ db = 0$. This simple relation can be used to define the economic optimum for any system of two variables. It states that at the economic optimum an additional dollar outlay yields an additional dollar return. If the return is more than a dollar, then the outlay should be increased, and if the return is less than a dollar then the outlay should be decreased. This assumes that there are no discontinuities in the immediate vicinity of the optimum values.

Minimum cost points as in Figure 1 can, in general, be used to obtain the optimum values of only two variables. But the relation of Equation 1 can be applied to any two variables of a number of variables and can be used to define the optimum values for systems of any number of variables. This is the basis of the present method. The example of Figure 1 just discussed is for the original design of a steam line. However, Equation 1 can be applied equally well to types of engineering variables other than equipment design. The remainder of this article will deal only with the process variables, the temperatures, pressures, flows, etc., of continuously operating plants.

Equation 1 can be used to define the economic optimum for any operation or design that can be reduced to two variables. In the extension of this relation to systems of more than two process variables the following nomenclature will be used:

a, b, $c \ldots e$ = process variables measured as units
A, B, $C \ldots E$ = cost or value in dollars of an incremental unit of the corresponding process variable

In general, the desired gains of a process will be taken as dependent variables, and the operating conditions by which they are accomplished will be taken as independent. Thus in the example of Figure 1, the steam loss can be considered to be a dependent function of the thickness of lagging. The signs of the cost terms $A, B, C \ldots E$ are taken as positive for product values and other plant gains, and negative for necessary outlays, such as compressing power or heat.

For a system of n process variables the relations for defining the optimum conditions corresponding to Equation 1 for two variables, can be written as follows:

$$A(\partial a/\partial b)_{c\ldots e} + B = 0^{*} \tag{2ab}$$

$$A(\partial a/\partial c)_{b\ldots e} + C = 0 \tag{2ac}$$

$$B(\partial b/\partial e)_{a\ldots c} + E = 0 \tag{2be}$$

etc., for any other combination of two variables

These equations are, of course, simply Equation 1 for two variables with other variables present but considered constant. Equation 2 is true for any combination of two variables at the optimum conditions and can be used to define completely the optimum operation. For a system of n process variables only $n-1$ of the equations of Equation 2 can be considered to be independent. The remaining relation necessary to solve for the n unknowns consists in the interrelations of the process variables of the plant.

In the use of Equation 2 to solve for the optimum conditions for a given operation, three types of data are required: First, the complete interrelations of the process variables must be known in the vicinity of the optimum conditions; second, the values of the partial terms—$(\partial a/\partial b)_{c\ldots e}$, $(\partial a/\partial c)_{b\ldots e}$, etc.—resulting from these interrelations are required; and third, the cost in dollars of additional units of the process variables—values of $A, B, C \ldots E$—must be known, either as constants or as functions of $a, b, c \ldots e$.

It will be noted that the cost terms are for incremental units of the process variables and are not averaged values of total cost divided by total number of units. Thus the cost of an additional M pounds of steam from a boiler would include the cost of the additional fuel required and would not include the labor or overhead costs which are constant and independent of small changes in the amount of steam.

For an operation with two variables a direct solution for the optimum values can be obtained as was shown in the steam loss–lagging illustration. For operations with three or more variables, however, such direct solutions are not generally possible, and trial and error methods must be used. The solutions are not difficult to obtain, and many variations in the trial and error procedures can be used. The requirements for the final operating conditions are that they be consistent within themselves and that they satisfy the system of equations of Equation 2. A simple procedure and one that is frequently the best is to estimate a consistent set of operating conditions and to substitute these values in Equation 2. The results are studied, and the changes required to make the equations more nearly true are estimated. The substitutions are then repeated. With practice a rapid approach to the optimum conditions can be made in this manner.

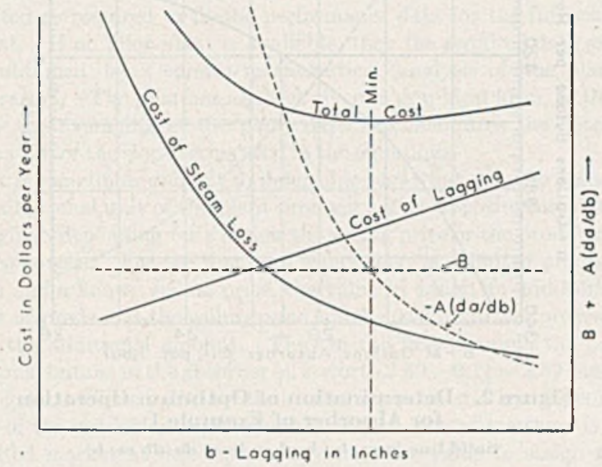

Figure 1. Determination of Optimum Thickness of Lagging for a Steam Line

A more elaborate and general trial and error procedure for solving for the optimum values of $a, b, c \ldots e$ from engineering and economic data is given below. One variable, a, is selected as being dependent and the remainder, $b, c \ldots e$, as being independent. The steps of the procedure are as follows:

1. Estimate a set of reasonable values for the independent variables $b, c \ldots e$ and determine the resultant value for the dependent variable a so as to obtain a complete estimated operation.
2. With the values from step 1 and the cost data substitute for A and B in Equation 2ab, and solve for the value of $(\partial a/\partial b)_{c\ldots e}$. Find the value of b required to give this partial with the other independent variables considered to remain constant at the estimated values. Similarly substitute for A and C in Equation 2ac, and solve for $(\partial a/\partial c)_{b\ldots e}$ and the resulting new value of c. This calculation is repeated for each of the independent variables so as to give a new set of values for $b, c \ldots e$.
3. These new values of the independent variables are used in place of the estimated values of step 1, and the calculation of step 2 is repeated. This is continued until the assumed and calculated values check. These final values are the desired optimum operating conditions.

Frequently modifications of this procedure are necessary, and these depend on the individual conditions.

EXAMPLES

Natural Gasoline Absorber. A twenty-plate absorber is operated to recover butanes and casinghead gasoline from a natural gas. The feed to this column is constant at 1.10 million (M) cubic feet per hour of gas which contains 448 gallons of iso- and n-butane. The butane recovery and the rate of flow of the lean oil are selected as the two principal variables of the operation, and the relation between them is shown by the solid line curve of Figure 2. This curve was obtained by smoothing and extending plant data with the aid of calculations so that the final curve represents averaged, most probable values. The market price on butane is 2.5 cents per gallon, and the cost of handling an

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[*] A discussion of the extreme values of functions of several variables and a rigorous derivation of this system of equations as a property of such values are given in Courant's "Differential and Integral Calculus," Vol. 2, pp. 183–208, New York, Nordemann Pub. Co., Inc., 1936.

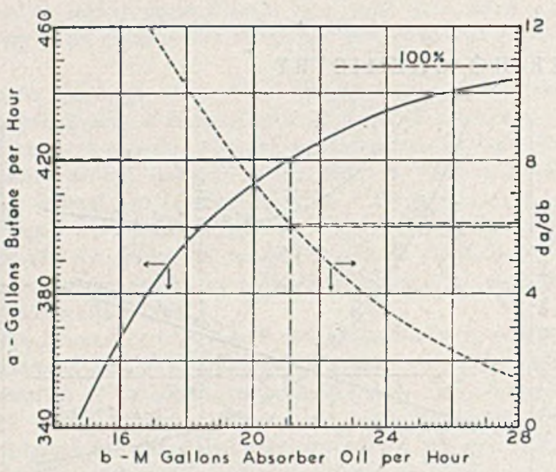

Figure 2. Determination of Optimum Operation for Absorber of Example 1

Solid line, a vs. b; broken line, da/db vs. b

additional gallon of butane in the remainder of the plant is 0.11 cent, so that the value of additional butane in the rich oil from the absorber is 2.50 − 0.11 = 2.39 cents per gallon. The cost of additional cold lean oil at the top of the absorber is 14.6 cents per million gallons. This includes the cost of stripping, pumping, and cooling the oil and of repressuring the additional light gases absorbed, but it does not include any costs such as equipment write-off or labor that does not change with the amount of oil pumped. This value of 14.6 cents per million gallons varies but slightly with total amount of absorption oil and can be considered to be constant for the range under consideration.

It is desired to know the optimum amount of absorber oil for this operation and the resultant butane recovery.

For the solution the dependent variable a is taken as the butane recovery in gallons per hour, and the independent variable b is taken as the flow of absorber oil in million gallons per hour. Then from the values given, $A = 2.39$ cents and $B = -14.6$ cents. The slopes of the curve of a vs. b of Figure 2 are measured and plotted to give the broken curve of da/db vs. b. For this operation Equation 1 becomes

$$A(da/db) + B = 2.39\,(da/db) - 14.6 = 0 \tag{1}$$

so that $da/db = 6.1$. The corresponding values of $a = 420$ gallons butane recovery and $b = 21.1$ M gallons of absorber oil are read from Figure 2 as marked. These are the desired optimum operating conditions and will give maximum plant profit.

As a further example, suppose that the price of butane is increased to 3.0 cents per gallon. Then the value of the butanes in the absorber oil is 3.0 − 0.11 = 2.89 cents per gallon and Equation 1 becomes

$$2.89\,(da/db) + 14.6 = 0 \tag{1}$$

so that $da/db = 5.5$. From Figure 2 the corresponding butane recovery is 427 gallons per hour with a lean oil flow of 22.2 M gallons per hour. Thus the recovery of an additional 427 − 420 = 7 gallons of butane per hour was made economic by the 0.5 cent increase in price.

Gas Reactor. A high temperature gas reactor operates with a constant fresh feed rate and has a catalyst of substantially constant activity. The feed gas is heated, mixed with hot recycle gas, and passed over the catalyst. The variables selected for the operation are:

a = yield of product, % of theoretical
b = inlet gas temperature, ° F.
c = recycle ratio, volumes of recycle gas/volume of fresh feed

where a is the dependent variable, and b and c are independent. Smoothed, averaged yield data for this reactor are given by the solid curves of Figure 3 as yield against inlet temperature for constant amounts of recycle (a vs. b at constant c). Cost studies show that 1% of theoretical product for one day is worth $73.00 at the discharge from the reactor. This value is the selling price less the cost of recovering and purifying the additional amount. To recirculate a volume of recycle gas equal to the constant volume of feed gas costs $54.00 per day, and this includes increased costs in the product recovery system because of dilution. An additional degree of temperature at the reactor inlet for one day costs $0.60 for the fresh feed to the reactor and $0.55 for a volume of recycle gas equal to the volume of fresh feed.

For this operation it is desired to know the optimum reactor inlet temperature and the optimum recycle ratio together with the resultant product yield in per cent.

The solid curves of Figure 3 give a vs. b at constant c, and the slopes of these lines are values of $(\partial a/\partial b)_c$. These slopes are measured and plotted against b to give the broken lines of Figure 3. The data of Figure 3 are then cross-plotted as yield in per cent against recycle ratio for constant inlet temperatures (a vs. c at constant b) to give the solid curves of Figure 4. The slopes of these curves are values of $(\partial a/\partial c)_b$ and are plotted as the broken lines of Figure 4.

From the costs given for one day's operation,

$$A = +73.0 \qquad B = -(0.60 + 0.55c) \qquad C = -54.0$$

Then Equations 2ab and 2ac become

$$73.0(\partial a/\partial b)_c - (0.60 + 0.55c) = 0 \tag{2ab}$$

and

$$73.0(\partial a/\partial c)_b - 54.0 = 0 \tag{2ac}$$

from which $(\partial a/\partial c)_b = 54.0/73.0 = 0.74$. The temperature and recycle ratio at which these two equations hold are the optimum ones and give maximum plant monetary return.

It is next necessary to select a convenient trial and error procedure for solving for the optimum conditions, and the one chosen is as follows: A reasonable amount of recycle c is assumed, and the corresponding temperature b is found from Figure 4 for the value

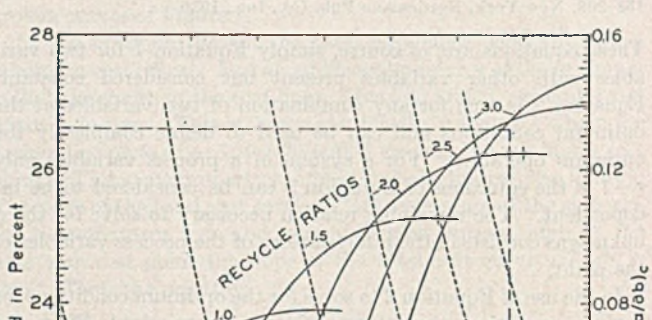

Figure 3. Interrelations of Process Variables for Gas Reactor of Example 2

Solid lines, a vs. b at constant c; broken lines, $(\partial a/\partial b)_c$ vs. b

$(\partial a/\partial c)_b = 0.74$. The value of $(\partial a/\partial b)_c$ corresponding to these values of c and b is then read from Figure 3. This is compared with the value of $(\partial a/\partial b)_c$ obtained by substituting for c in the above Equation 2ab. The recycle rate at which these two values of $(\partial a/\partial b)_c$ are equal satisfies Equations 2ab and 2ac and is the optimum recycle.

As a first estimate $c = 1.5$ is assumed. Then at $(\partial a/\partial c)_b = 0.74$ on Figure 4 the corresponding temperature b is 1264° F., and these values of b and c in Figure 3 give $(\partial a/\partial b)_c = 0.044$. The corresponding value found by substituting $c = 1.5$ in Equation 2ab is $(\partial a/\partial b)_c = 0.0195$. Evidently these two values of 0.044 and 0.0195 for $(\partial a/\partial b)_c$ do not check, and a higher recycle rate is required. The succeeding trial and error calculations are summarized in the following table:

c Estd.	b from Figure 4, ° F.	$(\partial a/\partial b)_c$ From Figure 3	$(\partial a/\partial b)_c$ From Equation 2ab
1.5	1264	0.044	0.0195
2.0	1279	0.029	0.0233
2.5	1291	0.025	0.0270
2.3	1287	0.0265	0.0256
2.35	1288	0.0260	0.0260

Evidently $c = 2.35$ gives the same values of $(\partial a/\partial b)_c$ by both methods and so satisfies Equations 2ab and 2ac. Then the desired optimum conditions are 2.35 for the recycle ratio and 1288° F. for the inlet gas temperature. The resultant product yield is 26.6% of the theoretical. These values are marked off on Figures 3 and 4. Operation at these conditions will give maximum plant profit.

SPECIAL REQUIREMENTS

The first step in the analysis of a plant by the method given here is the division of the total plant into subplants. In general these subplants should be the smallest possible units that can be completely separated from the remainder of the plant. The requirement is that all streams to and from the subplant be known. Thus in the first example the absorber could be considered independently of the stripper because the flows and compositions of all of the streams could be determined.

The next step, the selection of the variables of the operation, is an important one. In general these variables should be as few as possible and should include only the principal control conditions together with the resultant plant yields. Frequently it is possible to combine what would seem to be separate variables. There are many items that might seem to be variables but should not be included in the calculations for a number of reasons. Thus items that cannot be controlled, such as the atmospheric conditions, are omitted. Many minor variables can be omitted with negligible effect on the calculated optimums. Frequently economically important items are not variables simply because they do not vary. Thus in the first example the principal monetary return from the absorber operation results from the recovery of the pentanes and heavier hydrocarbons in the natural gas; but at the optimum lean oil rates substantially all (99.9%) of these heavier components are recovered, so that this absorption can be considered constant and independent of small changes in the lean oil rate. Then only the butane recovery need be considered for the product yield variable. It is the rates of change of the costs of the variables at the optimum conditions and not their total values that determine their comparative importance in an analysis of this type.

For the application of the method it is necessary to know the complete interrelations of the process variables of the subplant, and these are frequently difficult to determine. Data of this type are generally considered necessary for good operation. The values used should be based on the actual measured performance of the plant and should be as accurate as possible. The primary difficulty in obtaining these interrelations is in separating the effects of the various variables. The operation can be conveniently analyzed if a carefully scaled pilot plant is available. In a series of controlled runs the effects of changing each variable separately can be determined so that a complete set of operating curves for the pilot plant can be obtained. These curves can be shifted as required to fit the performance data for the full scale plant. If no pilot plant is available, then the required data can be obtained by a careful mathematical analysis of the plant operation. The relations are best given in graphical form, as this aids the averaging of the plant data and facilitates the determination of the slope terms used in the equations.

It is sometimes difficult to determine just what value to assign an additional unit of the plant product. Two opposite cases can be given depending on whether the selling price or the producing price govern. For the first case where there is a limited production and a known selling price, the value to assign an additional unit of product is the selling price less the cost of further processing the additional amount. Thus in the first example the additional butane in the absorber oil is worth 2.50 − 0.11 = 2.39 cents per gallon. This value is based on selling price and is independent of the producing cost. For the second case where there is a limited market at below-plant capacity, the value to assign an additional unit of product is the cost of the raw materials plus the cost of the processing done. The value assigned, then, is the cost of replacing the product unit and is independent of the selling price. Other cases between these extremes could be given and these must be analyzed individually on the basis of maximum plant profit.

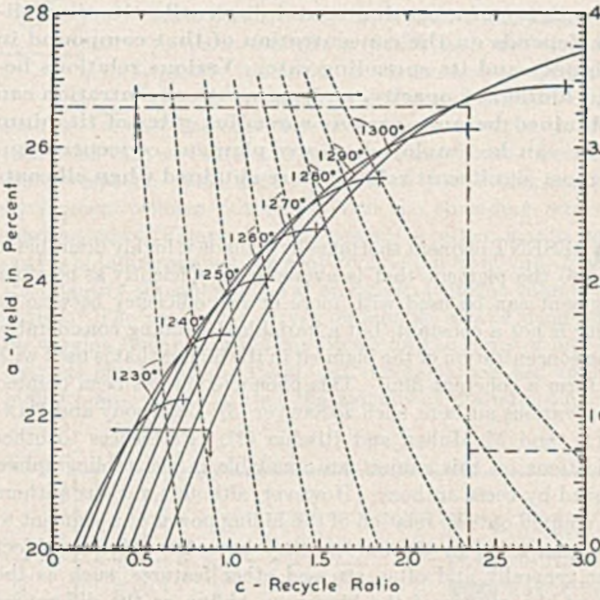

Figure 4. Cross Plot of Figure 3

Solid lines, a vs. c at constant b; broken lines, $(\partial a/\partial c)_b$ vs. c

An application of the method that is frequently useful is to select two variables for study and consider the remainder of the operation constant. Equation 1 is substituted to give the optimum value for the independent variable. In this way a quick check can be made on an operation suspected of being uneconomical without the necessity of the longer and more involved complete calculation. It will be noted that an optimum operation is a balance between at least two variables. Equation 1 contains two terms. It sometimes happens that the efficiency of a process is judged on the basis of a single variable, and uneconomical operation may result. Thus if the absorber operation of the first example were judged solely on the butane recovery, with the lean oil considered to have no cost, then excessive and expensive amounts of lean oil would probably be used. A butane recovery of 99% could be reached, but the over-all return would be decreased. As an additional point, factors of safety should not be included in these calculations. Thus in the same example more than the calculated amount of lean oil would not be used just to be safe.

Of fundamental importance in studies of this type is the fact that only the costs of additional units of the plant variables are required in determining the operating conditions that give maximum plant profit. In Figure 1 the slopes of the cost curves and not their total values determine the minimum cost point. In Equation 1 the term A is the cost per unit of the incremental amount da and is not an averaged total cost. The necessary fixed overhead costs of a plant, such as supervision, depreciation, taxes, etc., are substantially constant and change independently of small changes in the plant operating conditions. However important these fixed costs may be to total plant profit, they do not affect the operation that gives maximum plant profit. The reflux to a distillation column is not changed because a vice president's salary is increased. Then any elaborate and arbitrary system of proration of such fixed costs among subplants or products, however "fair" or "reasonable" it may be and however valuable to management as a "true picture," gives values that are of no use to an engineer in determining the optimum process conditions. Thus in determining the optimum amount of steam for a process, the cost of the steam should not be increased because the total steam production has decreased and the relatively constant boiler house overhead is distributed among fewer pounds of steam. A value obtained in this way has no connection with the actual dollars involved in changing the amount of steam. In general for the methods of this article any divisions of single costs that are necessarily arbitrary are also necessarily valueless. The cost calculations are for the single basis of maximum plant profits, and, as a result, the terms used do not need to have arbitrary values. Each cost term ($A, B, C \ldots E$) can have only one true numerical value at the optimum operation, however uncertain and difficult to determine this value may be.

Economical Use of Titanium Dioxide in Enamels

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The opacity of a coating containing rutile titanium dioxide depends on the concentration of that compound in the binder and its spreading rate. Various relations between hiding, or opacity, and pigment concentration can be obtained because various spreading rates of titanium dioxide can be employed at any pigment concentration. The most significant relations are obtained when all coatings are applied as they would be in actual use. Baking enamels applied at a constant dry film thickness show maximum hiding at a pigment volume of 25%. This hiding, however, can be duplicated with 25–30% less titanium dioxide per unit surface area by lowering the pigment volume to 16% and increasing the dry film thickness by about 10%.

PRESENT pigment shortages have made it highly desirable to use the pigment that is available as efficiently as possible. A pigment can be used with more or less efficiency because its opacity is not a constant, but a variable depending considerably on the concentration of the pigment in the binder that is used with it to form a coherent film. This phenomenon has been pointed out by various authors, such as Sawyer (*3*), Lightbody and Dawson (*1*), and McMullen and Ritchie (*2*). References to other publications on this subject are available in the bibliographies compiled by these authors. However, although various authors have pointed out the relation of the hiding power of a pigment to its concentration in the binder, they have treated the subject rather generally and often stressed other features, such as the effect of the nature of the binder on hiding or the differences between wet-film hiding and dry-film hiding. The intent of this paper is to show specifically how the phenomenon of change in hiding power with change in pigment concentration is related to the efficient use of rutile titanium dioxide in white enamels.

SOURCE OF DATA

Data were obtained by Lightbody and Dawson (*1*) on the hiding of white baking enamels made by incorporating increasing amounts of rutile titanium dioxide into a urea-alkyd vehicle of 40% nonvolatile matter by weight. Their method of determining hiding was described in detail in the original paper. Briefly, it consisted of using doctor blades to lay down films on black and white hiding power charts and determining contrast ratios from measurements made on the dried films with a Hunter reflectometer. The results that were obtained and several constants of the enamels are shown in Table I. The titanium dioxide ranged from 1 to 8 pounds per gallon, the pigment volumes from 7.9 to 46.5%, and the consistencies from 54 to 82 Krebs units. Five doctor blade clearances were used with each enamel. Actual spreading rates were determined by striping and ashing definite areas of film, considering the ash to be titanium dioxide, and relating this to the quantity of wet paint through the amount of titanium dioxide per gallon of paint indicated by the formulation. To expand the data, contrast ratios at spreading rates other than those actually used were determined by interpolation on curves of contrast ratio, or log (10 × contrast ratio), plotted against spreading rate of enamel. (Since contrast ratios are less than 1 their logarithms would be negative if they were not multiplied by some factor such as 10.) Since these relations were approximately linear, the interpolations should have been fairly accurate. Thus numerous relations between contrast ratio, pigment volume, and spreading rate of enamel are available from these data. Spreading rate of enamel was readily converted to the more useful quantity, spreading rate of titanium dioxide, since the titanium dioxide per gallon was known for all enamels.

FUNDAMENTAL RELATIONS

The relations of contrast ratio, pigment volume, and spreading rate of titanium dioxide obtained from these data are shown diagrammatically in Figure 1. Here contrast ratio is plotted against pigment volume with a family of curves showing various spreading rates of titanium dioxide, expressed as pounds per 1000

Table I. Tests on Enamels with Rutile Titanium Dioxide as Pigment

(Vehicle, 40% solids by weight; binder, 40% urea resin/60% alkyd resin by weight; thinner, mixture of toluol, xylol, and butanol)

TiO_2, Lb./Gal. of Enamel	Pigment Vol. in Solids, %	Consistency, Krebs Units	Blade Clearance, Inch	Spreading Rate, Sq. Ft./Gal. of Enamel	Hiding, Contrast Ratio
1.0	7.9	54	0.004	990.5	0.783
			0.006	653.8	0.824
			0.008	418.9	0.896
			0.010	349.7	0.919
			0.012	278.1	0.931
2.0	16.1	57	0.004	944.8	0.844
			0.006	586.2	0.913
			0.008	407.6	0.951
			0.010	314.0	0.968
			0.012	260.1	0.978
3.0	21.5	59	0.004	894.9	0.875
			0.006	578.0	0.938
			0.008	383.8	0.968
			0.010	314.2	0.977
			0.012	258.4	0.982
4.0	27.2	61	0.004	836.8	0.896
			0.006	526.3	0.950
			0.008	365.8	0.972
			0.010	288.9	0.983
			0.012	246.4	0.985
5.0	32.6	63	0.004	768.6	0.903
			0.006	485.6	0.950
			0.008	355.9	0.975
			0.010	287.3	0.982
			0.012	232.5	0.989
6.0	37.7	68	0.004	733.1	0.906
			0.006	483.7	0.953
			0.008	342.6	0.976
			0.010	277.5	0.985
			0.012	229.2	0.989
7.0	42.2	78	0.004	706.2	0.910
			0.006	453.1	0.954
			0.008	337.6	0.976
			0.010	274.4	0.985
			0.012	220.7	0.990
8.0	46.5	82	0.004	709.6	0.912
			0.006	448.6	0.958
			0.008	327.3	0.979
			0.010	265.6	0.987
			0.012	210.4	0.992

square feet of hiding chart. Other methods of plotting these three variables could be used if desired. Similar relations would exist with other binders, but they would differ slightly because of differences in such properties as the color and the pigment-dispersive powers of the binder. Using only pigment volume and spreading rate of titanium dioxide to determine hiding assumes that the thinners used will have a negligible effect on the results, but this is not an unreasonable assumption, since there is no apparent reason why the hiding of dry films should be affected by practicable variations in the thinners used for application purposes. On actual test Lightbody and Dawson (*1*) found that a change in the type of thinner and a change in the evaporation rate of one type of thinner had no effect on dry-film hiding.

As an illustration of the significance of these relations, suppose that a paint with a pigment volume of 17% were applied so that the spreading rate of the titanium dioxide was 5 pounds per 1000 square feet. This would give a contrast ratio of about 0.950. If it were desired to increase this hiding by increasing the titanium dioxide to 7 pounds per 1000 square feet, it could be done by applying more of the same paint, since the contrast ratio would rise to about 0.973, as indicated for 7 pounds of titanium dioxide per 1000 square feet at a pigment volume of 17%. On the other hand, it might be undesirable to increase the amount of wet paint applied, and an attempt would be made to obtain 7 pounds of titanium dioxide per 1000 square feet of surface by putting more pigment into the paint. If this necessitated an increase in pigment volume to 25%, no change in hiding would be obtained. If the new pigment volume were lower than 25%, some increase would be obtained. If it were over 25%, a decrease in hiding would be obtained.

This illustration serves to demonstrate that a knowledge of the fundamental hiding relations indicates certain possibilities but does not provide a conclusive answer to the question, "What is the best pigment volume to use in a white enamel made with rutile titanium dioxide?"

HIDING AT VARIOUS PIGMENT VOLUMES

Various curves showing hiding against pigment volume, or the equivalent, have appeared in the literature. These have been helpful to the formulator because they have shown that hiding tends to pass through a maximum, and that consequently there is no advantage in exceeding a certain pigment volume. The best pigment volume to use, however, has never been obvious, partly because the curves that have appeared have been dissimilar in many respects. This is to be expected since hiding is not fixed by pigment volume but varies with the spreading rate of the pigment also (Figure 1). Expressed in other words, various curves of hiding against pigment volume can be obtained, because the quantity of paint applied at any given pigment volume can be varied. The variety of curves obtainable can be demonstrated by varying the application conditions for the series of urea-alkyd enamels previously described. If these enamels are applied to hiding power charts so that the amount of titanium dioxide per

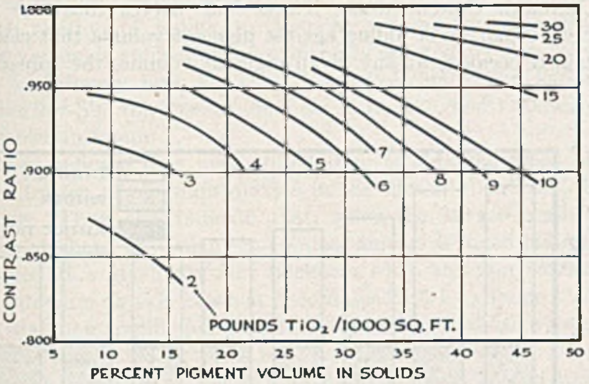

Figure 1. Fundamental Hiding Relations of Rutile Titanium Dioxide in a Urea-Alkyd Vehicle

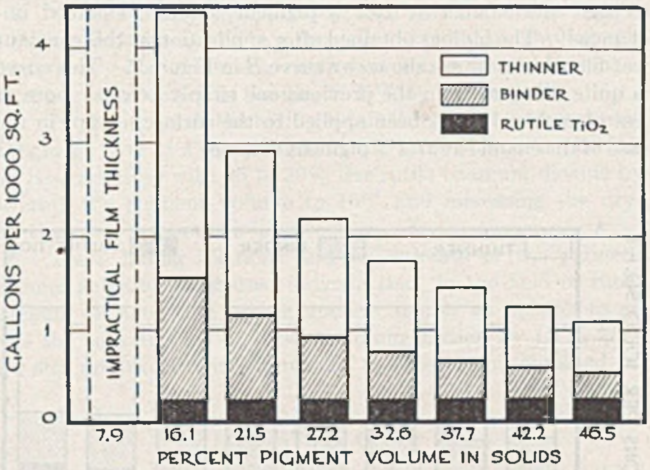

Figure 2. Application of a Series of Enamels at Constant Spreading Rate of Titanium Dioxide

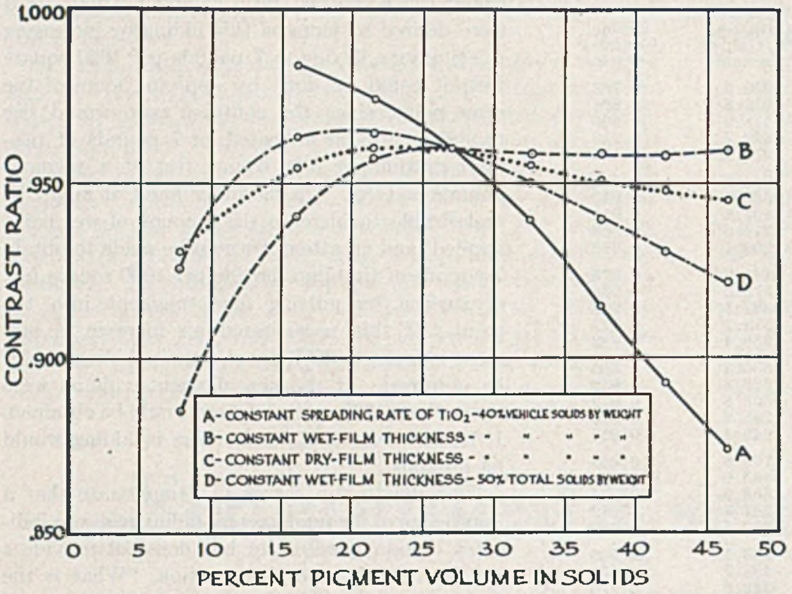

Figure 3. Hiding of Rutile Titanium Dioxide in a Urea-Alkyd Vehicle

square foot remains constant at some arbitrarily selected value, the films will be of the compositions shown in Figure 2. The wet-film thickness and the dry-film thickness decrease with increasing pigment volume. The amount of binder used with the constant quantity of titanium dioxide changes as required by the changing pigment volume. The hidings obtained under these conditions are shown by curve *A* in Figure 3. Since this curve represents a constant spreading rate of titanium dioxide, it is really one of the family of curves shown in Figure 1. It demonstrates once again how the hiding obtainable with a given amount of titanium dioxide is greatly enhanced by the presence of greater quantities of binder, even when that binder is very transparent and practically colorless. If these enamels were to be applied in practice, however, they would obviously not be applied at such unequal wet-film thicknesses.

If they are applied at a constant wet-film thickness the films will be as shown in Figure 4. The amount of titanium dioxide and the dry-film thickness increase with increasing pigment volume. To facilitate comparison of the results with those obtained by the previous system of application the wet-film thickness was selected so that the enamel at 27.2% pigment volume remained unchanged. The hidings obtained after application at this constant wet-film thickness are shown by curve *B* in Figure 3. This curve is quite different from the previous one simply because more or less of each paint has been applied to the surface, except in the case of the enamel at 27.2% pigment volume.

Again there is some question as to whether this system of application is representative of a practical application of these enamels, particularly since the enamels are of unequal consistency, increasing from 54 to 82 Krebs units as pigment volume increases (Table I). If they are applied so that a constant dry film thickness is obtained, with this thickness selected so that again the 27.2% pigment volume paint remains unchanged, the films will be of the compositions shown in Figure 5, and the hidings will be those shown by curve *C* in Figure 3. This curve reaches a peak at about 25% pigment volume and shows a much more distinct drop in hiding above this pigment volume than does curve *B*, which was obtained at a constant wet-film thickness.

HIDING AFTER MODIFYING THINNER CONTENT

The three curves discussed were obtained with a particular series of paints by specifying certain application conditions. Another series of paints made with similar materials would be expected to give similar results on application at the same spreading rate of titanium dioxide or the same dry-film thickness, but various results could be obtained on application at any given wet-film thickness, because the hiding of any paint would be influenced by the quantity of thinner that it contained.

In the series under discussion, the thinner in the vehicle was held constant at 60% by weight regardless of the pigmentation. If this series were modified by adding or subtracting thinner so that the total solids in each paint were 50% by weight, and then these paints were applied at a constant wet-film thickness, the films would be of the compositions indicated in Figure 6. The areas below the dashed lines indicate the compositions before modification. There is no significance in the selection of 50% total solids by weight, since under these conditions the paints decrease considerably in consistency as pigment volume increases. It has been used merely to illustrate how the selection of certain conditions can cause differences in the hiding power–pigment volume relations. The probable hidings of these modified paints were obtained from the data on hand by calculating the spreading rate of the titanium dioxide at each pigment volume and using the hiding actually obtained at this spreading rate and pigment volume. The results are shown as curve *D* in Figure 3. This curve is quite different from curve *B*, which was also obtained at a constant wet-film thickness. It has a more distinct peak and reaches this peak at a lower pigment volume.

General Conclusions. These four curves illustrate the variety of curves of hiding against pigment volume that can be obtained because, at any given pigment volume, the spreading

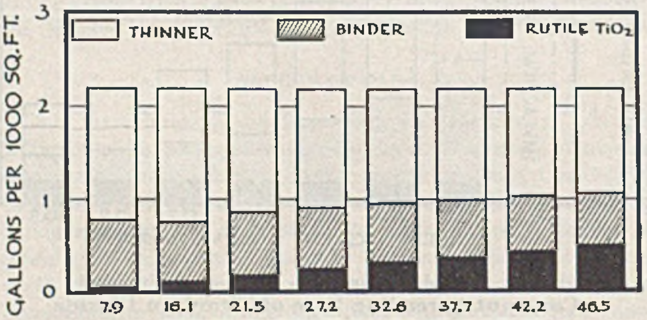

Figure 4. Application of a Series of Enamels at Constant Wet-Film Thickness

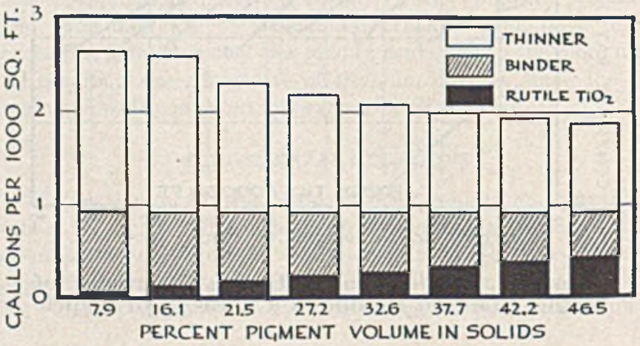

Figure 5. Application of a Series of Enamels at Constant Dry-Film Thickness

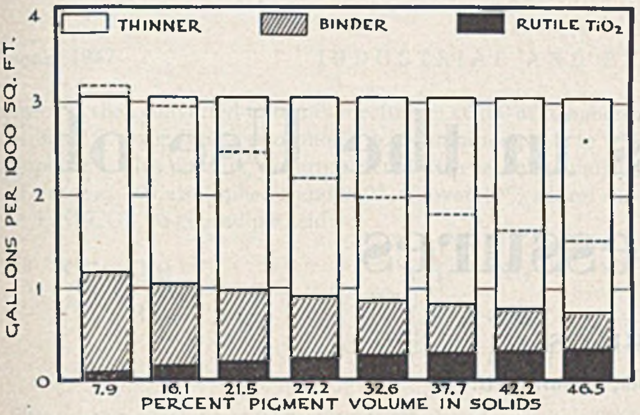

Figure 6. Application of Constant Wet-Film Thickness after Adjusting Thinner Content so Each Enamel Contains 50% Solids by Weight

rate of the titanium dioxide, which determines the hiding at that pigment volume, can be varied by changing the quantity of thinner or the wet-film thickness.

PRACTICAL CONSIDERATIONS

The most significant curve of hiding against pigment volume is the one that is obtained when each product is thinned and applied as it would be when put into practical use. In the case of air-drying, brushing, architectural enamels, it is probable that enamels of different pigment volume would be applied at about equal consistency and a constant wet-film thickness. All enamels would have to be thinned to about the same consistency to obtain brushing properties, and all would tend to go on at about the same wet-film thickness, because sagging would be encountered at too thick an application, and hard brushing would be encountered at too thin an application. Hiding curves obtained under these conditions using titanium dioxide and a binder suitable for an architectural enamel are not available at this time, but the data on hand give some practical information on baking enamels because the application conditions are somewhat different.

Baking enamels are usually applied by spraying to specified dry-film thickness; hence the hiding relations at various dry-film thicknesses are important. Film thickness is probably not so closely related to consistency as in brushing enamels because baking enamels are usually quick setting, and quite a range in film thickness can be obtained at any usable consistency by varying the spraying technique.

The relation of hiding to pigment volume for urea-alkyd baking enamels applied at one arbitrarily selected dry-film thickness has already been shown. Results calculated for various specific dry-film thicknesses—namely, 1.00, 1.25, and 1.50 mils—are shown in Figure 7.

These indicate that maximum hiding is obtained when the concentration of titanium dioxide in the film is about 25% by volume. They also indicate that, since the curves begin to flatten at about 16% pigment volume, almost as much hiding is obtained at a given dry-film thickness when the film contains 16% titanium dioxide as when it contains 25% by volume. Actual trial on a specific job would be required to establish whether this difference in hiding would be of practical significance.

On the other hand the hiding obtainable at 25% pigment volume and a thickness of 1.0 mil could be completely duplicated by using a 16% pigment volume and a film thickness of about 1.1 mils. The latter method employs 25 to 30% less rutile titanium dioxide per unit surface area, even though the same hiding is obtained. Since the increase in film thickness required would be only 10%, it could probably be tolerated from the standpoint of properties other than hiding. A 25% pigment volume is a pigment-to-binder ratio of about 1.18/1.00 by weight, and a 16% pigment volume is a pigment-to-binder ratio of about 0.68/1 by weight. Use of the lower ratio would save about 10% of the titanium dioxide required at an 0.8/1 ratio and about 25% of the titanium dioxide required at a 1/1 ratio by weight.

There is a possibility of effecting greater savings by using pigment volumes even lower than 16%, but the great increase in film thickness required to obtain adequate hiding at lower pigment volumes would probably introduce various undesirable features.

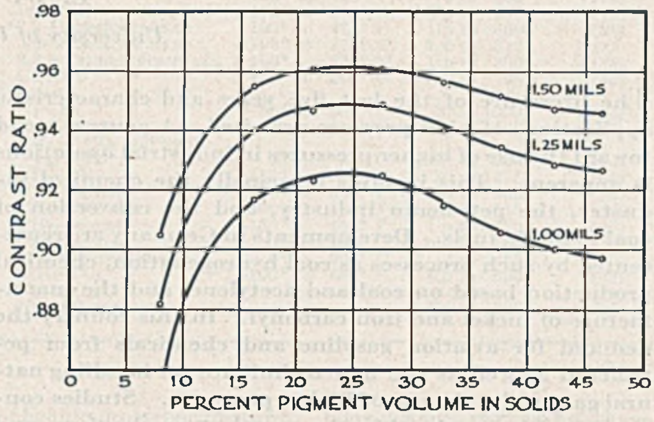

Figure 7. Hiding of Rutile Titanium Dioxide in a Urea-Alkyd Vehicle at Several Dry-Film Thicknesses

CONCLUSIONS

1. The hiding of a coating made with rutile titanium dioxide and any given binder is determined primarily by the pigment volume concentration in the binder and the spreading rate of the titanium dioxide.

2. Various relations between the hiding of such a coating and the pigment volume concentration in the binder can be obtained because a variety of spreading rates of titanium dioxide can be employed at any given pigment volume.

3. Significant relations between the hiding of a coating and the pigment concentration in the binder can be obtained by employing spreading rates of pigment that are typical of those that would be used in practical application.

4. When baking enamels made with rutile titanium dioxide at various concentrations in a urea-alkyd binder are applied at a constant dry-film thickness, maximum hiding is obtained at a pigment concentration in the film of 25% by volume.

5. In such enamels the hiding obtainable with a given amount of pigment used at a concentration of 25% by volume in the film can be duplicated with 25 to 30% less rutile titanium dioxide by lowering the pigment volume to 16% and increasing the dry-film thickness by about 10%.

6. These hiding relations and an estimate of the pigment volumes actually being used indicate that, in the field of rutile titanium dioxide white baking enamels, it may be possible to reduce the consumption of rutile titanium dioxide by 10 to 25% and still produce results equivalent to those being obtained today.

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Recent Advances in the Use of High Pressures

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The literature of the last five years and characteristic applications of high pressure are cited. A general trend toward the use of higher pressures in industrial operations is apparent. This involves principally the chemical industry, the petroleum industry, and the conversion of coal to liquid fuels. Developments in Germany are represented by such processes as coal hydrogenation, chemical production based on coal and acetylene, and the manufacture of nickel and iron carbonyl. In this country the demand for aviation gasoline and chemicals from petroleum as well as the new techniques for handling natural gas involve the use of higher pressures. Studies concerned with reaction kinetics, catalyst mechanism, and thermodynamics of reactions have a direct bearing on the use of high pressures. The importance of heat transfer, mass transfer, catalyst size, and gas flow conditions on the design of catalytic reactors is indicated. Much work has been done on the physical and thermal properties of pure compounds and their mixtures and on the phase equilibria of binary and multicomponent mixtures. Equipment for use at high pressures is noted.

PRESSURES from 100 to 30,000 pounds per square inch have been used in both chemical and physical industrial processes, and it is likely that higher pressures will be utilized. A comprehensive review of the literature in all fields mentioned has not been attempted, but it is apparent that the industrial applications of high pressures are becoming more numerous and involve larger scale apparatus. This is reflected in the greater interest in chemical and physical processes carried out under pressure, in the physical and thermal properties of gases, in phase equilibria, reaction kinetics, and equipment for use at high pressures (*13*).

The capacity for synthetic ammonia production was greatly expanded during the war (*25, 27, 60, 86, 100, 104*). The reaction pressures used in the new plants in this country are in the range from 250 to 800 atmospheres. The water gas shift reaction for converting steam and carbon monoxide to hydrogen for use in the synthesis of ammonia was carried out in Germany under 25 atmospheres to save power in compressing the carbon dioxide formed in the reaction.

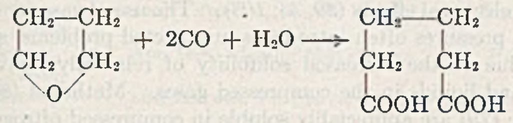
Methanol (*61*) and higher alcohols (*43*) have been synthesized for years. When carbon monoxide and hydrogen react at atmospheric pressure and 380° C. over nickel, methane is formed. At temperatures as low as 180° C. and higher, and with the more active cobalt-thoria catalyst, paraffin hydrocarbons of higher molecular weight are produced, as in the Fischer-Tropsch process. At pressures of 300 atmospheres and 450° C. with thoria-alumina or zinc oxide–alumina catalyst, the products are isomerized to branched hydrocarbons. The zinc oxide–alumina catalyst shows a tendency to alcohol formation. This would be suspected since a zinc oxide–chromium oxide or zinc oxide–copper oxide catalyst at 300 atmospheres and 300–350° C. yields methanol. Higher temperatures increase the yield of the higher alcohols, and for this purpose the methanol catalyst is alkalized with 2% potassium oxide, and the methanol produced is recycled.

Both methanol and isobutanol react with ammonia under 60 to 220 atmospheres to form methylamine and isobutylamine, respectively (*55*). Toluene synthesis was carried out in a commercial plant by the reaction of benzene and methanol at 340° to 380° C. and 30 to 35 atmospheres.

Inadequate sources of petroleum caused the Germans to use coal as a raw material for liquid fuels and chemical products. Increased demand and limited reserves will eventually have a similar effect in this country (*116*). Coal was hydrogenated under high pressure by the Bergius process (*9, 10, 104, 141*) or coke was gasified in a water gas reactor, and the resulting carbon monoxide and hydrogen were converted to liquid products catalytically at atmospheric pressure as in the Fischer-Tropsch synthesis (*40, 90, 159*). The latter yields low octane gasoline, but research results indicate that by operating at 300 atmospheres and 420–450° C. with an alumina-thoria catalyst, good yields of isoparaffins from C_3 to C_5 and higher are obtained (*28*). These would be useful in preparing high octane gasoline. Increasing the pressure beyond this point gives increasing percentages of oxygenated products until at 1000 atmospheres the principal product is dimethyl ether. The liquid-phase hydrogenation of coal was carried out in Germany by the Bergius process at 700 atmospheres (*21, 55, 56*) and 480° C., and in general this process proved preferable to the Fischer-Tropsch synthesis (*60*) to the extent that over six times as much liquid product was produced by the former process. The gasoline and middle oil from the 700-atmosphere liquid-phase hydrogenation was hydrogenated in a two-stage vapor-phase process. The first was a saturation stage at 300 atmospheres and 400–410° C. over a tungsten and nickel sulfide on activated alumina catalyst, and the second was a splitting stage at 300 atmospheres and 410–420° C. over tungsten sulfide. A single-stage vapor-phase hydrogenation, resulting in direct splitting, was also operated at 700 atmospheres and 450° C. Lower octane gasolines, of not very high aromatic content (naphthenes), were dehydrogenated at 510–520° C. under 25–70 atmospheres by the D.H.D. process to improve the octane rating. The Arobin process (*55*) is also a method of manufacturing aromatics from the high boiling residues of the latter process. It operates at 390° to 455° C. and 200 atmospheres. In another type of reaction embodied in the O X O process (*55*), olefins react with the hydrogen and carbon monoxide of water gas to give aldehydes. These are then hydrogenated to mixed alcohols and used for detergent manufacture. The first step is carried out at 200 atmospheres and 150–160° C. with Fischer-Tropsch catalyst while the hydrogenation step is at 200 atmospheres and 170–195° C.

A fraction (Kogasin) from the Fischer-Tropsch process was hydrogenated at 200 atmospheres and 300–350° C. with a nickel tungstate catalyst to convert its olefin content to saturated hydrocarbons for use in preparing sulfonyl chlorides as detergents (*55*).

Numerous other applications of high pressure were found in the German chemical industry (*6, 55*). Acetylene from calcium carbide and from the iron arc process occupied a major position. This was made possible by the discovery of methods for handling this compound safely at pressures up to 20 atmospheres and 200° C. Several of the products derived from acetylene result from reactions under pressure at some step in the process. Thus 1,4-butylene glycol was hydrogenated to 1,4-butanediol at 200–300 atmospheres and 80–130° C. over copper-nickel catalyst. The latter was then converted to tetrahydrofurane at 100 atmospheres and 300° C. over liquid phosphoric acid containing 0.5 to 1% phosphine. This product, in turn, reacted with carbon monoxide and water at 200 atmospheres and 270° C. over 10% nickel carbonyl, $Ni(CO)_4$, to give adipic acid:



The experimental direct hydration of ethylene to produce 20% ethanol is claimed by carrying out the reaction at 200–300 atmospheres and 300° C. in the presence of a mixture of WO_2 and WO_3 promoted with 5% zinc oxide carried on silica gel. High-viscosity polyethylene, with a molecular weight of 15,000 to 20,000, was made by polymerizing ethylene in the presence of oxygen as a catalyst at 2000 atmospheres. A product of lower viscosity, with a molecular weight of 2000 to 3000, was made at 60–200 atmospheres (*56*) in alcoholic solution with benzoyl peroxide as catalyst.

At higher pressures (up to 5000 atmospheres) and 320° C. Uhde (*115*) indicates that, according to experiments, methane becomes quite reactive with water. Experimental reactions with natural gas at 5000 atmospheres (*87*) and methane with butylene at 12,000 atmospheres (*126*) are described elsewhere.

Other applications of high pressures carried out in Germany include the following: Nickel carbonyl was made in quantities of several hundred tons a month by the reaction between crushed nickel matte and carbon monoxide at 200 atmospheres and 250–260° C., and iron carbonyl, $Fe(CO)_5$, was made at 70–200 atmospheres and 200–220° C. (*22*). These carbonyls were decomposed to form nickel and iron powders, and the carbon monoxide was recirculated. Hydrazine hydrate, $NH_2NH_2.H_2O$, for jet propulsion and rocket fuels was made by the reaction of sodium hypochlorite and ammonia solutions at 40 to 50 atmospheres and 180° C. (*42*). This material reacted in the rocket combustion chamber under 30 to 40 atmospheres pressure (*60*). Concentrated nitric acid (*55*) was made directly from the ammonia oxidation gases by first condensing water formed in the reaction and removing it as weak acid. The gases were then cooled to −10° C., and the liquid NO_2 formed was treated at 80–100 atmospheres and 70° C. with dilute nitric acid and oxygen to yield pure nitric acid and N_2O_4 which, on distillation, gave 99% nitric acid.

Pressures used in the petroleum industry are not, as a rule, so high as some of those mentioned above. The Isomate process (*145*) operates at 700–800 pounds per square inch and 240–250° F. (116–121° C.) and isomerizes low octane pentanes and hexanes to compounds of higher octane number and volatility. A liquid aluminum chloride–hydrocarbon complex promoted with anhydrous hydrogen chloride is used as a catalyst in the presence of hydrogen. The thermal alkylation process operates at 3000–5000 pounds per square inch and 950° F., and causes reactions such as that of ethylene with propane or butane to form branched pentanes and hexanes. The use of a homogeneous catalyst allows operation at lower temperatures and pressures (*52, 70*). Some catalytic polymerization processes are carried out at 600 to 900 pounds per square inch (*162*). A method of hydrogenating isooctene to isooctane requires 300 pounds per square inch (*14*). The hydrogenation of petroleum is described (*102, 103*) as well as the synthesis of toluene by hydroforming (*41*).

The processing of natural gas at high formation pressures has been introduced in the last few years (*155*). This normally involves absorbing natural gasoline at pressures of 2000 pounds per square inch and compressing the lean gas to 3500 pounds per square inch for reinjection of the stripped gas into the well. Pressures as high as 8000 pounds have been encountered in these wells. The equilibria between gas and liquid in the retrograde region are of particular interest here as well as in the separation of light hydrocarbon mixtures. Long-distance gas pipe lines have also made higher pressures necessary to increase the capacity. Water vapor in the gas is undesirable because of its tendency to form solid hydrocarbon hydrates (*3*) which act like ice. The water vapor is removed at high pressures by one of several methods (*19*).

Nitroparaffins are produced by the vapor-phase nitration of propane at about 150 pounds per square inch. An entire series (*77*) of nitroparaffin derivatives (aminohydroxy compounds) is produced by the reduction of the corresponding nitrohydroxy compound, using hydrogen and catalyst at 500–2000 pounds per square inch in autoclaves. Incidentally, pressures in excess of 400,000 atmospheres have been reached experimentally (*11*).

Table I. Pressure-Volume-Temperature Relations

System	Range		Citation
	Temp.	Atm.	
Compounds			
H_2	0° to 150° C.	Up to 3000	(*98*)
N_2	−70° to 500° C.	20 to 6000	(*125*)
CO	−70° to 1000° C.	50 to 1200	(*125*)
CH_4	0° to 150° C.	10 to 1000	(*125*)
CH_4	100° to 490° F.	0 to 680	(*110, 114*)
C_2H_4	0° to 150° C.	Up to 3000	(*97*)
C_2H_6	100° to 460° F.	0 to 680	(*122*)
n-C_4H_8	100° to 460° F.	0 to 680	(*111*)
Iso-C_4H_{10}	150° to 275° C.	Up to 250	(*2*)
2,2-Dimethylbutane	100° to 275° C.	Up to 300	(*39*)
2,3-Dimethylbutane	100° to 275° C.	5.6 to 312	(*71*)
2,2,4-Trimethylpentane	100° to 250° C.	Up to 300	(*38*)
CH_3OH	170° to 290° C.	10 to 95	(*85*)
Mixtures			
N_2–$3H_2$	−50° to 200° C.	50 to 1000	(*125*)
N_2–CO_2	25° to 125° C.	Up to 500	(*51*)
CH_4 + CO_2 and hydrocarbons	0° to 50° C.	Up to 250	(*114*)
CH_4–NH_3	150° to 300° F.	80 to 1675	(*69*)
CH_4–n-C_4H_{10}	100° to 300° F.	Up to 350	(*2*)
CH_4–iso-C_4H_{10}	100° to 460° F.	Up to 318	(*112*)
CH_4–decane	100° to 460° F.	Up to 680	(*118*)
CH_4–N_2–H_2	0° to 200° C.	100 to 700	(*81*)
Propane–pentane	0° to 300° C.	2 to 80	(*150*)
C_2H_6–CO_2	100° to 460° F.	Up to 680	(*123*)
Natural gas	Pseudocritical method		(*31*)
Natural gas	....	Up to 200	(*139*)

REACTION KINETICS

The mechanism of a number of the reactions just described, as well as the applications of thermodynamics, catalysts, studies, and catalyst mechanism, are important in the successful design and operation of high pressure processes. The kinetics of the ammonia synthesis (*33, 73*) and the thermodynamics of the synthesis of ethanol from ethylene and water (*154*) have been studied recently. The theory of the cracking of petroleum products (*36*) and the effect of the numerous variables which control it need further clarification. Contributions have been made toward a more adequate understanding of the factors which control reaction rates (*26, 35, 57*). These include catalytic activity, catalyst particle size and porosity, flow conditions in the reactor, catalyst

Table II. Thermodynamic Properties

System	Range		Citation
	Temp.	Pressure	
Compounds			
N_2	—75° to 200° C.	1000 to 6000 atm.	(*8, 32, 93*)
NH_3	150° to 300° C.	20 to 1000 atm.	(*68*)
SO_2	−100° to 500° F.	Up to 68 atm.	(*128*)
CO_2	−75° to 1800° F.	Up to 3000 lb./sq. in.	(*32, 146*)
CH_4	−70° to 200° C.	Up to 1000 atm.	(*32, 88*)
CH_4	70° to 220° C.	Up to 1500 lb./sq. in.	(*18, 94*)
C_2H_4	Up to 500° F.	Up to 300 atm.	(*32, 163*)
C_3H_8	−80° to 200° F.	Up to 40 atm.	(*140*)
Pentane	100° to 460° F.	Up to 680 atm.	(*130*)
CH_3OH	....	10 to 250 atm.	(*84*)
Benzene	200° to 420° C.	1 to 190 atm.	(*46*)
Mixtures			
N_2–H_2–NH_3	150° to 300° C.	50 to 1000 atm.	(*67*)
Natural gas	32° to 700° F.	Up to 680 atm.	(*15*)
Wet gas	58° to 120° F.	Up to 225 atm.	(*16*)
N_2–H_2	....	....	(*7, 66*)
CH_4–C_2H_6	70° to 310° F.	Up to 1500 lb./sq. in.	(*17*)

TABLE III. VAPOR-LIQUID EQUILIBRIUM OF MIXTURES

System	Range Temp.	Range Atm.	Citation
C_2H_5OH–H_2O	Up to 345° F.	Up to 190	(*50*)
C_2H_6–H_2O	100° to 460° F.	Up to 680	(*119*)
n-Butane–H_2O	100° to 340° F.	Up to 680	(*121*)
Benzene–toluene	Up to 280° C.	Up to 34	(*49*)
Benzene	100° to 500° F.	Up to 41	(*30*)
Toluene	100° to 500° F.	Up to 41	(*30*)
Methylcyclohexane	100° to 500° F.	Up to 41	(*30*)
Hydrocarbons	−10° to 450° F.	Up to 34	(*132*)
HCl–*n*-C_4H_{10}	70°, 120°, 180° F.	Up to 37	(*113*)
H_2–*n*-C_4H_{10}[a]	24°, 82°, 116° C.	Up to 100	(*105*)
H_2–hexane	35° C.	Up to 150	(*131*)
H_2–cyclohexane	35° C.	Up to 150	(*131*)
H_2–benzene	35° C.	Up to 150	(*131*)
H_2–*m*-xylene	35° C.	Up to 150	(*131*)
H_2–isobutane	100° to 250° F.	34 to 200	(*27*)
H_2–2,2,4-trimethylpentane	100° to 302° F.	12 to 340	(*27*)
H_2–dodecanes	200° to 300° F.	34 to 340	(*27*)
CH_4–iso-C_4H_{10}	100° to 460° F.	Up to 318	(*112*)
CH_4–C_2H_4–isobutane	38°, 71° C.	34, 68	(*4*)
CH_4–C_2H_6–C_3H_8	99° F.	96	(*153*)
CH_4–decane	100° to 460° F.	Up to 680	(*118*)
C_2H_6–propylene	−30° to 90° C.	Up to 50	(*91*)
C_2H_4–propylene	54° to 59° C.	Critical region	(*134*)
CO_2–CH_4	100° to 460° F.	7 to 680	(*120*)
He–CH_4	90°, 105° K.	Up to 160	(*48*)
Propylene–isobutane	100° to 250° F.	Up to 41	(*47*)
Propane–H_2S	125° to 225° F.	Up to 41	(*47*)
Propane–*n*-butane	100° to 280° F.	Up to 41	(*109*)
Propylene–acetylene	....	....	(*92*)
Propane–*n*-pentane	130° to 370° F.	Up to 34	(*129*)
Propane–acetylene	....	....	(*92*)
Propane–isopentane	0° to 300°	2 to 80	(*149*)
Natural gas–95% dimethylene glycol	100° F.	Up to 136	(*127*)
Natural gas–crude oil	....	Up to 560	(*138*)
Petroleum fractions	300° to 800° F.	1 to 68	(*160*)
CH_4–absorber oil	33° to 180° F.	Up to 340	(*76, 157*)
C_2H_6–absorber oil	33° to 180° F.	Up to 340	(*76, 157*)
C_3H_8–absorber oil	33° to 180° F.	Up to 340	(*76, 157*)
Iso-C_4H_{10}–absorber oil	33° to 180° F.	Up to 340	(*157*)
n-C_4H_{10}–absorber oil	33° to 180° F.	Up to 340	(*76, 157*)
Iso-C_5H_{12}–absorber oil	33° to 180° F.	Up to 340	(*157*)
n-C_5H_{12}–absorber oil	33° to 180° F.	Up to 340	(*76, 157*)
n-C_6H_{14}–absorber oil	33° to 180° F.	Up to 340	(*157*)
Benzene–N_2[b]	35° to 100° C.	1100	(*79*)
CH_3OH–N_2[b]	0° to 75° C.	Up to 700	(*80*)
CH_3OH–N_2[b]	0° to 75° C.	Up to 700	(*80*)
CH_3OH–CH_4[b]	0° to 75° C.	Up to 700	(*80*)
CH_3OH–CO_2	0° to 75° C.	Up to 700	(*80*)
NH_3–N_2	90° to 148° C.	9650	(*82*)
NH_3–CH_4	45° to 100° C.	9650	(*82*)
NH_3–N_2–H_2	100° C.	5300	(*82*)

[a] Two regions of isobaric retrograde condensation (*65*).

[b] These have minima in the curve of solubility *vs.* pressure; they represent solubility of a liquid in a compressed gas.

poisons, physical properties of the reactants and products, and heat and mass transfer (*59, 161*). It has been proposed that the assumption of "active points" on a jagged surface is not necessary to explain the action of poisons on catalysts, but that the same results could be obtained if the poisoned molecules or centers were in plane crystal surfaces (*53*).

PHYSICAL PROPERTIES AND PHASE EQUILIBRIA

A large amount of experimental work has been reported recently on pure compounds and mixtures at elevated pressures. This may be broadly classified as pressure-volume-temperature relations for pure compounds and mixtures, thermodynamic properties of pure compounds and mixtures which are largely derived from the *P-V-T* data, vapor-liquid equilibrium for binary and multicomponent mixtures, and a number of other contributions mentioned later. The recent literature on *P-V-T* relations is summarized in Table I, on thermodynamic properties in Table II, and on vapor-liquid equilibria in Table III. These tables include the majority of the work reported during the last five years.

Progress has been made in arriving at correlations useful in predicting the effects of high pressures. New experimental determinations of high-pressure gas viscosity are reported for nitrogen (*136*), carbon dioxide (*23*), methane (*23*), ethylene (*23, 37*), ethane (*23, 137*), propane (*23, 137*), pentane (*58*), and natural gas (*5*), as well as correlations (*23, 137, 147*) for predicting the effect of pressure on gas viscosity.

A beginning has been made in obtaining similar data (*78, 148, 149*) and a correlation (*24*) for the effect of pressure on the thermal conductivity of gases. The effect of high pressure on the viscosity of lubricants (*54*) is of interest. A number of other correlations are available for use in engineering design for predicting the critical properties of hydrocarbon mixtures (*83*), phase equilibria (*45, 64, 75, 101*), and the thermodynamic properties of liquids (*156*). Some information is available on the effect of pressure on the surface tension of methane-propane mixtures (*158*) and on certain electrical effects (*20, 44, 108*). The use of gases or vapors at high pressures often introduces unexpected problems, such as those due to the increased solubility of relatively nonvolatile solids and liquids in the compressed gases. Methanol (*80*) and benzene (*79*) are appreciably soluble in compressed nitrogen and hydrogen. Sodium hydroxide, potassium hydroxide, sodium chloride, and sodium sulfate become sufficiently soluble in steam as the critical pressure and temperature (*142*) of the latter is approached to cause trouble from turbine blade deposits. Related effects are noted with silicic acid in steam (*143, 144*). The action of extremely high pressures, up to 100,000 atmospheres (*12*), on the properties of many solids has been observed, and the melting point of mercury (*99*) has been measured up to 3000 atmospheres.

DESIGN OF EQUIPMENT

Attention has been given during recent years to both the structural design (*107*) of high pressure apparatus and to the separate effects of heat transfer (*161*), mass transfer, and reaction rate at the surface of catalysts on reactor design. In this connection the concept of H.R.U. (height of an over-all reaction unit) and H.C.U. (height of catalytic unit) have been introduced (*59*) and should be as useful for high pressure reactions as for low.

Pressure vessels are now built up in layers to obtain the thick walls required, or preformed steel tape is wound on a thin-walled tube to make a *Wickel* vessel in the process invented by Schierenbeck (*133*). This made possible the manufacture of pressure vessels in Germany on a production basis and the limitation of the forging process was thus avoided. Several patents (*72, 105, 117*) have been issued involving these new techniques, and they are also described elsewhere (*55, 62*). Apparatus for chemical reactions at 5000 atmospheres and 400° C. has been constructed (*29, 152*), and methods for designing high pressure vessels (*63*) for lower pressures and the principles of closures (*95, 96*) for such vessels are described. A simple O-ring rubber or plastic packing (*1, 89*) has been found unusually effective up to 20,000 pounds per square inch for nonmoving seals and at somewhat lower pressures for moving seals.

A packing gland of another design for use with a $^3/_8$-inch-diameter stirrer shaft operating at 1725 revolutions per minute and 5000 pounds per square inch is described (*34*). The design of cracking coil tubes for use at high pressures and temperatures is better understood (*52, 124*). In another situation a solid catalyst is introduced into a high pressure reactor (*145*) as a slurry, using a specially designed pumping system arranged for continuous flushing of the slurry from the system.

Piezoelectric elements (*164*) are employed to measure pressure differences, and a range to 10,000 atmospheres is claimed for a free piston type manometer (*151*). A refractometer (*135*) can be used on liquids flowing under high pressure, and there is a high speed agitator (*74, 106*) for pressure vessels.

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Guanidine Nitrate from Dicyandiamide and Ammonium Nitrate by Pressure Reaction

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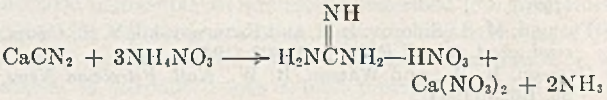
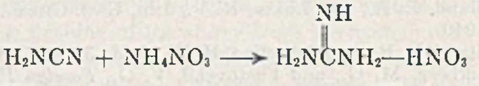
LARGE quantities of nitroguanidine were desired by the British early in the recent war for use in flashless powder. A plant to produce this material was built by the American Cyanamid Company in Canada and operated throughout the war. For the quantities of nitroguanidine required, a process for the intermediate guanidine nitrate was necessary. This material had been made on a small scale for some time, but the processes used did not seem suitable for the contemplated scale of operations. The present work was undertaken to select the most suitable method for the purpose. It resulted in the development of a new process which involved the heating of dicyandiamide with ammonium nitrate in anhydrous ammonia solution (*12*).

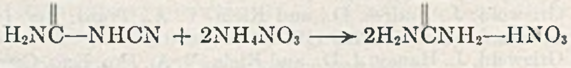
A great deal of work has been recorded in the literature on the preparation of guanidine nitrate. The starting materials which have received most attention and are pertinent to this investigation are calcium cyanamide, free cyanamide, and dicyandiamide:



$$CaCN_2 + 3NH_4NO_3 \longrightarrow H_2N\overset{NH}{\overset{\|}{C}}NH_2{-}HNO_3 + Ca(NO_3)_2 + 2NH_3 \qquad (1)$$



$$H_2NCN + NH_4NO_3 \longrightarrow H_2N\overset{NH}{\overset{\|}{C}}NH_2{-}HNO_3 \qquad (2)$$



$$H_2N\overset{NH}{\overset{\|}{C}}{-}NHCN + 2NH_4NO_3 \longrightarrow 2H_2N\overset{NH}{\overset{\|}{C}}NH_2{-}HNO_3 \qquad (3)$$

The reaction involving calcium cyanamide (*2, 3, 10, 11, 18, 20*) has some obvious drawbacks, including the fact that three moles of ammonium nitrate are required per mole of guanidine nitrate produced. Also, the carbonaceous materials always present in crude cyanamide must be heated with ammonium nitrate, which constitutes an explosion hazard (*3*). Consequently, it was

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The usual starting materials for guanidine nitrate production are cyanamide or its dimer, dicyandiamide, and ammonium nitrate. The reaction of these materials to produce guanidine nitrate is highly exothermic. It can be readily carried out by fusion on a small scale to give excellent yields, but it appeared to be hazardous on the contemplated scale. Experiments using various diluents to control the exothermic nature of the reaction resulted in the selection of liquid ammonia as the most suitable. It had the disadvantage of producing higher pressures, but these were well within the range of accepted commercial usage. The advantages of the process over those involving fusion or the use of water as a diluent were controllability of the reaction, higher yields, and purity of product. The product could be used for nitroguanidine production directly without purification.

thought preferable to isolate the cyanamide from the crude calcium cyanamide and utilize either free cyanamide or dicyandiamide as the starting material.

The reaction of aqueous cyanamide solution with ammonium salts has been the subject of several investigations (*1, 2, 13*). Blair and Braham (*1, 2*) reported the most comprehensive study. Their optimum conditions gave a maximum conversion of 80% based on cyanamide; this yield does not take into account losses that would be involved in isolating the product; our results (not recorded here) check theirs closely. This process was feasible, but the yields were not entirely satisfactory and large excesses of ammonium salt were required for optimum yield.

Anhydrous cyanamide, as well as the aqueous solution, has been used in the preparation of guanidine salt (*7, 8, 16*). These reactions were carried out either as fusions or in solution in anhydrous solvents. Excellent yields may be obtained in this way, but since the comparatively insoluble dicyandiamide is more easily isolated and dried than the very soluble, low melting cyanamide, the former is preferable for anhydrous reactions where its use is permitted.

The simplest method of converting dicyandiamide to guanidine nitrate involves fusion with ammonium nitrate (*1, 4, 5, 17, 19, 22*). On a small scale this is a smooth reaction providing good yields of product (*5*). The reaction is quite exothermic (*5*), however, and it was thought that, in a large scale fusion, temperatures might be reached which would be dangerous in view of the nature of the reactants.

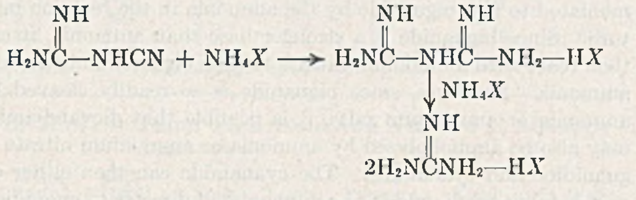
Davis reported yields of guanidine nitrate, ranging from 85% (*4*) to quantitative (*6*), by heating dicyandiamide with ammonium nitrate in water under pressure. Our maximum yields in this reaction were about 80% after a heating period of 6 hours. This yield again represents conversion and not finished product. The indications were that hydrolytic side reactions were consuming considerable of the dicyandiamide in this reaction. We therefore tried a series of experiments using aqueous ammonia as the solvent to determine whether this might not increase the yield. Under the conditions tried the yields were of the same order of magnitude as those obtained in water. The highest was 78.4%, obtained over a comparatively long heating period at a relatively low temperature. In general, the yields did not exceed 70%, and here again they represent product formed in solution and not isolated.

Since none of the exploratory experiments with these alternative reactions gave the yields which we had previously obtained by heating dicyandiamide with ammonium nitrate in anhydrous ammonia, further attention was directed to this process. It was found to give yields of better than 90% guanidine nitrate when the theoretical proportions of reactants were heated for periods of about one hour or less. The product obtained was satisfactory for making nitroguanidine without purification, and it could be easily isolated from the reaction mixture without loss. The only impurity present in any considerable quantity was unchanged ammonium nitrate. These advantages were not offered by any of the previously discussed procedures.

A wide variety of guanidine salts have also been produced by a similar procedure (*12*).

MECHANISM OF REACTION

Little information was obtained that would contribute to previous studies on the mechanism of the reaction of dicyandiamide with ammonium salts (*1, 4, 22*). The best evidence indicates that biguanide is an intermediate in this reaction:



$$H_2N\overset{\overset{NH}{\|}}{C}\text{—}NHCN + NH_4X \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}\text{—}NH\overset{\overset{NH}{\|}}{C}\text{—}NH_2\text{—}HX \xrightarrow{NH_4X} 2H_2N\overset{\overset{NH}{\|}}{C}NH_2\text{—}HX$$

No biguanide was detected in any of our reaction mixtures, but a few tests indicated that a biguanide salt was much more unstable in liquid ammonia in the presence of ammonium salts than in the

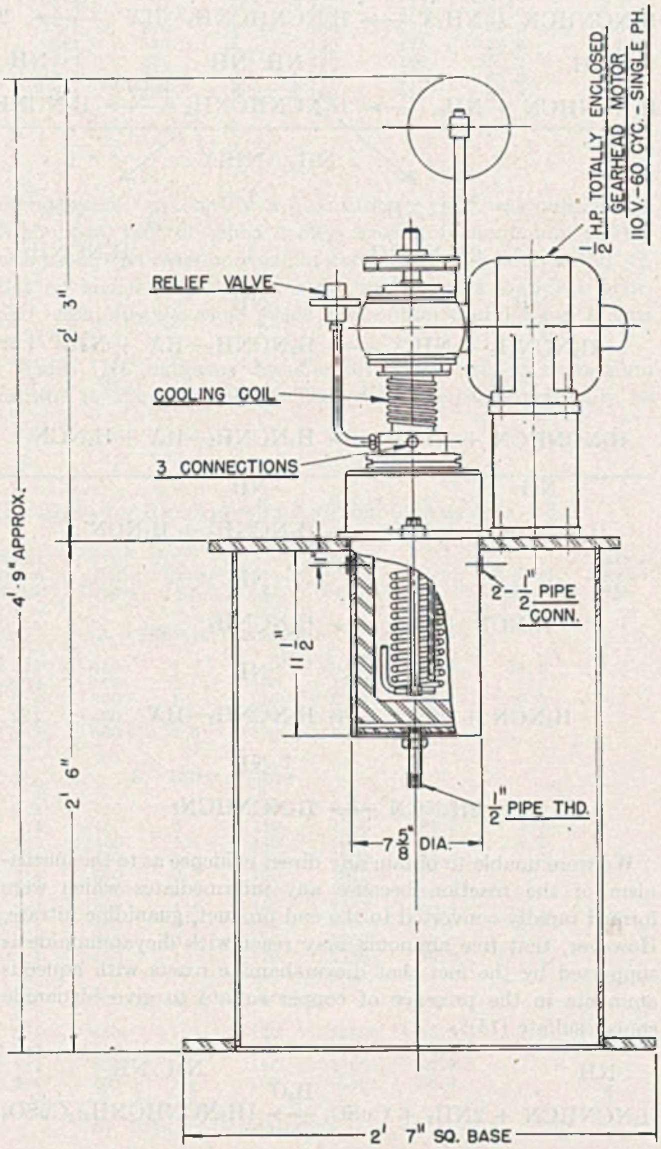
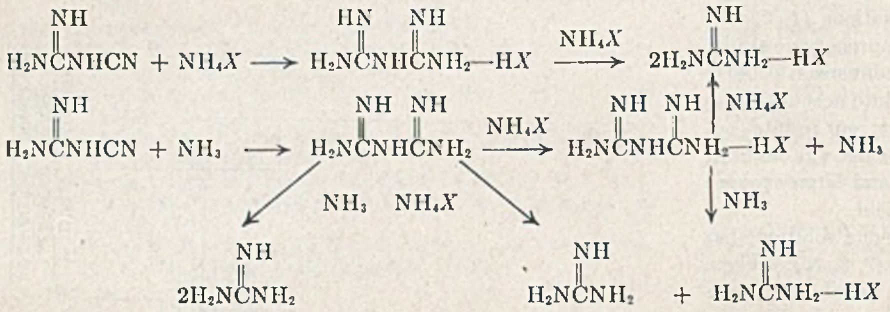
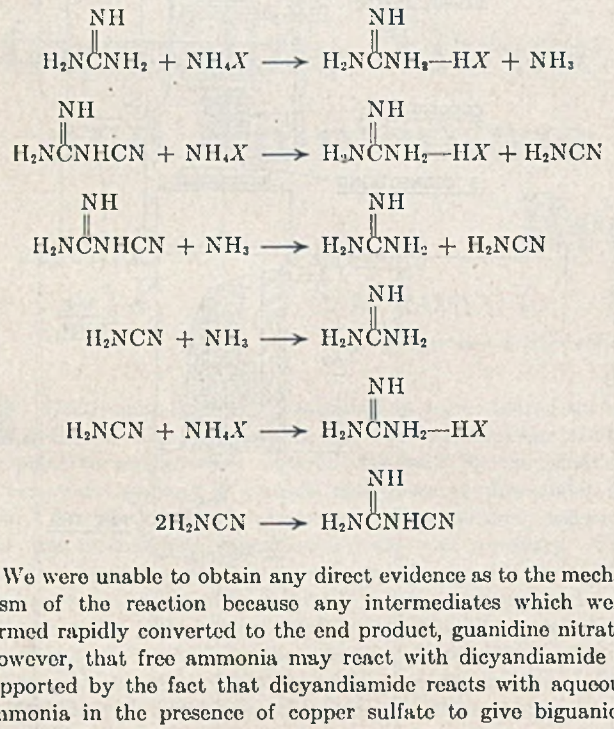


Figure 1. Autoclave for Small Scale Experiments

fusion mixtures which had been used in previous studies on mechanisms. Biguanide in our reaction mixture was rapidly cleaved to guanidine below 140° C., the minimum temperature of the experiments included in this report, so that its concentration would never become appreciable. Therefore, this reaction may proceed through biguanide nitrate even though none was detected.

It is possible that in our system reactions may occur in addition to the formation of biguanide salt followed by cleavage to guanidine salt. For example, dicyandiamide may be ammoniated to free biguanide by the ammonia in the reaction mixture. Since biguanide is a stronger base than ammonia, it can then react with ammonium nitrate to give biguanide nitrate and ammonia. Similarly, since biguanide is so readily cleaved by ammonia or ammonium salts, it is possible that dicyandiamide may also be ammonolyzed by ammonia or ammonium nitrate to guanidine and cyanamide. The cyanamide can then either dimerize to dicyandiamide or be ammoniated directly to guanidine. Such considerations indicate that a great variety of reactions may occur, as summarized by the following equations:





$$H_2N\overset{\overset{NH}{\|}}{C}NH_2 + NH_4X \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NH_2{-}HX + NH_3$$

$$H_2N\overset{\overset{NH}{\|}}{C}NHCN + NH_4X \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NH_2{-}HX + H_2NCN$$

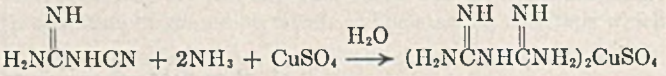
$$H_2N\overset{\overset{NH}{\|}}{C}NHCN + NH_3 \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NH_2 + H_2NCN$$

$$H_2NCN + NH_3 \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NH_2$$

$$H_2NCN + NH_4X \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NH_2{-}HX$$

$$2H_2NCN \longrightarrow H_2N\overset{\overset{NH}{\|}}{C}NHCN$$

We were unable to obtain any direct evidence as to the mechanism of the reaction because any intermediates which were formed rapidly converted to the end product, guanidine nitrate. However, that free ammonia may react with dicyandiamide is supported by the fact that dicyandiamide reacts with aqueous ammonia in the presence of copper sulfate to give biguanide copper sulfate (*15*):



$$H_2N\overset{\overset{NH}{\|}}{C}NHCN + 2NH_3 + CuSO_4 \xrightarrow{H_2O} (H_2N\overset{\overset{NH}{\|}}{C}NH\overset{\overset{NH}{\|}}{C}NH_2)_2CuSO_4$$

Presumably the role of copper sulfate is to remove the biguanide from the reaction medium as the stable complex and thus prevent its destruction by ammonolysis, hydrolysis, etc. It seems reasonable to assume that a similar ammoniation of dicyandiamide to biguanide might occur in anhydrous ammonia solution.

It is possible that, in the fusion of dicyandiamide with ammonium salts, the ammonolysis to a guanidine salt and cyanamide could also occur to a certain extent along with the ammoniation to biguanide followed by ammonolysis to guanidine.

SMALL SCALE EXPERIMENTS

All the small scale reactions were carried out in either a 3-quart Struthers-Wells autoclave (Figure 1), fabricated of Type 347 stainless steel, or a steel Hadfield autoclave of the same size and somewhat similar design. Liners of stainless steel were used with both autoclaves, and all material in contact with the charge was of stainless steel. Both autoclaves had top-driven stirrers, providing good agitation, with a thermocouple well and cooling coils in the charge. The autoclaves were heated by means of strip heaters outside a Dowtherm jacket. The temperature was recorded and controlled by a Micromax, Model R.

The reactions were carried out by placing the dicyandiamide, ammonium nitrate, and water (or ammonium hydroxide) in the liner of the autoclave, closing the autoclave, and heating to the temperature indicated in the tables. Usually 30 minutes to 1 hour was required to reach reaction temperature. At the end of the heating period the temperature of the charge was quickly (5–10 minutes) reduced to room temperature by circulating water through the coils. The autoclave was then opened, and the contents were prepared for analysis. In most cases the charge at room temperature was a slurry. In such cases the solids were filtered and dried, and both solid and mother liquor were weighed and analyzed for guanidine and dicyandiamide. All analyses were performed by the Analytical Laboratory. Guanidine was determined by a modification of the Vozarick method (*21*), dicyandiamide by the method of Garby (*9*), and ammonium nitrate by formaldehyde titration (*14*).

In those experiments where anhydrous ammonia was used, the dicyandiamide and ammonium nitrate were placed in the liner of the autoclave which was then closed. The ammonia was weighed into a small transfer bomb from a storage cylinder. This bomb was then connected to the autoclave in an inverted position, and the ammonia was forced into the autoclave by warming with steam.

At the end of the heating period, the charge was cooled as described above and the pressure vented until it was atmospheric. The autoclave was then opened, the liner removed, and the remaining ammonia allowed to evaporate. The solid was dried and analyzed as described above. In all cases a material balance was taken, and the yields given in the tables are based on actual recoveries.

REACTIONS OF DICYANDIAMIDE AND AMMONIUM NITRATE IN WATER

In one series of experiments dicyandiamide and ammonium nitrate were heated in aqueous solution under pressure. Ratios of ammonium nitrate to dicyandiamide (theoretical ratio, 2:1), time, temperature, and dilution were varied, as will be seen in Table I.

The maximum yield obtained in any of these experiments was 80.5%, which was not sufficiently high to be attractive. It is obvious from the results that side reactions consumed much of the dicyandiamide. These were probably hydrolytic reactions to give the hot water insolubles, ammeline, ammelide, etc., as well as guanylurea, ammonia, carbon dioxide, etc.

REACTIONS IN AQUEOUS AMMONIA

A series of experiments was also carried out in aqueous ammonia, using ordinary concentrated ammonium hydroxide as the solvent. It was hoped that, by having some ammonia present, some of the hydrolytic side reactions might be repressed sufficiently to result in higher yields. Table II shows that the hope for higher yields was not realized. A 78.4% yield was obtained in experiment 19, but this required the rather long reaction time of 3 hours at 140° C. and the use of a 50% excess of ammonium nitrate. From a production angle this was not attractive.

Comparison of experiment 9, Table I, with experiment 3, Table II, indicates that the presence of the ammonia greatly increased the rate of the reaction. This effect was not apparent when a 3:1 ratio of reactants was used, however (experiment 13 and 14, Table I, compared with experiments 17 and 18, Table II). Comparison of experiments 3 and 5 with experiments 2 and 4, Table II, indicates that guanidine nitrate is unstable in the reaction mixture at 160° C., since the yields are lower in 3 hours than in 1 hour. For this reason longer reaction times which gave increased yields in aqueous systems were not tried in these experiments.

In the experiments in aqueous ammonia the dicyandiamide was more completely reacted than in water, and also the formation of water-insoluble materials, ammelide, ammeline, etc., was largely repressed.

Table I. Reactions of Dicyandiamide with Ammonium Nitrate in Water

Expt. No.	Dicy., Grams	AN, Grams	Molar Ratio, AN:Dicy.	H_2O, Grams	Time, Hr.	Temp., ° C.[a]	Yield, % GN	% Dicy. Unchanged	Hot H_2O Insol., Grams
8	252	480	2:1	750	3	160	36.4	47.5	90
9	252	480	2:1	750	1	160	27.9	..	..
10	252	480	2:1	750	1	180	58.4	18.6	26
11	252	480	2:1	750	1	170	66.0	15.3	..
12	252	480	2:1	750	0.5	180	54.3	28.6	..
13	210	600	3:1	1000	3	160	63.0	7.1	21
14	168	480	3:1	800	1	160	69.1	..	13
15	168	480	3:1	800	1	180	70.5	3.3	10
16	168	480	3:1	800	0.5	180	63.6	10.7	..
25	405	850	2.2:1	850	2	160	67.9	13	..
249	405	850	2.2:1	850	6	160	80.5	0.0	3.1

[a] The pressures in these experiments were 130 pounds per square inch or less.

Table II. Reactions of Dicyandiamide with Ammonium Nitrate in Aqueous Ammonia

Expt. No.	Dicy., Grams	AN, Grams	Molar Ratio, AN:Dicy.	28% NH_4OH, Grams	Time, Hr.	Temp., ° C.	Max. Pressure, Lb./Sq. In.	Yield. % GN	% Dicy., Unchanged
2	252	480	2:1	750	3	160	575	45.8	0.6
3	252	480	2:1	750	1	160	420	63.8	0.0
4	252	480	2:1	1040	3	160	495	49.2	0.5
5	202	384	2:1	830	1	160	300	57.8	10.5
6	202	384	2:1	830	3	140	180	57.1	..
7	202	384	2:1	830	1	140	200	47.0	..
17	168	480	3:1	830	3	160	275	61.6	..
18	168	480	3:1	830	1	160	230	69.4	5.0
19	168	480	3:1	830	3	140	175	78.4	7.7
20	168	480	3:1	830	1	140	180	50.2	43.5
21	168	480	3:1	830	0.5	170	210	66.3	0.7
22	168	480	3:1	830	1	180	410	47.8	0.1

REACTIONS IN ANHYDROUS AMMONIA

Since the exploratory experiments with aqueous and aqueous ammonia systems had indicated that yields of approximately 80% were the most to be expected, and these involved the use of comparatively long reaction times and large excesses of ammonium nitrate, attention was turned again to the use of anhydrous ammonia as a solvent. Preliminary experiments had shown that 90% yields were obtainable when the theoretical quantities of ammonium nitrate and dicyandiamide were heated in ammonia solution at 160° C. Consequently, an investigation of the variables involved in this reaction was undertaken.

Table III*A* shows the effect of temperature. In a reaction period of 1 hour, 160° C. is required to obtain a 90% yield. The yield is not increased by raising the temperature to 180° C., but the reaction time is halved. In these experiments the concentrations were not held constant, but the general effect of temperature is accurately shown by the results.

The effect of time is shown in Table III*B*. The main points are: A 90% yield was obtained in 3 hours at 140° C. using the theoretical ratio of reactants; practically a quantitative yield was obtained in 3 hours at 140° C. when a 50% excess of ammonium nitrate was used; the reaction was not complete in 0.5 hour at 160° C. but no higher yield was obtained in 1.5 hours than in 1 hour, and essentially the same yields were obtained in 0.5 and 1 hour at 170° C.

Table III*C* indicates the effect of molar ratio of ammonium nitrate to dicyandiamide. The yield decreases gradually as

Table III. Data on Reactions in Anhydrous Ammonia

Expt. No.	Dicy., Grams	AN, Grams	Molar Ratio, AN:Dicy.	NH_3, Grams	Time, Hr.	Temp., ° C.	Max. Pressure, Lb./Sq. In.	Yield, % GN	% Dicy. Unchanged	Ratio, Solids: NH_3
				A. Effect of Temperature						
23	168	320	2:1	450	1	140	1085	53.5	38.0	..
33	336	640	2:1	600	1	150	1110	84.7	..	..
32	168	320	2:1	300	1	160	1270	93.1	0.0	..
37	168	320	2:1	450	1	170	1725	89.9	..	..
41A	336	640	2:1	600	0.5	180	1560	90.2	..	..
				B. Effect of Time						
23	168	320	2:1	450	1	140	1085	53.5	38.0	..
24	168	320	2:1	450	3	140	1235	91.2	2.7	..
29	168	480	3:1	450	1	140	1065	88.6	9.7	..
28	168	480	3:1	450	3	140	1030	98.7	..	..
38	336	640	2:1	900	0.5	160	1815	77.5	..	..
34	336	640	2:1	600	1	160	1350	88.3	..	..
60	336	640	2:1	600	1.5	160	1330	88.4	..	..
27	168	320	2:1	450	3	160	1700	89.0	0.0	..
36	168	320	2:1	450	0.5	170	1750	89.9	..	..
37	168	320	2:1	450	1	170	1725	89.9	..	..
				C. Effect of Molar Ratio						
30	168	480	3:1	450	1	160	1360	95.2	1.6	..
52	336	704	2.2:1	600	1	160	1250	92.2	..	..
45	336	672	2.1:1	600	1	160	1405	89.8	..	..
34	336	640	2:1	600	1	160	1350	88.3	..	..
				D. Effect of Concentration						
23	168	320	2:1	450	1	140	1085	53.5	38.0	1.08
24	168	320	2:1	450	3	140	1235	91.2	2.7	1.08
25	168	320	2:1	900	1	140	1670	26.2	65.5	0.54
26	168	320	2:1	900	3	140	1700	67.4	22.6	0.54
50	336	640	2:1	400	1	160	1050	91.8	0.0	2.44
34	336	640	2:1	600	1	160	1350	88.3	..	1.63
57	336	704	2.2:1	400	1	160	940	93.2	..	2.6

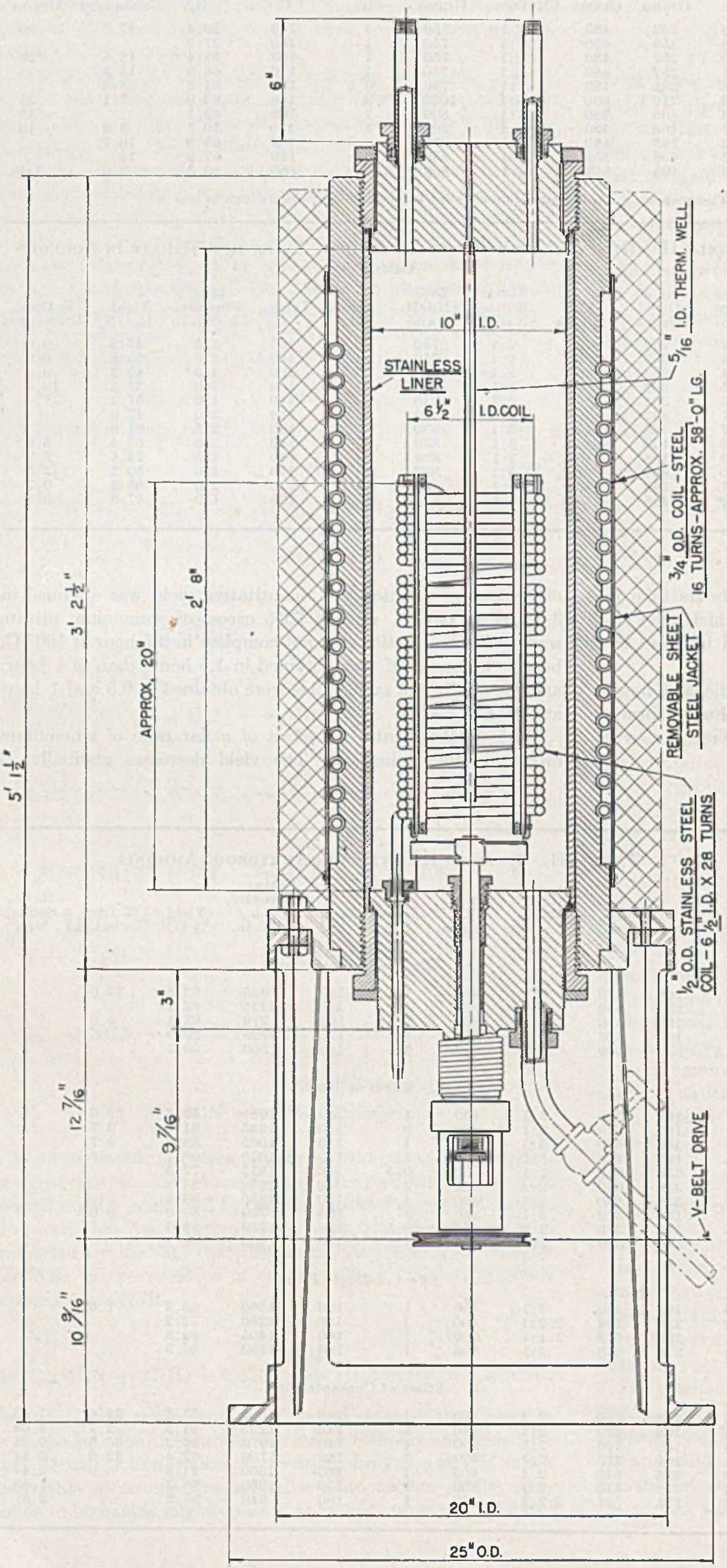


Figure 2. Autoclave for Pilot Plant Experiments

the molar ratio decreases from 3:1 to 2:1. Later work on a larger scale showed that with the 2:1 ratio the yield was 91–92%, and, for reasons to be discussed later, it was desirable to keep this ratio as low as possible.

The effect of concentration (ratio of solids to ammonia) is shown in Table III*D*. The first four experiments were run at a low enough temperature to illustrate the effect of dilution with ammonia on the reaction rate. Since it was obviously advantageous to use as little ammonia as possible, no further experiments were run at these dilutions. The last three experiments show that in 1 hour at 160° C. the ratio of solids to ammonia could be varied from 2.6:1 to 1.6:1 with little effect on yield.

The conclusions were that a minimum temperature of 160° C. was necessary to obtain a reaction time of 1 hour or less. Because of the nature of the reaction mixture it was desirable to maintain the temperature as low as possible consistent with a reasonable reaction time. A 90% yield was obtained with the theoretical ratio of reactants, and slight excesses over the theoretical of ammonium nitrate improved the yield only slightly. A ratio of solids to ammonia in the range 1.6:1 to 2.6:1 was indicated. No spontaneous temperature rises due to the exothermic reaction were noted. The maximum pressure observed was about 2000 pounds per square inch.

Experiments conducted by K. D. Ashley, of these laboratories, on the conversion of some of the above products to nitroguanidine had shown that the crude material was satisfactory without purification. Thus it was necessary only to flash off the ammonia to obtain a product which was satisfactory for the desired use. This meant, however, that any impurities which were present would remain in the product and that there would be no opportunity to recover an excess of either reagent used. For this reason it was decided not to use higher ratios of ammonium nitrate to dicyandiamide even though practically quantitative yields could be obtained in this manner. When the theoretical ratio was used, a product containing 4–6% ammonium nitrate was obtained. This product, which had a purity of 91–92%, was entirely satisfactory for the nitration step. Slightly higher yields could be obtained with a 5 or 10% excess of ammonium nitrate, but this material remained in the product and lowered the purity to below 90%.

A product of 98.5 to 99.5% purity could be obtained from the crudes by a single recrystallization from water.

PILOT PLANT WORK

A 10-gallon stainless-steel-lined autoclave (Figure 2) with bottom stirring was used along with the auxiliary equipment illustrated in Figure 3. This consisted of two 9-gallon stainless steel tanks with working pressures of 300 pounds per square inch, equipped with sight glasses; ammonia was stored in one and made-up solutions in the other. Between these tanks was a 2.2-gallon stainless steel autoclave with a working pressure of 500 pounds per square inch and a bottom-driven stirrer. This vessel was used as a mix tank for preparing the solutions, although its size was not suitable for the purpose. These three vessels were arranged so that the flow of liquids through them was by gravity. A Proportioneers pump was used to transfer the solutions from the storage tank to the autoclave. A 30-gallon aluminum drum served as the receiver for the product. The autoclave discharge entered this drum tangentially near the center, the solid settled to the bottom, and the ammonia was led off through the top. The vaporized ammonia was led through a bag filter to a scrubber but was not recovered in this work. It was essentially pure ammonia, however, which was recycled without difficulty in the plant. All lines, valves, etc. in contact with the reactants were of stainless steel.

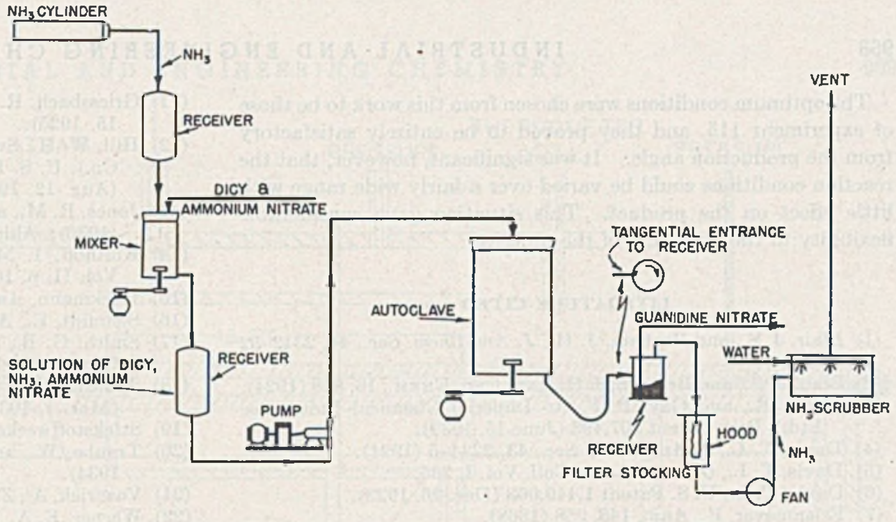


Figure 3. Flow Sheet for Production of Guanidine Nitrate

The autoclave was heated by liquid Dowtherm which circulated through both inner and outer coils. Cold Dowtherm could be pumped through the coils to cool the charge when desired. The temperature was recorded by a Micromax which also controlled the Dowtherm circulating pump. Excellent temperature control was maintained. The small mixing autoclave was jacketed and could be heated with steam or cooled with water.

The ammonia was run from cylinders to the ammonia storage tank. The solid dicyandiamide and ammonium nitrate were charged to the mixing autoclave through a one-inch valve in the top. The autoclave was then closed and the ammonia measured in from the ammonia storage tank by volume. Five-minute stirring at room temperature was sufficient to dissolve the reactants completely, after which the solution was allowed to run into the lower storage tank. Because of the small size of the mixing autoclave it was necessary to make four or five batches for each autoclave charge.

Table IV gives data on a representative series of runs in this equipment. In most cases the charge was pumped into a hot autoclave. Since the pump was of low capacity, the pumping-in period was proportionately much too long (about 1 to 1.25 hours). In those cases where a run was started in a cold autoclave, the charge was blown into the autoclave by ammonia pressure in a few minutes. The charge was held at temperature for the stated time after it had been pumped in.

It was found possible to discharge the autoclave cleanly at operating temperature in about 5 minutes. The sensible heat of the charge was sufficient to flash all but 5–10% of the ammonia when discharged to atmospheric pressure. Thus when the autoclave was discharged into a receiver of the proper design at atmospheric pressure under conditions allowing the flashing of ammonia, a free-flowing, finely divided, colorless product was obtained. Only a short drying operation was required to remove the residual ammonia and give a product which was suitable for use. On the other hand, if the autoclave was discharged under conditions which kept an appreciable amount of ammonia in the product (i.e., if the charge was cooled prior to discharging), a mush was obtained which dried to a hard cake and was difficult to handle.

The experiments summarized in Table IV bore out the results obtained in the small scale experiments. No difficulties of a chemical or mechanical nature manifested themselves. In this scale work no exothermic reactions were observed even when very small quantities of ammonia were used (experiment 75); however, in one case with such a small quantity of ammonia difficulty was experienced in discharging the autoclave; consequently it was considered advisable to use larger amounts of ammonia.

The test for exothermic reactions consisted of charging the autoclave cold and heating. After the temperature reached 100° C. (at which point the reaction occurs very slowly), the heat was turned off every 10° C. In all cases the temperature leveled off immediately and the pressure began to drop after 1–2 minutes.

The discrepancies between the columns headed "Purity" and "Yield" represent mechanical losses which were from 1 to 4% in our set up. In larger scale operation this loss would be much less; it was to be expected, therefore, that the yields in larger scale operation would be about 91–93%, the purities in most of these runs.

Table IV shows that the ratio of ammonium nitrate to dicyandiamide could be varied from 1.94:1 to 2.04:1 without appreciably affecting the yield. However, the higher ratio left 5–7% of ammonium nitrate in the product, whereas with the lower ratios only 3–4% was left. For reasons already discussed, it was desirable to use the lower ratio. On the other hand, when the ratio was lowered to 1.94:1, appreciable quantities of melamine were found in the product. This was undesirable as an impurity because of difficulties which might occur in further processing. Consequently, a ratio of approximately 2:1 was chosen.

Table IV. Pilot Plant Experiments

Expt. No.	Dicy., Lb.	AN, Lb.	Molar Ratio, AN:Dicy.	NH_3, Lb.	Time, Hr.	Temp., ° C.	Max. Pressure, Lb./Sq. In.	Yield, % GN	Purity[a], % GN	% AN in Product
69	10.8	20.4	1.98:1	19.2	1	160	1450	89.1	92.9	3.2
70	10.8	20.4	1.98:1	19.2	0.5	170	1650	91.1	92.8	3.7
71	10.8	20.4	1.98:1	19.2	1.5	170	1800	93.0	93.4	3.4
73	10.8	20.4	1.98:1	19.2	0.5	180	1950	86.5	89.9	4.9
75	10.8	21.0	2.04:1	12.8	1	160	1180	87.5	87.7	7.3
90	15.25	29.7	2.04:1	27.1	1	160	1610	89.7	91.2	5.3
107	13.5	25.0	1.94:1	24.0	1	160	1490	90.3	93.2	3.0
115	13.5	25.5	1.98:1	24.0	1	160	1520	88.7	91.9	4.1

[a] The guanidine nitrate and ammonium nitrate analyses never add up to more than 96–97%. Minor amounts of impurities made up the balance, and included melamine, dicyandiamide, small quantities of water insolubles, etc.

The optimum conditions were chosen from this work to be those of experiment 115, and they proved to be entirely satisfactory from the production angle. It was significant, however, that the reaction conditions could be varied over a fairly wide range with little effect on the product. This situation gave considerable flexibility to the operation of the process.

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Heat Transfer in a 3-1 Hydrogen-Nitrogen Mixture at High Pressure

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Experiments were conducted for flow inside a 5-foot length of $^5/_8$-inch i.d. steel tubing heated by steam, at gas pressures from 30 to 900 atmospheres. The Reynolds numbers extend from 40,000 to the unusually high value of 440,000. The results are in good agreement with the usual relations for heat transfer. In the correlations the effects of pressure on the relevant properties of the mixture are taken into account. Methods of estimating these effects, which were not pronounced over the pressure range studied, are presented. Concurrence of the data with those for better known gases is shown by inclusion of experimental data for air at 5 to 8 atmospheres and at Reynolds numbers from 9000 to 50,000.

IN DESIGNING equipment for heating or cooling gases at high pressure, it is of great importance to know whether formulas deduced from data for ordinary pressures can be applied or whether pressure exerts some specific influence on the transfer of heat not sensible at low pressures. No experimatal data have been found in the published literature for pressures higher than 14 atmospheres; Nusselt's data (*18*) on gases at 1 to 14 atmospheres show no effect of pressure. What indirect evidence was available from the operation of plant equipment was conflicting. To resolve the conflict, experiments were carried out with a mixture of hydrogen and nitrogen at 900 atmospheres that is used in the synthesis of ammonia.

An apparatus for heat transfer studies should be so designed that both the temperature rise of the material flowing and the temperature differences between that material and the heating medium may be adequately measured without elaborate instrumentation. Preliminary calculations on the basis of existing data showed that about a 5-foot length of $^5/_8 \times 1^1/_2$ inch steel tubing fulfilled these conditions. A double steam jacket was provided, as shown in Figure 1. Thus, the condensate from the test section could be collected without including that arising from heat losses to the surroundings. The outer jacket was connected to a steam trap, and the inner jacket was connected to a condensate chamber provided with a gage glass that permitted the level of the condensate to be determined. A line from the bottom of the condensate chamber led to a cooler and a collecting vessel. Vents on the steam line before and after the heat exchanger permitted the lines to be freed from condensate and the heat exchanger to be purged of any air which might enter with the steam.

The gas mixture entered the heat exchanger through two high pressure valves which were used in regulating the flow and pressure. From the heat exchanger the gas passed through another regulating valve by which the pressure was reduced to 30 atmospheres, the pressure for which the flowmeter was designed.

The steam temperature was determined from the pressure, using the corresponding temperatures for saturated steam. The quality of the steam was estimated with an Ellison calorimeter. The temperature of the gas was measured by thermocouples in wells which projected axially in from the two ends of the experimental tube. The test section was taken as the distance between the ends of wells (4.71 feet); the well at the cold end projected 2.0 inches beyond the inner condensate jacket. The gas pressure was measured by calibrated Bourdon gages. The gas flow was read from a Bailey flowmeter equipped with a sharp-edged eccentric orifice; the readings were corrected for the difference between the conditions for which the meter was calibrated and the pressure, temperature, and composition of the actual gas.

The flow rate was adjusted until the pressure and rate were in the desired region, and the pressure at the flowmeter was near the value for which it was calibrated. Then the flow was held steady for 15 or 20 minutes until the temperatures became constant. At this time the condensate chamber was drained until the level in the gage glass was at some predetermined point. Readings were then taken at 5-minute intervals for 30 minutes, while the level in the condensate chamber was kept nearly con-

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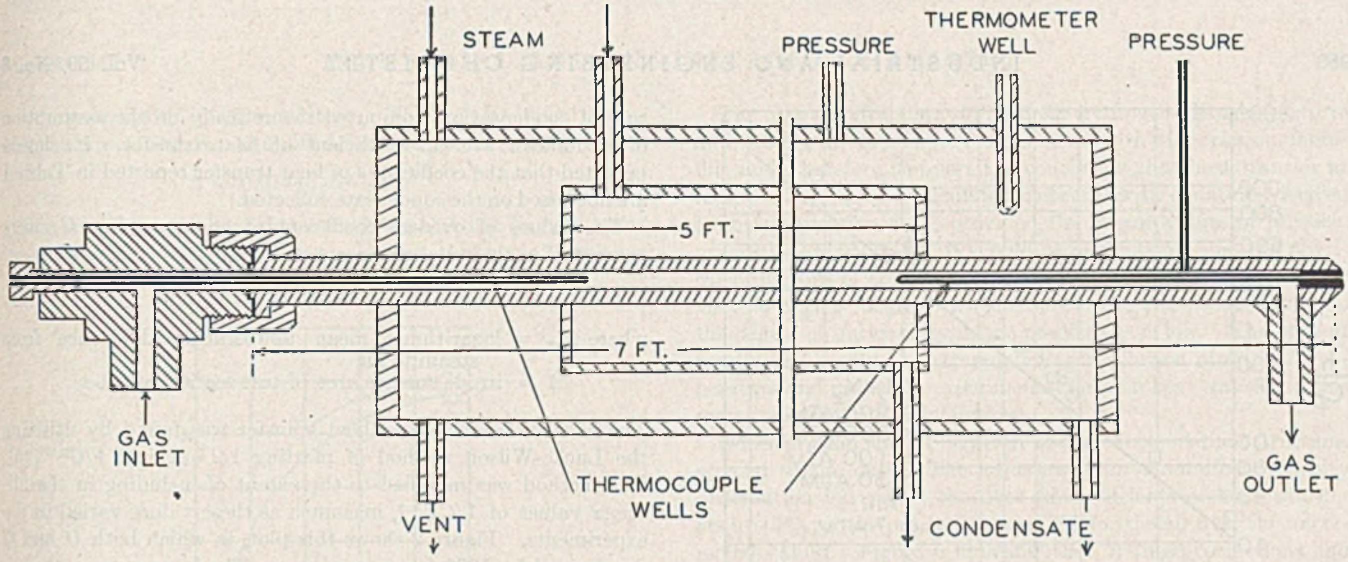

Figure 1. Experimental Heat Exchanger

stant. At the end of the run the level in the condensate chamber was brought carefully to the starting point, and the flow cut off. The condensate was weighed as a basis for a heat balance.

For the runs on air the apparatus was altered by the substitution of diaphragm pressure regulators for the hand-operated valves used with the gas mixture, and a concentric orifice was used.

DATA AND CALCULATIONS

Table I gives pertinent observed data and calculated results. The readings of the thermocouples in the two wells are given, as well as corrected inlet and outlet temperatures, as explained later.

The values of steam temperature are those corresponding to the observed steam pressures. The observed values of flow rate are reported as mass velocities.

To obtain the correct average gas temperatures at the inlet and exit of the test section from the thermocouple readings, corrections were made for nonuniform temperature distribution and also, in the case of the air runs, for radiation to the thermocouple wells. Because of the high coefficients of heat transfer in the tests with the process gas, the radiation was negligible in those tests. A calculation was also made of the effect of heat conduction along the thermocouple wells on the observed temperatures, and even in the air runs no correction was found necessary. The corrections for radiation from the hot tube wall to the thermocouple wells in the air runs were made with an assumed value of 0.9 for emissivity and with a combined emissivity and area factor of 0.87. Inasmuch as the net coefficients of heat transfer by radiation are estimated to be 2.1 P.c.u./(hr.) (sq. ft.) (° C.) at the air inlet and 2.9 at the exit, compared with coefficients of heat transfer of from 10 to 40 by convection, the corrections are small but appreciable. In the process gas tests the coefficients of heat transfer are from 100 to 600, so that radiation can be ignored. The observed air temperatures, corrected for radiation are, for runs 24 to 27, respectively: inlet, 42.9°, 40.6°, 40.7°, and 41.8° C.; exit, 138.0°, 141.4°, 148.2°, and 155.9° C.

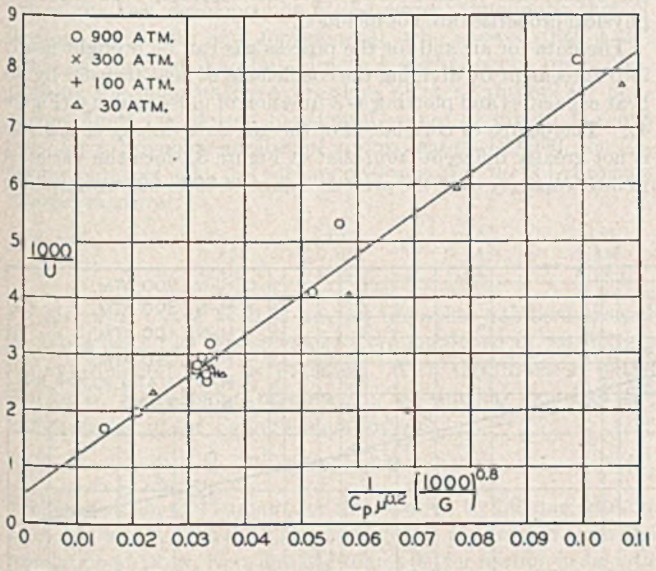

Figure 2. Determination of Combined Resistance of Condensate and Metal Wall

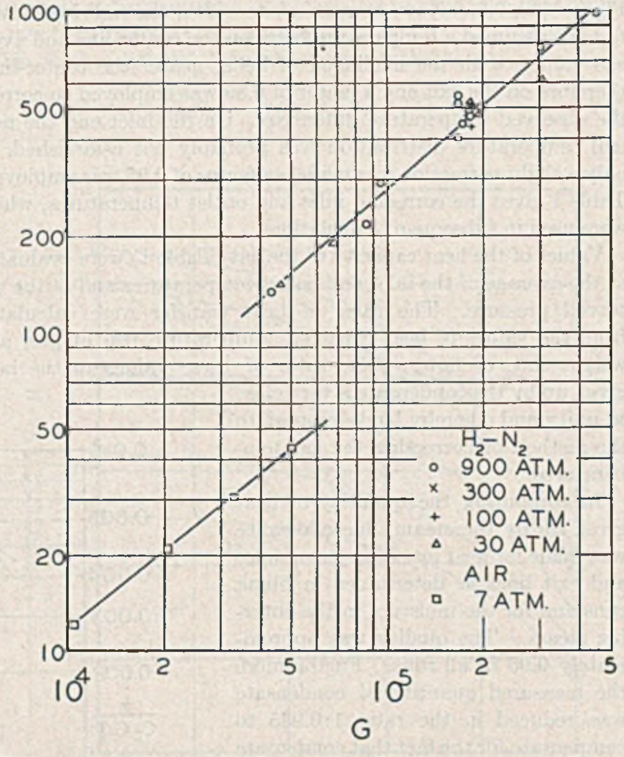

Figure 3. Observed Gas-Side Coefficients of Heat Transfer

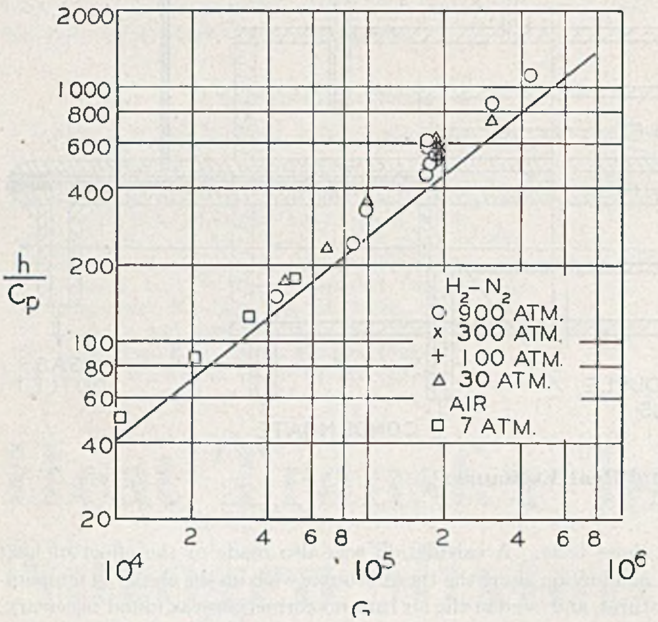

Figure 4. Comparison of Gas and Air Data with McAdams' Simplified Formula for Air (Equation 4)

Corrections for nonuniform temperature distribution were applied to both the process gas and air data. The thermocouple wells were located in the center of the tube and extended 0.219/0.625 or 0.35 of the diameter. Obviously the wells tend more to the center-line temperature than to the "mixed-mean" or average value. Boelter, Martinelli, and Jonassen (*2*) developed a relation between the mean and maximum temperature differences as a function of Prandtl and Reynolds numbers. For $N_{Pr} = 0.45$ and $N_{Re} = 100{,}000$, $\Delta t_{mean}/\Delta t_{max.}$ is given by their Figure 4 as 0.8. Now, because of its width, the well is believed to have assumed a temperature between the center-line and average values, with the likelihood of being nearer the center-line; therefore on the exit end a factor of 0.85 was employed to correct the observed temperature difference. On the inlet end the normal temperature distribution was probably not established, so only a slight correction was made—a factor of 0.95 was employed. Table I gives the corrected inlet and outlet temperatures, which were used in subsequent calculations.

Values of the heat capacity of the gas (Table I) were evaluated at the average of the inlet and outlet temperatures and at the observed pressure. The rates of heat transfer were calculated from the values of heat capacity, temperature rise of gas, and weight rate of flow. The ratio of these values to the heat given up by the condensate is very close to unity and, thereby lends support to the method of correcting the gas temperatures.

In computing the quantity of heat given up by the steam, due allowance was made for heat loss from steam inlet and exit lines as determined in blank runs and for the moisture in the entering steam. The quality was approximately 0.95 in all runs. Furthermore the measured quantity of condensate was reduced in the ratio 1:0.935 to compensate for the fact that condensate was collected from a slightly greater length of tube than that over which the temperature rise was measured. This factor was deduced from a consideration of the variation along the tube of the rate of condensation, computed theoretically on the assumption of a uniform over-all coefficient of heat transfer. It should be noted that the coefficients of heat transfer reported in Table I are not based on the condensate collected.

The values of over-all coefficient of heat transfer, U, were computed in the usual manner:

$$U = q/A\,\Delta t_m \tag{1}$$

where Δt_m = logarithmic mean temperature difference from steam to air
A = inside surface area of test section of tube

The gas-side coefficient of heat transfer was found by utilizing the Lucke-Wilson method of plotting $1/U$ against $1/G^{0.8}$ (*15*). The method was modified to the extent of including in the abscissa values of $1/C_p\mu^{0.2}$, inasmuch as these values varied in the experiments. Figure 2 shows this plot, in which both U and G are divided by 1000 for convenience. The intercept on the Y-axis is 0.0005 (hr.) (sq. ft.) (° C.)/(P.c.u.), and it should represent the combined thermal resistance of tube wall and steam. For comparison, the steam and wall resistance, as calculated from Nusselt's formula for film condensation and an assumed thermal conductivity of steel of 31 P.c.u./(hr.) (sq. ft.) (° C./ft.), is approximately 0.00082. An average of the two values is 0.00066, which is not so significantly different from either of the predicted values that it cannot be accounted for by uncertainties in the value of thermal conductivity ascribed to the steel and in the location of the line in Figure 2. The values of gas coefficients h as listed in Table I were obtained by the equation:

$$1/h = 1/U - 0.00066 \tag{2}$$

Gas viscosity μ_f (Table I) was evaluated at an average film temperature defined as:

$$t_f = t_w - {}^1/_2(t_w - t_g)$$

$$= t_s - \Delta t_m\ (1 - U/2h) \tag{3}$$

RESULTS

The gas coefficients of heat transfer for the 3-1 hydrogen-nitrogen mixture and for air are plotted in Figure 3 against the mass velocity. It is evident that pressure has no great effect on the coefficients of heat transfer for the mixture, even when the physical properties are not included.

The data for air and for the process gas can be brought nearly into agreement by dividing the coefficients of heat transfer by the heat capacities and plotting as a function of mass velocity (Figure 4). The degree of correlation of the gas data among themselves is not greatly different from that of Figure 3, since the variation in heat capacity over the pressure range of 30 to 900 atmospheres

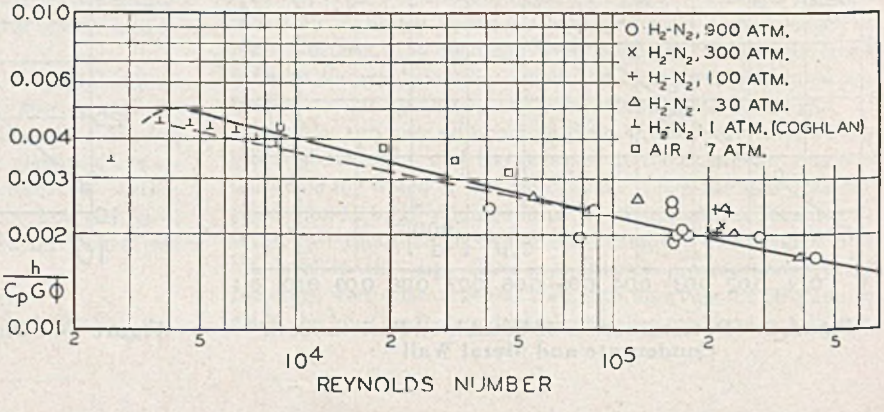

Figure 5. Comparison of Data with Various Formulas: Solid Line, Equations 5 and 6; Dashed Line, Equation 7

is only around 10% for this mixture. The line drawn on Figure 4 represents McAdams' simplified formula for air (*14*):

$$h = 0.0144 C_p G^{0.8}/D^{0.2} \tag{4}$$

The air data are only slightly above the line, but the values for the process gas lie enough higher to suggest that some factor has been omitted in the correlation.

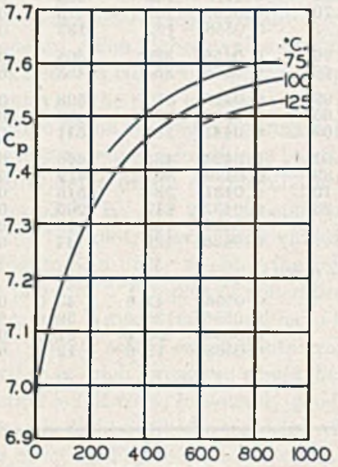

Figure 6. Molal Heat Capacity at Constant Pressure, MC_p, of 3-1 Hydrogen-Nitrogen Mixture

More general correlations include the viscosity to a power around 0.2, and the Prandtl number $C_p\mu/k$, in various functions. As Table I shows, the viscosity of the mixture varies some 30% from 30 to 900 atmospheres, but the values for air are essentially the same as for the mixture at the highest pressure. The Prandtl number is quite different for the two gases, however, being 0.73 for air and around 0.45 for process gas. A general correlation is provided in Figure 5, where the "j-factor," $h/C_pG\phi$, is plotted against Reynolds number, DG/μ_f. In this expression of j-factor, ϕ is a function of Prandtl number and, to a slight degree, of Reynolds number. Although various powers of Prandtl number such as $^2/_3$ and 0.6 have been employed in the past, for values of N_{Pr} appreciably less than unity, these simple functions are inadequate. One of the best developments of the correct function is that of Boelter, Martinelli, and Jonassen (*2*), who showed that ϕ depends not only on N_{Pr}, but also to a slight extent upon N_{Re}. Utilizing the quantitative expressions of these authors for nonviscous fluids (as plotted for typical values in Figure 11), one finds, for a Reynolds number of approximately 100,000, the following values of ϕ at the various pressures (for the 3 hydrogen–nitrogen mixture):

p, atm.	30	100	300	900
$C_p\mu/k$	0.45	0.452	0.448	0.433
ϕ	1.42	1.42	1.42	1.45

For air, with $C_p\mu/k$ = 0.73 and at Reynolds numbers around 20,000, ϕ = 1.12. These values were employed in calculating the experimental data as j-factors. With this function ϕ the j-factor is, furthermore, predicted to be equal to one half the friction factor in the Fanning equation, or:

$$h/C_pG\phi = f/2 \tag{5}$$

Boelter *et al.* showed support for this relation by reliable data on gases and water. The solid line on Figure 5 is obtained from the correlation of Drew, Koo, and McAdams (*9*) for friction in smooth pipes, and is expressed as

$$f/2 = 0.00070 + 0.0625\,(DG/\mu)^{-0.32} \tag{6}$$

It is of interest that this equation is substantially identical with that of Nikuradse (*17*) over the range covered by the plot.

The experimental data on both the hydrogen-nitrogen mixture and air are in satisfactory agreement with the friction factor line and, therefore, support the conclusion that heat transfer at high pressure can be calculated correctly with equations derived from low pressure data, provided the proper values of physical properties are utilized. It should be remembered that the physical properties of the gases employed in the investigation do not vary to a great degree with pressure up to 900 atmospheres, so the degree of uncertainty in the predictions is low. The present results can hardly be extrapolated to the region of critical temperature and pressure; experimental data on heat transfer in this region would be of special interest.

Consideration should be given to the effects of the corrections applied to the data. The adjustment for nonuniform velocity distribution has raised the over-all coefficients of heat transfer about 15% for the process gas and 7% for the air over the uncorrected values. Figure 5 indicates that, if these corrections had not been made so that the data were lower by these amounts, the agreement with the curves would have been as satisfactory. If the corrections for radiation had not been made to the air data, they would lie around 10 to 15% higher than plotted; such a change would mean poor agreement of the air and process gas data. Fortunately there is little question in the validity of the radiation correction.

Since these high pressure experiments were carried out, heat transfer results on hydrogen-nitrogen mixtures at atmospheric pressure have been reported (*6*). These results for a mixture of 55% hydrogen (a composition having about the same value of N_{Pr} as the 75% mixture) are included in Figure 5. In this case, for N_{Pr} = 0.45 and N_{Re} = 7000, ϕ = 1.45. These results are slightly lower than the solid curve based on Equation 6. It should be recalled that these data were obtained in an apparatus with a long calming section whereas the apparatus for the high pressure data involved a slight expansion just at the beginning of the test length, inasmuch as the cross-sectional area of the thermocouple well was 12% of the cross-sectional area of the tube. This slight expansion would be expected to cause the heat transfer rate to be raised a small amount.

The dashed line on Figure 5 represents the equation:

$$h/C_pG\phi = 0.023\,(DG/\mu_f)^{-0.2} \tag{7}$$

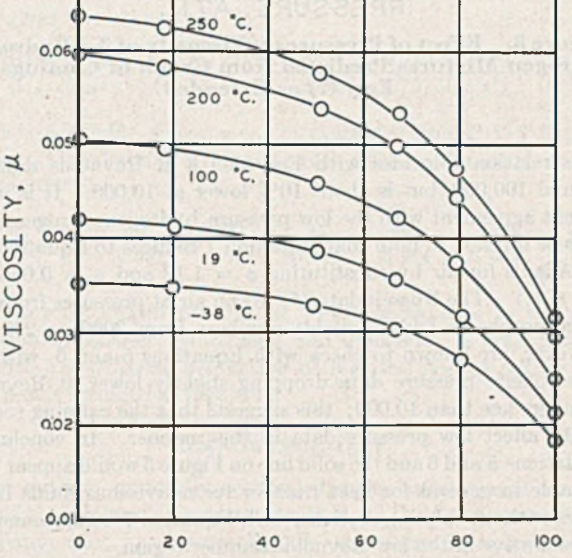

Figure 7. Viscosity of Hydrogen-Nitrogen Mixtures at 1 Atmosphere (*19*)

Table I. Summary of Data

Run No.	Pressure, Atm.	Mass Velocity, G	Temperature, ° C. Observed		Temperature, ° C. Corrected		Temperature, ° C. Steam,	Heat Capacity, C_p	Heat to Gas, q_a	Heat Balance Ratio, q_a/q_s	Viscosity, μ_f	Over-all Coefficient, U	Gas Coefficient, h	$\frac{h}{C_pG\phi}$	$\frac{DG/\mu_f}{1000}$
			t_1	t_2	t_1	t_2	t_s								
Process Gas (74% H_2, 24.4% N_2, 1.6% CH_4, CO, etc., Mol. Wt. = 8.69)															
16	810	463,000	37.7	87.1	44.8	101.0	180.2	0.878	87,600	1.07	0.0549	602	998	0.00169	440
15	819	309,000	40.1	101.4	47.1	113.3	181.1	0.878	68,900	1.07	0.0551	511	771	0.00196	292
3	868	186,000	42.2	87.4	46.8	94.3	133.3	0.875	29,600	0.92	0.0559	358	470	0.00199	173.6
12	906	184,000	46.4	115.5	53.1	125.4	181.7	0.875	44,600	0.96	0.0576	367	485	0.00208	166.7
14	890	175,000	45.0	113.1	51.7	123.3	180.9	0.878	42,100	....	0.0573	342	443	0.00199	159.1
8	886	170,000	35.5	117.0	49.8	132.7	187.0	0.877	47,800	0.98	0.0571	383	513	0.00237	155.0
9	863	170,000	38.8	119.9	45.8	128.9	179.4	0.875	47,400	1.01	0.0569	400	543	0.00252	155.5
2	846	168,300	44.2	111.2	51.2	121.8	182.0	0.875	40,000	1.04	0.0563	316	400	0.00187	155.9
13	889	97,100	48.0	129.7	54.7	137.7	183.1	0.877	27,100	1.01	0.0575	245	293	0.00237	88.0
18	790	86,900	41.9	118.2	48.9	127.7	181.6	0.877	23,000	0.70[a]	0.0567	189	216	0.00195	79.7
17	809	43,700	43.0	131.8	49.9	139.1	180.3	0.875	13,080	....	0.0558	122	133	0.00240	40.8
4	347	194,000	68.0	101.2	71.3	106.0	133.1	0.858	22,200	0.96	0.0458	379	505	0.00214	221
5	333	183,000	70.9	128.1	77.1	137.0	183.9	0.855	35,900	1.00	0.0476	354	463	0.00208	200
7	99	185,000	62.8	99.3	69.1	106.8	132.4	0.824	22,000	0.99	0.0415	380	508	0.00235	232
6	102	184,000	71.0	127.8	76.6	136.2	183.6	0.822	34,500	1.05	0.0438	339	437	0.00204	219
10	121	183,000	72.1	131.5	77.5	138.8	180.0	0.826	35,600	1.09	0.0441	381	511	0.00238	216
22	32.2	310,000	73.0	116.2	78.4	125.9	180.6	0.811	45,800	1.01	0.0423	434	606	0.00170	382
21	32.0	196,000	73.0	129.0	78.4	137.0	182.2	0.811	35,600	0.89	0.0429	363	479	0.00202	238
11	32.2	184,400	77.0	135.4	82.2	142.7	182.0	0.808	34,600	1.10	0.0431	384	516	0.00243	223
20	32.2	99,300	65.8	140.0	71.8	146.4	183.1	0.811	23,100	0.83	0.0432	247	295	0.00258	119.8
23	31.0	69,300	77.3	142.8	82.5	149.8	182.3	0.811	14,260	....	0.0435	169	190	0.00238	83.0
19	31.2	46,800	65.0	144.9	71.0	151.7	183.6	0.811	11,600	....	0.0435	129	141	0.00262	56.0
								Air		Av. = 0.995[b]					
24	7.8	50,300	49.9	141.3	49.9	144.8	183.1	0.241	44,100		0.0556	41.6	43.0	0.00316	47.1
25	6.5	33,300	50.3	145.1	47.6	147.5	182.2	0.241	30,700		0.0556	30.0	30.6	0.00341	31.2
26	6.0	20,600	54.6	152.7	48.0	153.6	183.8	0.241	20,200		0.0568	20.7	21.0	0.00376	18.9
27	5.4	10,300	63.9	161.4	48.8	159.8	182.9	0.241	10,560		0.0568	12.0	12.1	0.00434	8.90

[a] There is reason to believe the apparatus was not fully heated up in this run.
[b] This average excludes the value 0.70 marked *a*.

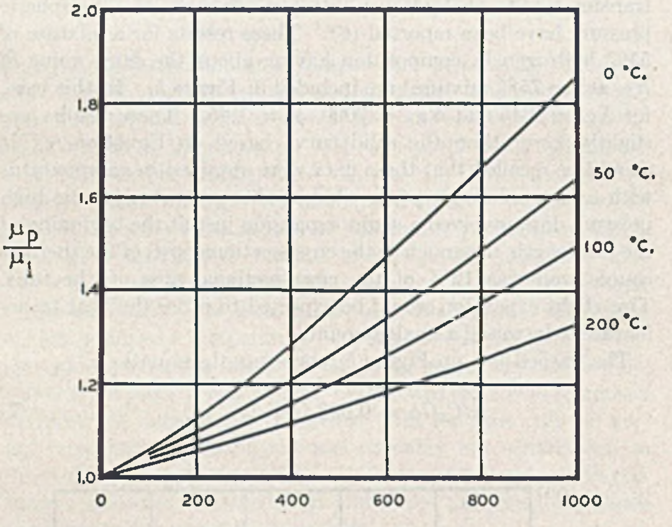

Figure 8. Effect of Pressure on Viscosity of 3-1 Hydrogen-Nitrogen Mixtures Predicted from Graph of Comings and Egly (*7*) as Extended

This relation coincides with Equation 6 at Reynolds numbers around 100,000, but is about 10% lower at 10,000. It is in excellent agreement with the low pressure hydrogen-nitrogen data. It is of interest to note that Equation 7 reduces to Equation 4 of McAdams for air by substituting ϕ = 1.12 and μ = 0.056 lb./(hr.) (ft.). The Nusselt data (*5*, *18*) on air at pressures from 2 to 14 atmospheres and Reynolds numbers from 3000 to 200,000, however, are known to check with Equations 5 and 6, with the atmospheric pressure data dropping slightly lower at Reynolds numbers less than 10,000; this suggests that the calming section might affect low pressure data in this manner. In conclusion, Equations 5 and 6 and the solid line on Figure 5 would appear to be suitable in general for heat transfer for nonviscous fluids inside pipes without calming sections, with Equation 7 being somewhat conservative in the low Reynolds number region.

ESTIMATION OF THERMOPHYSICAL PROPERTIES

Heat Capacity. The molal heat capacities at constant pressure, MC_p, as derived by Deming and Shupe (*8*) for the pure constituents, were selected at the pressure and temperature of the mixture. These values were combined linearly in accord with the mole fractions: 0.75 hydrogen, 0.25 nitrogen. The results, shown in Figure 6, vary only slightly with small variations of composition. The method of combination used is not consistent with the *P-V-T* data for hydrogen-nitrogen mixtures, but the molal heat capacities of hydrogen and nitrogen are not far different and, consequently, more elaborate methods of combination give only slightly different results. The specific heat, C_p, is obtained by dividing the value of MC_p read from Figure 6 by the molecular weight of the gas mixture used in the tests—namely, 8.69.

Viscosity. Kleint (*13*) and Trautz and Baumann (*19*) determined the viscosities of hydrogen-nitrogen mixtures at ordinary

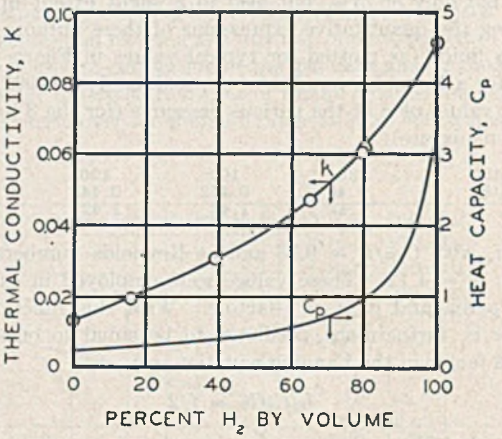

Figure 9. Thermal Conductivity (*12*) and Heat Capacity at Constant Pressure of Hydrogen-Nitrogen Mixtures at 32° F. and 1 Atmosphere

pressures. Kleint's values for the mixture are somewhat higher than those of Trautz and Baumann, although his values for the constitutents agree quite well with theirs. The results of the latter workers have been accepted as the more reliable and are shown in Figure 7.

The only data found on the viscosity of the mixtures at elevated pressures are those of Boyd (*3*) which extend to 200 atmospheres, but they scatter too much to permit reliable conclusions; furthermore, his data on pure nitrogen are not in agreement with the very consistent data of Michels and Gibson (*16*) on nitrogen to 1000 atmospheres at 25°, 50°, and 75° C. These data form part of the basis of a generalized plot by Comings and Egly (*7*), where μ/μ_1 is plotted against reduced pressure with reduced temperature as parameter. The highest value of reduced temperature on this plot is 2.80. A curve for reduced temperature of 7.25 was added by employing the pure hydrogen data of Gibson (*11*), and then values were found for the 3 hydrogen-1 nitrogen mixtures by interpolating at reduced conditions based on the pseudo-critical temperature and pressure of the mixture; these values were calculated as 62.3° K. and 24 atmospheres, respectively. From a convenient cross plot, interpolated values were obtained and plotted on Figure 8 in order to show the relative effects of temperature and pressure. The plot of generalized reduced viscosities of Uyehara and Watson (*20*) could have been utilized in a similar manner. While actual experimental values of the viscosity of the mixture at high pressures would be desirable, this method of prediction is felt to be reasonably good. Fortunately a considerable error in estimating the viscosity at high pressures would have little effect on Figure 5 and no effect on the conclusions drawn from it.

THERMAL CONDUCTIVITY. Figure 9 shows Ibbs and Hirst's data (*12*) on the thermal conductivity of hydrogen-nitrogen mixtures at 0° C. and 1 atmosphere. Weber's single point for 57.4% nitrogen at 0° C., as given in the International Critical Tables (*12A*), is in agreement. No data have been found on the effect of pressure, although estimation can be made from viscosity data as described later.

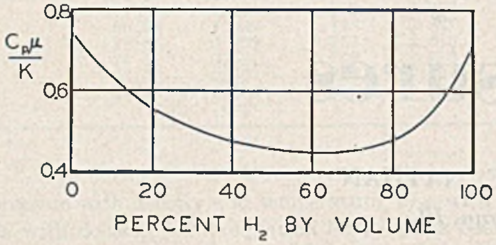

Figure 10. Prandtl Number of Hydrogen-Nitrogen Mixtures at 0° C. and 1 Atmosphere

PRANDTL NUMBER. Figure 10 shows the value of $C_p\mu/k$ for 0° C. and 1 atmosphere, calculated from the values of C_p, μ, and k derived as stated above. This curve is in substantial agreement with a similar plot of Brunot (*4*), also based on literature data. If the temperature coefficient of k for the mixture is assumed to be that given by International Critical Tables for the constituents, the calculated variation of $C_p\mu/k$ with the temperature is negligible. This agrees with the results for the pure constituents which are in accord with elementary kinetic theory. Actually, however, extended kinetic theory does not indicate invariance with the temperature, but the precision of the experimental determinations of k and of the temperature coefficient is inadequate to permit a test of theory.

For the effect of pressure, theoretical relations derived by Enskog (*10*) can be utilized. His equation of state is:

$$p + a\rho^2 = \frac{RT\rho}{M}(1 - b\rho\kappa) \tag{8}$$

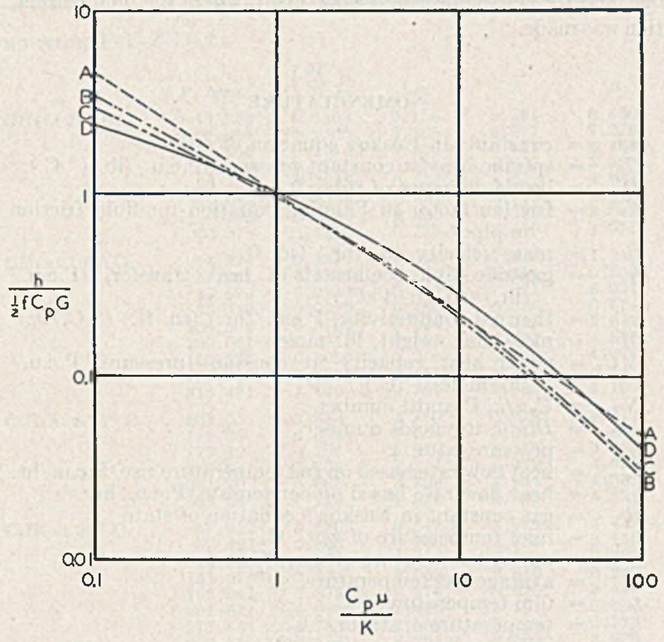

Figure 11. Relation between $h/{}^1/{}_2fC_pG$, N_{Pr}, and N_{Re} According to Empirical Relation and Equations of Boelter, Martinelli, and Jonassen (2, 5)

A. Empirical relation, $1/N_{Pr}{}^{2/3}$
B. N_{Re} = 5000
C. N_{Re} = 10,000
D. N_{Re} = 100,000

It may be shown (*16*) that

$$b\rho\kappa = \frac{M\left(\frac{dp}{dT}\right)_\rho}{R\rho} - 1 \tag{9}$$

Enskog gives the following equations for constant temperature, though in slightly different form:

$$\kappa\left(\frac{\mu_{p,t}}{\mu_{1,t}}\right) = 1 + 0.8b\rho\kappa + 0.7164(b\rho\kappa)^2 \tag{10}$$

$$\kappa\left(\frac{k_{p,t}}{k_{1,t}}\right) = 1 + 1.2b\rho\kappa + 0.7574(b\rho\kappa)^2 \tag{11}$$

Because of the deviation term on the left-hand side, neither of these equations can be solved directly for the effect of pressure, even though they contain only the relatively easily obtainable $b\rho\kappa$ on the right-hand side. However, dividing one equation by the other and multiplying both sides of the equation by $(C_p)_p/(C_p)_1$ gives

$$\frac{(C_p\mu/k)_{p,t}}{(C_p\mu/k)_{1,t}} = \frac{(C_p)_{p,t}\,(1 + 0.8b\rho\kappa + 0.7614b^2\rho^2\kappa^2)}{(C_p)_{1,t}\,(1 + 1.2b\rho\kappa + 0.7574b^2\rho^2\kappa^2)} \tag{12}$$

which is calculable, since $b\rho\kappa$ can be evaluated from *P-V-T* data of Bartlett, Cupples, and Tremearne (*1*). The results are given below for 100° C.:

Pressure, atm.	32	100	300	600	800	900
$\frac{(C_p\mu/k)_{p,t}}{(C_p\mu/k)_{1,t}}$	1.001	1.004	0.996	0.974	0.965	0.962

EFFECT OF PRANDTL NUMBER. For convenience in use, the equation of Boelter, Martinelli, and Jonassen (*2*) was plotted (*5*) with $h/{}^1/{}_2fC_pG$ as a function of N_{Pr} and N_{Re} as parameter. This plot is included as Figure 11.

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NOMENCLATURE

a,b = constants in Enskog equation of state
C_p = specific heat at constant pressure, P.c.u./(lb.)(° C.)
D = inside diameter of tube, ft.
f = friction factor in Fanning equation for fluid friction in pipes
G = mass velocity, lb./(hr.) (sq. ft.)
h = gas-side film coefficient of heat transfer, (P.c.u./(hr.) (sq. ft.) (° C.)
k = thermal conductivity, P.c.u./(hr.) (sq. ft.) (° C./ft.)
M = molecular weight, lb./mole
MC_p = molal heat capacity at constant pressure, P.c.u./(lb. mole) (° C.)
N_{Pr} = $C_p\mu/k$, Prandtl number
N_{Re} = DG/μ, Reynolds number
p = pressure, atm.
q_a = heat flow rate based on gas temperature rise, P.c.u./hr.
q_s = heat flow rate based on condensate, P.c.u./hr.
R = gas constant in Enskog's equation of state
t_1 = inlet temperature of gas, ° C.
t_2 = outlet temperature of gas, °C.
t_g = average gas temperature, ° C.
t_f = film temperature, ° C.
t_s = temperature of steam, ° C.
t_w = inside wall temperature ° C.
T = absolute temperature, ° K.
U = over-all coefficient of heat transfer based on inside diameter of tube, P.c.u./(hr.) (sq. ft.) (° C.)

$$\Delta t_m = \frac{t_2 - t_1}{\ln \dfrac{t_s - t_1}{t_s - t_2}}$$

κ = deviation factor, greater than unity, in Enskog's equation of state
μ = viscosity, lb./(hr.) (ft.)
ρ = density, lb./cu. ft.
ϕ = function of N_{Pr}

Subscripts

f = value of physical property at film temperature t_f
p = value of physical property at pressure p and prevailing temperature

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Thermal Conductivity of Gases at High Pressures

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THE increasing use of high pressure gas-phase processes has made a knowledge of the effect of pressure on the physical properties of gases necessary. Many pressure-volume-temperature measurements with the common gases, as well as equations of state and compressibility factor correlations for these, are available. Within the last few years a considerable amount of high pressure gas-viscosity data has appeared. Comings, Mayland, and Egly (*5*) summarized the viscosity data available and correlated the viscosity ratio, μ/μ_1, as a function of reduced temperature and reduced pressure.

Few experimental measurements of the thermal conductivity of gases at high pressures have been reported. Comings *et al.* (*5*) pointed out that as a first approximation the correlation of viscosity ratio could be used to predict the thermal conductivity ratio, k/k_1, at high pressure by assuming that the latter ratio is equal to the viscosity ratio. This follows from the transport theory based on the kinetic theory of gases. It was realized that these two ratios are not exactly equal for actual gases at high pressures. The difference between them will eventually need to be established by accurately determining the thermal conductivity of several gases under high pressures. The thermal conductivity measurements by Sellschopp (*15*) on carbon dioxide to 90 atmospheres were used to compare the two ratios, and the agreement was not very close (*5*). It has been shown (*8*) that convection existed in Sellschopp's experiments and his data are therefore not correct. Vargaftik (*19*) obtained a limited amount of thermal conductivity data on nitrogen up to 90 atmospheres. The relation between thermal conductivity and viscosity predicted by the kinetic theory is: $k = C\, C_v\mu$. The deviation from this relation becomes progressively greater as the pressure is increased. In the absence of adequate experimental data another method for predicting the relative magnitudes of the viscosity and thermal conductivity ratios was sought.

Enskog (*4*) derived equations which use the same constants to

Table I. Values Obtained from *P-V-T* Data

	P, Atm.	$\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_v$	$b\rho x$	A	B
N_2 at 0° C.	40	1.117	0.110	9.965	10.364
	60	1.177	0.157	7.274	7.673
	80	1.244	0.222	5.468	5.867
	100	1.294	0.275	4.645	5.044
	200	1.507	0.559	3.013	3.411
	300	1.632	0.848	2.625	3.021
	400	1.666	1.091	2.547	2.943
	500	1.692	1.345	2.568	2.962
	600	1.642	1.502	2.609	3.003
	800	1.639	1.946	2.796	3.188
	1000	1.547	2.191	2.925	3.316
N_2 at 20° C.	40	1.098	0.091	11.848	12.247
	60	1.146	0.114	9.663	10.063
	80	1.202	0.199	5.982	6.381
	100	1.236	0.239	5.169	5.569
	200	1.422	0.499	3.185	3.583
	300	1.551	0.773	2.682	3.079
	400	1.583	0.986	2.565	2.961
	500	1.600	1.199	2.547	2.942
	600	1.572	1.358	2.570	2.965
	800	1.583	1.773	2.714	3.107
	1000	1.499	1.997	2.821	3.214
N_2 at 50° C.	40	1.079	0.081	13.162	13.562
	60	1.117	0.124	8.978	9.378
	80	1.154	0.167	6.901	7.301
	100	1.184	0.206	5.809	6.208
	200	1.362	0.462	3.317	3.716
	300	1.450	0.618	2.889	3.287
	400	1.485	0.863	2.616	3.013
	500	1.499	1.037	2.554	2.950
	600	1.496	1.201	2.547	2.942
	800	1.509	1.564	2.630	3.024
	1000	1.444	1.779	2.717	3.110
N_2 at 100° C.	40	1.055	0.065	16.227	16.627
	60	1.079	0.097	11.170	11.569
	80	1.103	0.113	9.736	10.136
	100	1.131	0.169	6.860	7.259
	200	1.224	0.334	4.054	4.453
	300	1.311	0.527	3.099	3.496
	400	1.360	0.703	2.758	3.155
	500	1.374	0.841	2.630	3.026
	600	1.378	0.976	2.568	2.964
	800	1.398	1.277	2.556	2.950
	1000	1.378	1.514	2.613	3.007
C_3H_8 at 116.4° C.	91.66	1.905	1.901	2.773	3.166
	70.70	1.396	1.429	2.588	2.982
	61.78	1.037	1.106	2.546	2.942
	57.32	0.789	0.922	2.587	2.983
	53.80	0.593	0.807	2.654	3.051
	49.05	0.411	0.669	2.804	3.201
	40.71	0.245	0.490	3.216	3.614
C_3H_8 at 152.3° C.	161.48	1.972	2.003	2.824	3.216
	121.97	1.454	1.530	2.619	3.013
	99.88	1.082	1.198	2.547	2.942
	85.86	0.802	0.953	2.575	2.971
	74.82	0.581	0.769	2.686	3.083
	63.52	0.397	0.614	2.896	3.294
	49.28	0.235	0.433	3.439	3.838

	P, Atm.	$\left(\frac{\partial P}{\partial T}\right)_v$	$b\rho x$	A	B
CH_4 at 25° C.	43.829	0.1803	0.136	8.281	8.680
	52.826	0.2265	0.165	6.971	7.370
	65.504	0.2974	0.209	5.747	6.146
	70.367	0.3770	0.255	4.909	5.308
	93.445	0.4799	0.312	4.242	4.641
	111.082	0.6129	0.381	3.717	4.116
	135.293	0.8161	0.480	3.250	3.648
	203.379	1.465	0.776	2.680	3.077
CH_4 at 100° C.	44.523	0.1342	0.094	11.546	11.946
	57.251	0.1787	0.126	8.854	9.253
	69.676	0.2233	0.149	7.621	8.021
	87.616	0.2926	0.189	6.225	6.624
	106.362	0.3706	0.234	5.249	5.648
	129.061	0.4711	0.288	4.491	4.890
	156.593	0.6020	0.356	3.879	4.278
	195.961	0.8025	0.455	3.344	3.743
	312.491	1.445	0.751	2.703	3.100
C_2H_4 at 8.25° C.	108.65	3.856	2.360	3.020	3.411
	119.35	4.034	2.456	3.077	3.468
	173.39	4.796	2.870	3.333	3.722
	259.67	5.702	3.334	3.638	4.025
	381.70	6.663	3.796	3.954	4.338
	552.36	7.716	4.274	4.288	4.671
C_2H_4 at 30° C.	57.952	0.5203	0.547	3.044	3.442
	67.483[a]	0.840	0.706	2.755	3.152
	73.566[a]	1.156	0.838	2.631	3.028
	151.676[a]	3.298	2.053	2.850	3.242
	192.647	3.873	2.374	3.029	3.419
	207.63	4.080	2.495	3.101	3.491
	277.68	4.788	2.863	3.329	3.717
	383.31	5.645	3.291	3.609	3.996
	525.82	6.575	3.733	3.910	4.295
C_2H_4 at 50° C.	47.647	0.2569	0.316	4.207	4.606
	68.179	0.5041	0.499	3.184	3.582
	84.180	0.8288	0.682	2.785	3.182
	96.909	1.1737	0.866	2.614	3.011
	112.754	1.6060	1.107	2.546	2.942
	126.614	1.9325	1.295	2.558	2.953
	168.997	2.7018	1.741	2.700	3.093
	218.50	3.355	2.106	2.879	3.270
	270.72	3.899	2.397	3.042	3.433
	289.05	4.054	2.473	3.087	3.478
	337.37	4.774	2.851	3.322	3.710
	495.80	5.598	3.255	3.585	3.972
	656.44	6.499	3.678	3.872	4.258
C_2H_4 at 95° C.	49.779	0.1941	0.216	5.583	5.982
	58.935	0.2481	0.271	4.700	5.099
	90.452	0.4866	0.447	3.377	3.775
	121.201	0.8107	0.646	2.840	3.238
	149.726	1.1737	0.866	2.614	3.011
	185.22	1.6166	1.121	2.546	2.941
	213.808	1.9490	1.315	2.562	2.957
	290.261	2.6918	1.731	2.696	3.089
	368.60	3.320	2.073	2.861	3.253
	444.96	3.826	2.333	3.005	3.396
	470.70	3.993	2.421	3.056	3.447
	585.03	4.633	2.738	3.250	3.639

[a] Data in range in which isometric passes through an inflection point—therefore, not very accurate.

relate pressure with density and temperature, μ/μ_1 with density, and k/k_1 with density. The equation for μ/μ_1 has been shown (*4, 11, 13*) to agree well with the viscosity measurements on carbon dioxide and nitrogen. Leipunsky (*9*) investigated the applicability of this equation to the viscosity of several gases. These equations cannot be used to predict thermal conductivity or viscosity ratios from *P-V-T* data alone. It is possible to evaluate the constants in them by using both *P-V-T* data and viscosity data, and then to predict the thermal conductivity. This has been done, and the calculated thermal conductivity ratios for nitrogen agree with Vargaftik's data within about 1% over the range of his data.

A method for predicting the thermal conductivity of a gas at high pressures is described. This requires only a knowledge of the critical pressure, the critical temperature, and the thermal conductivity at atmospheric pressure and the temperature in question for the gas. Enskog's equation of state and his two equations relating viscosity ratio with density and thermal conductivity ratio with density are used as a basis. The constants in all these equations are the same. These constants are evaluated from available *P-V-T* data and high pressure gas-viscosity data, and are then used to predict the thermal conductivity ratio at high pressures. The calculated ratios are arranged as a function of reduced pressure and reduced temperature. The effect of pressure on the Prandtl number ratio has also been determined. A graph is presented showing this ratio as a function of reduced pressure and reduced temperature.

The method has been used to predict k/k_1 ratios over a considerable range of temperatures and pressures, and these have been arranged in the same form as the viscosity ratio correlation as a function of reduced pressure P_r, at various constant values of reduced temperature, T_r.

METHOD OF CALCULATION

The equations developed by Enskog based on the kinetic theory are as follows:

Equation of state for a static gas relating P, ρ, and T,

$$P + a\rho^2 = \frac{RT}{M}\rho(1 + b\rho x) \tag{1}$$

Equation relating viscosity ratio and density,

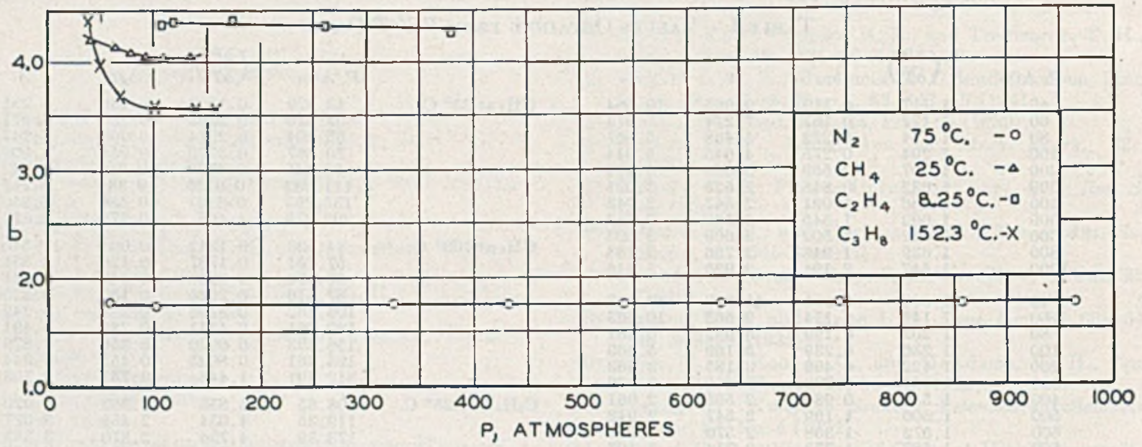

Figure 1. Effect of Pressure on Constant *b* for Several Gases

Table II. Summary of Source and Range of Viscosity and *P-V-T* Data

P-V-T				Viscosity			
Gas	Source	T_r	Max. P_r	Gas	Source	Max. Pr	Source of data at 1 atm.
N_2	(*6*)	2.36	28.8	N_2	(*11*)	28.8	(*17*)
N_2	(*6*)	2.56	28.8	N_2	(*11*)	28.8	(*17*)
N_2	(*6*)	2.76	28.8	N_2	(*11*)	28.8	(*17*)
CH_4	(*12*)	1.56	4.44	CH_4	(*5*)	3.0	(*5*)
CH_4	(*12*)	1.96	7.09	CH_4	(*5*)	3.6	(*5*)
C_2H_4	(*10*)	0.995	10.9	C_3H_8	(*16*)	8.1	(*18*)
C_2H_4	(*10*)	1.072	10.3	C_2H_4	(*5*)	2.7	(*5*)
				C_3H_8	(*16*)	8.1	(*18*)
C_2H_4	(*10*)	1.143	12.9	C_2H_4	(*5*)	2.7	(*5*)
				C_3H_8	(*16*)	8.1	(*18*)
C_2H_4	(*10*)	1.302	11.5	C_2H_4	(*5*)	2.7	(*5*)
C_3H_8	(*3*)	1.053	2.4	C_3H_8	(*16*)	8.1	(*18*)
C_3H_8	(*3*)	1.15	4.0	C_3H_8	(*16*)	8.1	(*18*)

$$\mu/\mu_1 = b\rho\left(\frac{1}{b\rho x} + 0.8 + 0.7614b\rho x\right) \qquad (2)$$

Equation relating thermal conductivity ratio and density,

$$k/k_1 = b\rho\left(\frac{1}{b\rho x} + 1.2 + 0.7574b\rho x\right) \qquad (3)$$

If it is assumed that x is a function of density only and that a and b are constants, the term $b\rho x$ may be evaluated along an isometric from Equation 1. Thus,

$$b\rho x = \frac{M}{R\rho}\left(\frac{\partial P}{\partial T}\right)_v - 1 \qquad (4)$$

The values of $\left(\frac{\partial P}{\partial T}\right)_v$ determined by Deming and Shupe (*6*) for nitrogen based on Bartlett's *P-V-T* data (*1*, *2*) were used for this gas. The values for propane, ethylene, and methane were calculated graphically from the *P-V-T* data of Beattie *et al.* (*3*), Michels and Geldermans (*10*), and Michels and Nederbragt (*12*), respectively, using a method of residuals (*21*). A straight-line relation was used to connect the ends of an isometric. The equation of this line was $p' = sT + g$. The residual r was defined as the difference between actual pressure P and p' or

$$P = sT + g + r \qquad (5)$$

Residual r was then plotted against temperature and $\left(\frac{\partial r}{\partial T}\right)_v$ was obtained graphically from the smoothed curves.

$\left(\frac{\partial P}{\partial T}\right)_v$ was calculated from the equation

$$\left(\frac{\partial P}{\partial T}\right)_v = s + \left(\frac{\partial r}{\partial T}\right)_v \qquad (6)$$

This method of using residuals is highly accurate since s is usually large compared to $\left(\frac{\partial r}{\partial T}\right)_v$. Table I gives calculated values of $\left(\frac{\partial P}{\partial T}\right)_v$ or $\frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_v$, $b\rho x$, A, and B.

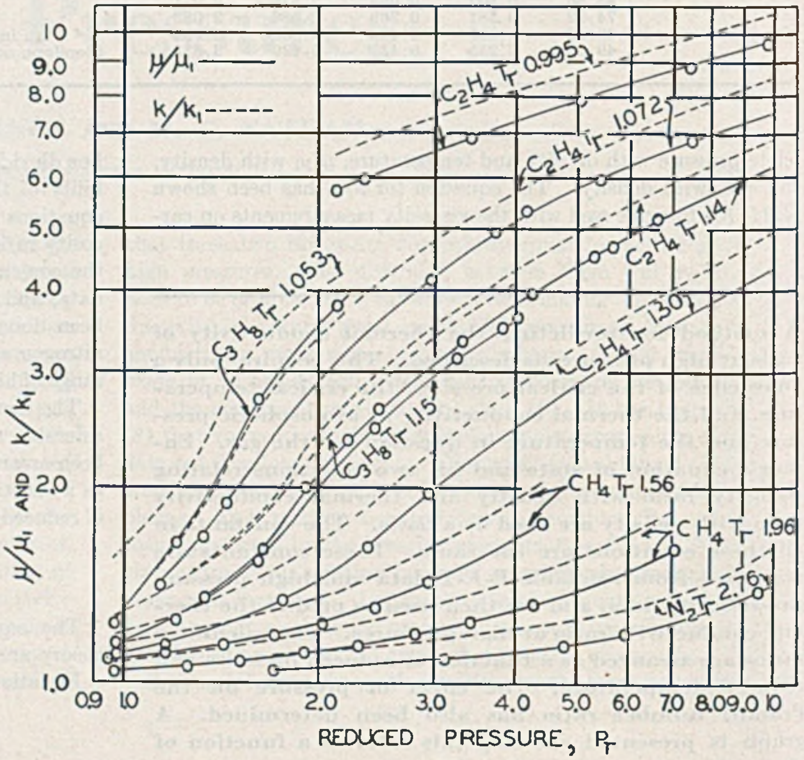

Figure 2. Comparison of Experimental Viscosity Ratio with Calculated Thermal Conductivity Ratio

Table III. Values Obtained from Viscosity and P-V-T Data for Nitrogen, Propane, and Methane

	P, Atm.	μ/μ_1 Measured	ρA	b	ρB	k/k_1 Calcd.	$\frac{k/k_1}{\mu/\mu_1} = \frac{B}{A}$
N_2 at 25° C.	48.22	1.055 (*11*)	0.552	1.91	0.568	1.09	1.03
	57.59	1.067 (*11*)	0.555	1.92	0.576	1.11	1.04
	92.31	1.122 (*11*)	0.584	1.92	0.621	1.19	1.06
	320.4	1.565 (*11*)	0.836	1.87	0.960	1.80	1.15
	430.2	1.817 (*11*)	0.978	1.86	1.126	2.09	1.15
	541.7	2.058 (*11*)	1.111	1.85	1.288	2.39	1.16
	630.4	2.263 (*11*)	1.220	1.86	1.409	2.61	1.15
	742.0	2.494 (*11*)	1.350	1.85	1.552	2.87	1.15
	854.1	2.719 (*11*)	1.472	1.85	1.686	3.11	1.15
	965.7	2.947 (*11*)	1.580	1.87	1.807	3.37	1.14
N_2 at 50° C.	57.60	1.058 (*11*)	0.562	1.88	0.586	1.10	1.04
	104.5	1.115 (*11*)	0.617	1.81	0.656	1.19	1.06
	212.4	1.268 (*11*)	0.669	1.90	0.748	1.42	1.12
	320.4	1.462 (*11*)	0.794	1.84	0.906	1.67	1.14
	430.2	1.671 (*11*)	0.915	1.83	1.056	1.93	1.15
	541.7	1.874 (*11*)	1.038	1.81	1.196	2.16	1.15
	630.4	2.022 (*11*)	1.128	1.79	1.303	2.34	1.16
	742.1	2.225 (*11*)	1.237	1.80	1.426	2.57	1.15
	854.1	2.431 (*11*)	1.338	1.82	1.551	2.82	1.16
	965.8	2.624 (*11*)	1.420	1.85	1.672	3.09	1.18
N_2 at 75° C.	57.61	1.053 (*11*)	0.574	1.83	0.600	1.10	1.05
	104.5	1.097 (*11*)	0.629	1.75	0.672	1.17	1.07
	320.3	1.385 (*11*)	0.764	1.81	0.868	1.57	1.14
	430.2	1.553 (*11*)	0.870	1.79	0.996	1.78	1.15
	541.7	1.729 (*11*)	0.975	1.77	1.127	2.00	1.16
	630.3	1.867 (*11*)	1.059	1.76	1.221	2.15	1.15
	742.0	2.026 (*11*)	1.131	1.79	1.335	2.39	1.18
	854.1	2.201 (*11*)	1.255	1.75	1.450	2.54	1.16
	965.7	2.373 (*11*)	1.360	1.75	1.557	2.72	1.14
C_3H_8 at 116.4° C.	40.84	1.244 (*16*)	0.260	4.79	0.322	1.54	1.14
	51.06	1.654 (*16*)	0.389	4.25	0.455	1.94	1.16
	68.07	2.755 (*16*)	0.767	3.79	0.887	3.37	1.16
	90.00	3.689 (*16*)	0.968	3.81	1.105	4.21	1.14
	102.1	4.032 (*16*)	1.057	3.81	1.182	4.51	1.12
C_3H_8 at 152.3° C.	40.84	1.152 (*16*)	0.263	4.38	0.289	1.27	1.10
	51.06	1.263 (*16*)	0.312	4.05	0.349	1.41	1.12
	68.07	1.547 (*16*)	0.417	3.71	0.477	1.77	1.14
	102.1	2.473 (*16*)	0.688	3.59	0.795	2.86	1.16
	136.1	3.150 (*16*)	0.884	3.56	1.013	3.61	1.15
	160.0	3.528 (*16*)	0.990	3.56	1.127	4.02	1.14
	170.1	3.688 (*16*)	1.028	3.58	1.165	4.18	1.13
CH_4 at 25° C.	43.829	1.089 (*5*)	0.257	4.24	0.269	1.14	1.05
	52.826	1.114 (*5*)	0.265	4.21	0.280	1.18	1.06
	65.504	1.150 (*5*)	0.276	4.16	0.295	1.23	1.07
	78.367	1.182 (*5*)	0.288	4.11	0.311	1.28	1.08
	93.445	1.233 (*5*)	0.303	4.07	0.332	1.35	1.09
	111.082	1.307 (*5*)	0.322	4.06	0.357	1.45	1.11
	135.293	1.429 (*5*)	0.350	4.08	0.393	1.60	1.12
	203.379	1.77 (*5*)	0.432	[a]	0.406	2.03	1.15
CH_4 at 100° C.	44.523	1.047 (*5*)	0.277	3.78	0.286	1.08	1.03
	57.251	1.065 (*5*)	0.275	3.88	0.287	1.11	1.04
	69.676	1.084 (*5*)	0.289	3.75	0.304	1.14	1.05
	87.616	1.111 (*5*)	0.299	3.72	0.318	1.18	1.06
	106.362	1.141 (*5*)	0.308	3.71	0.331	1.23	1.08
	129.061	1.183 (*5*)	0.321	3.69	0.349	1.29	1.09
	156.593	1.24 (*5*)	0.336	[b]	0.371	1.37	1.10
	195.961	1.33 (*5*)	0.360	[b]	0.403	1.49	1.12
	312.491	1.61 (*5*)	0.436	[b]	0.500	1.85	1.15

[a] Beyond the range of viscosity data, b was taken as 4.10.
[b] Beyond the range of viscosity data, b was taken as 3.70.

The viscosity and P-V-T data listed in Table II were used to calculate the values of b which are given in Tables III and IV,

$$b = \mu/\mu_1/\rho A \qquad (7)$$

Tables III and IV also list the calculated thermal conductivity ratio, k/k_1, and $(k/k_1)/(\mu/\mu_1) = B/A$. This ratio varies in the range considered from 1.0 to 1.16.

The thermal conductivity ratio, k/k_1, was then calculated from Equation 3 or

$$k/k_1 = b\rho B \qquad (8)$$

using the values of b obtained from viscosity and P-V-T data and B from P-V-T data, both at the same temperature and pressure for which the k/k_1 ratio is evaluated.

CALCULATED RESULTS

For a given temperature the calculated values of b remain relatively constant with a variation in pressure except near the critical pressure. In the latter region the calculations are quite sensitive to small errors, a 1% error in $\left(\frac{\partial P}{\partial T}\right)_v$ producing an 8% error in the calculated viscosity ratio when using a constant value of b. As the pressure is increased, the viscosity ratio becomes less sensitive to errors in $\left(\frac{\partial P}{\partial T}\right)_v$ and b tends to remain constant over a considerable pressure range. However, as the pressure is increased, especially at low reduced temperatures, a slight variation appears in b which follows a definite trend. Figure 1 shows the typical variation of b with pressure for several gases at constant temperatures as calculated from viscosity data. No attempt was made to calculate the thermal conductivity ratio beyond a reduced pressure of 10, except in the case of nitrogen where viscosity data were available to nearly 1000 atmospheres. This limit was set because of the variation in b at the higher pressures in the region of low reduced temperatures.

Table V compares Vargaftik's experimental values (*19*) of the thermal conductivity of nitrogen expressed as k/k_1 with these ratios calculated by Enskog's equation. The calculated values agree with the experimental within 1%.

Figure 2 shows the effect of reduced pressure on the calculated thermal conductivity ratio for several gases at constant reduced temperatures. The curves are compared with those of the measured viscosity ratio. Figure 3 gives the thermal conductivity

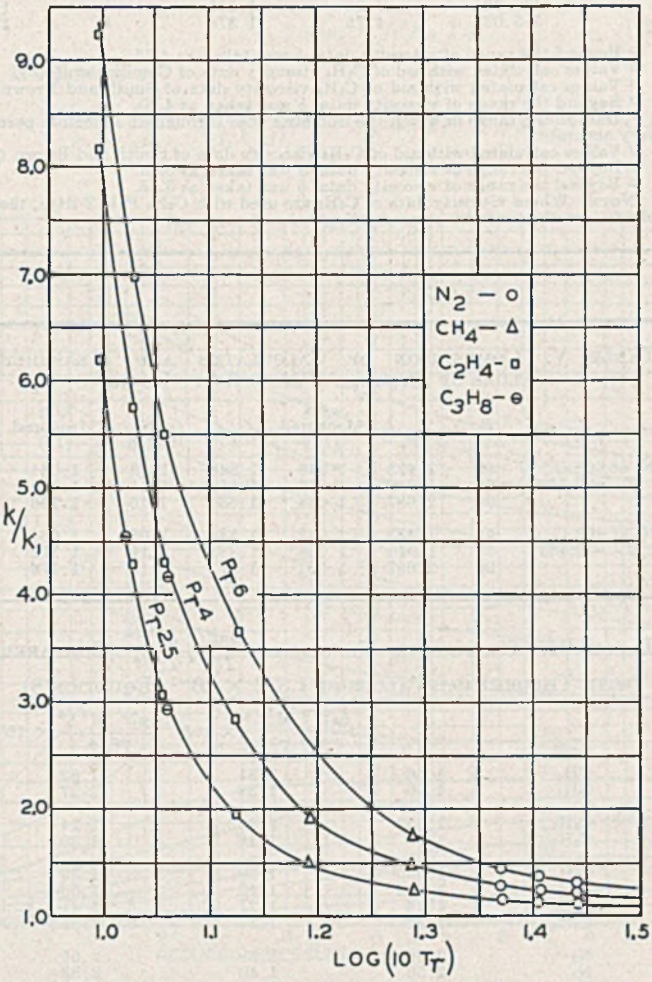

Figure 3. Calculated Thermal Conductivity Ratio *vs.* Reduced Temperature

TABLE IV. VALUES CALCULATED FROM VISCOSITY AND P-V-T DATA FOR ETHYLENE

Temp., ° C.	P, Atm.	μ/μ_1 Measured		ρA	b		ρB	k/k_1 Calcd.		$\frac{k/k_1}{\mu/\mu_1} = \frac{B}{A}$
8.25	108.65	5.782		1.184	4.88		1.337	6.53		1.13
	119.35	6.012		1.227	4.90		1.383	6.77		1.13
	173.39	6.954		1.411	4.93		1.576	7.77		1.12
	259.67	7.946		1.635	4.86		1.809	8.79		1.11
	381.70	8.985		1.876	4.79		2.059	9.86		1.10
	552.36	10.18		2.143	[a]		2.334	11.09		1.09
30	57.952	1.385[b]	1.417[c]	0.350	3.96[b]	4.05[c]	0.395	1.57[b]	1.60[c]	1.13
	67.483	1.684[b]	1.673[c]	0.464	3.63[b]	3.61[c]	0.530	1.93[b]	1.91[c]	1.14[e]
	73.566	2.040[b]	1.880[c]	0.565	3.62[b]	3.33[c]	0.651	2.36[b]	2.17[c]	1.15[e]
	151.676		4.196[c]	1.052		3.99[c]	1.196		4.77[c]	1.14[e]
	192.647		4.944[c]	1.188		4.16[c]	1.341		5.58[c]	1.13
	207.63		5.160[c]	1.236		4.17[c]	1.392		5.80[c]	1.13
	277.68		5.973[c]	1.410		4.24[c]	1.574		6.67[c]	1.12
	383.31		6.847[c]	1.622		4.22[c]	1.796		7.58[c]	1.11
	525.82		7.79[c]	1.856		[d]	2.038		8.56[c]	1.10
50	47.647	1.185[b]	1.130[f]	0.281	4.22[b]	4.03[f]	0.307	1.30[b]	1.24[f]	1.09
	68.179	1.391[b]	1.355[f]	0.366	3.80[b]	3.71[f]	0.411	1.56[b]	1.52[f]	1.12
	84.180	1.674[b]	1.604[f]	0.469	3.57[b]	3.42[f]	0.536	1.91[b]	1.83[f]	1.14
	96.909	2.031[b]	2.014[f]	0.562	3.62[b]	3.58[f]	0.647	2.34[b]	2.32[f]	1.15
	112.754	2.443[b]	2.353[f]	0.663	3.69[b]	3.55[f]	0.766	2.83[b]	2.72[f]	1.16
	126.614	2.756[b]	2.625[f]	0.736	3.75[b]	3.57[f]	0.849	3.18[b]	3.03[f]	1.15
	168.997		3.333[f]	0.909		3.67[f]	1.041		3.82[f]	1.15
	218.50		3.955[f]	1.062		3.72[f]	1.207		4.49[f]	1.14
	270.72		4.528[f]	1.193		3.80[f]	1.346		5.11[f]	1.13
	289.05		4.706[f]	1.231		3.82[f]	1.387		5.30[f]	1.13
	337.37		5.250[f]	1.406		3.73[f]	1.571		5.86[f]	1.12
	495.80		6.17[f]	1.611		[g]	1.785		6.84[f]	1.11
	656.44		7.04[f]	1.838		[g]	2.020		7.74[f]	1.10
95	49.779	1.111		0.304	3.65		0.326	1.19		1.07
	58.935	1.150		0.314	3.67		0.340	1.25		1.08
	90.452	1.348		0.388	3.48		0.434	1.51		1.12
	121.201	1.628		0.478	3.41		0.545	1.86		1.14
	149.726	1.952		0.562	3.47		0.647	2.25		1.15
	185.220	2.29		0.663	[h]		0.766	2.64		1.16
	213.808	2.54		0.737	[h]		0.850	2.93		1.15
	290.261	3.13		0.908	[h]		1.040	3.59		1.15
	368.60	3.64		1.056	[h]		1.200	4.14		1.14
	444.96	4.06		1.178	[h]		1.331	4.59		1.13
	470.70	4.20		1.219	[h]		1.374	4.74		1.13
	585.03	4.75		1.376	[h]		1.541	5.32		1.12

[a] Beyond the range of viscosity data, b was taken as 4.75.
[b] Values calculated with aid of C_2H_4 viscosity data of Comings *et al.* (*5*).
[c] Values calculated with aid of C_3H_8 viscosity data of Smith and Brown (*16*).
[d] Beyond the range of viscosity data, b was taken as 4.20.
[e] Data in the range in which the isometric goes through an inflection point; therefore, calculated data are not very accurate.
[f] Values calculated with aid of C_3H_8 viscosity data of Smith and Brown (*16*).
[g] Beyond the range of viscosity data, b was taken as 3.83.
[h] Beyond the range of viscosity data, b was taken as 3.45.
NOTE: Where viscosity data of C_3H_8 are used with C_2H_4 P-V-T data, the P is that of the C_2H_4, and the values of μ/μ_1 are those at the corresponding reduced pressure.

TABLE V. COMPARISON OF CALCULATED AND MEASURED VALUES OF THERMAL CONDUCTIVITY RATIO

	P, Atm.	P_r	μ/μ_1 Measured (*11*)	b	k/k_1 Calcd.	k/k_1 Measured (*19*)
N_2 at 60° C., $T_r = 2.642$	48	1.433	1.038	1.848	1.08	1.084
	65	1.940	1.056	1.853	1.11	1.109
	90	2.687	1.084	1.834	1.16	1.166
N_2 at 40° C., $T_r = 2.483$	48	1.433	1.041	1.88	1.08	1.084
	65	1.940	1.058	1.88	1.11	1.112
	90	2.687	1.091	1.87	1.16	1.176

TABLE VI. CALCULATED VALUES OF $\frac{b\mu_1^{3/2}M^{1/4}}{T_r^{3/4}T_c^{3/4}}$ COMPARED WITH THEORETICAL VALUES OF 1.872×10^{-7} (EQUATION 9)

Gas	T_r	$\frac{b\mu_1^{3/2}M^{1/4}}{T_r^{3/4}T_c^{3/4}} \times 10^7$	$\frac{b\mu_1^{3/2}M^{1/4}}{T_c^{3/4}} \times 10^7$
CH_4	1.56	1.31	1.82
CH_4	1.96	1.38	2.27
C_3H_8	1.053	1.20	1.24
C_3H_8	1.15	1.18	1.30
C_2H_4	0.995	1.39	1.39
C_2H_4	1.072	1.43	1.50
C_2H_4	1.14	1.27	1.41
C_2H_4	1.30	1.34	1.63
N_2	2.36	1.39	2.65
N_2	2.56	1.40	2.83
N_2	2.73	1.40	3.00

ratio as a function of reduced temperature at constant reduced pressures. Cross plots such as this were used to construct the final correlation.

The value b represents the actual volume of the molecules as given by Enskog's equation (*9*). This equation, expressed in terms of reduced temperature, is:

$$b = \frac{1.872 \times 10^{-7} \times T_r^{3/4}\,T_c^{3/4}}{\mu_1^{3/2}\,M^{1/4}} \tag{9}$$

where the numerical constant is that predicted by Enskog. Table VI gives b as obtained by using the values of b calculated from viscosity data. The values obtained are closer to 1.4×10^{-7} than to 1.872×10^{-7}. Figure 4 is a plot of:

$$\frac{b\mu_1^{3/2}\,M^{1/4}}{T_c^{3/4}} \text{ vs. } T_r \tag{10}$$

The greatest deviation from the curve appears at low values of the reduced temperature.

CORRELATION OF THERMAL CONDUCTIVITY RATIO

The calculated values of the thermal conductivity ratio were then plotted as a function of reduced pressure at several values of reduced temperature, and these curves were smoothed somewhat with the aid of Figure 3. Figure 5 represents a correlation of the calculated values of k/k_1 against reduced pressure at constant

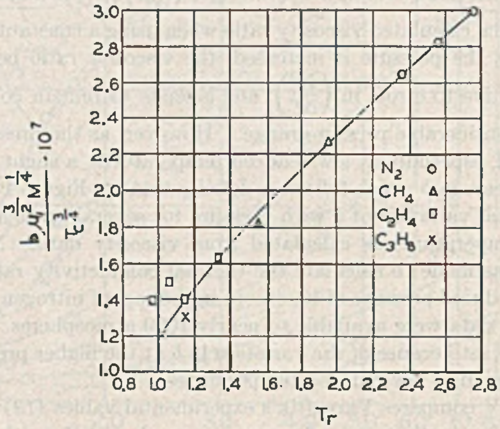

Figure 4. $\frac{b\mu_1^{3/2}M^{1/4}}{T_c^{3/4}}$ as a Function of Reduced Temperature

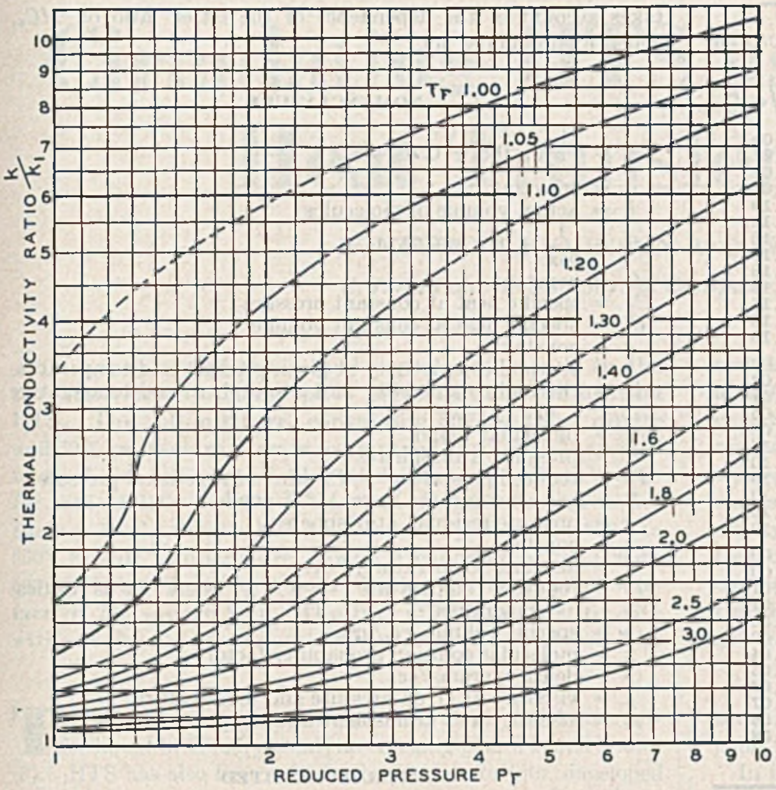

Figure 5. General Correlation of Thermal Conductivity Ratio as Function of Reduced Pressure and Reduced Temperature

reduced temperature. This figure may be used to predict the effect of pressure on the thermal conductivity of any gas when its critical temperature, critical pressure, and thermal conductivity at atmospheric pressure are known.

EXAMPLE. The use of the correlations for predicting thermal conductivity is illustrated by the following example for ethylene at 150° F. and 300 atmospheres absolute:

$$P_c = 50.9 \text{ atm.};\quad T_c = 509° \text{ R.}$$

$$k_1 = 0.0140 \frac{\text{B.t.u.}}{\text{hr.} \times \text{ft.} \times {}^\circ\text{F.}}$$

$$P_r = \frac{300}{50.9} = 5.6;\quad T_r = \frac{150 + 460}{509} = 1.20$$

From Figure 5, $k/k_1 = 4.61$; therefore,

$$k = 0.0140 \times 4.61 = 0.0645 \frac{\text{B.t.u.}}{\text{hr.} \times \text{ft.} \times {}^\circ\text{F.}}$$

CORRELATION OF PRANDTL NUMBER RATIO

In the design of heat transfer equipment at high pressure, it is often necessary to know the effect of pressure on the Prandtl number, $C_p\mu/k$. Saunders (*14*) found it possible to correlate heat transfer data on nitrogen from 1 to 1000 atmospheres by assuming $C_p\mu/k$ independent of pressure at relatively high reduced temperatures. This number for nitrogen at 0°, 50°, and 100° C. from 1 to 1000 atmospheres was calculated using the k/k_1 ratios obtained above and the C_p data of Deming and Shupe. These values, listed in Table VII, show a slight increase with pressure. A correlation of the Prandtl number ratio, $(C_p\mu/k)/(C_{p_1}\mu_1/k_1)$ as a function of reduced pressure at several values of reduced temperature would be useful. This requires that the ratio C_p/C_{p_1} be the same for all substances in corresponding states. Dodge (*7*) prepared charts of C_p/C_{p_1} against reduced pressure at several values of reduced temperature, but did not show that these are generalized correlations. Watson and Smith (*20*) derived a generalized expression and showed that the difference $M(C_p - C_{p_1})$ must be the same for all gases in corresponding states. It is clear that the ratio of C_p to C_{p_1} and their difference cannot both be functions of only the reduced temperature and the reduced pressure, since this could only be true if MC_p and MC_{p_1} were also each functions of reduced temperature and reduced pressure alone. It is well known that MC_p and MC_{p_1} differ from one chemical compound to another and hence cannot be the same for all compounds in corresponding states. It is concluded that only $M(C_p - C_{p_1})$ and not C_p/C_{p_1} is a function of P_r and T_r only. This may be stated as:

$$MC_p - MC_{p_1} = f_1(P_r, T_r) \tag{11}$$

From Figure 5,

$$k/k_1 = f_2(P_r, T_r) \tag{12}$$

and from Comings *et al.* (*5*)

$$\mu/\mu_1 = f_3(P_r, T_r) \tag{13}$$

It follows that

$$\frac{C_p\mu}{k} \Big/ \frac{C_{p_1}\mu_1}{k_1} = \frac{f_3}{f_2}\left(\frac{f_1}{MC_{p_1}} - 1\right) = f_4(P_r, T_r, MC_{p_1}) \tag{14}$$

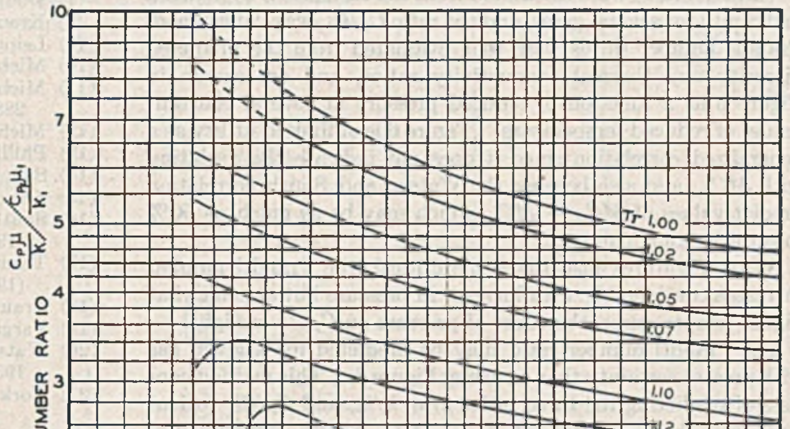

Figure 6. Variation in Prandtl Number Ratio with Reduced Pressure and Reduced Temperature (Not a General Correlation)

Table VII. Effect of Pressure on the Prandtl Number of Nitrogen

Temp., ° C.	T_r	P, Atm.	C_p (6), Cal./Mole	$\frac{C_p\mu}{k}$	$\frac{C_p\mu}{k} \bigg/ C_{p1}\frac{\mu_1}{k_1}$
0	2.17	1	6.91	0.706	1.00
		20	7.20	0.727	1.02
		40	7.51	0.737	1.04
		60	7.83	0.758	1.07
		80	8.15	0.776	1.10
		100	8.44	0.793	1.12
		200	9.25	0.834	1.18
		300	9.46	0.839	1.19
		400	9.39	0.830	1.18
		500	9.28	0.821	1.16
		600	9.21	0.817	1.16
		800	9.11	0.816	1.16
		1000	9.04	0.814	1.15
50	2.56	1	6.92	0.700	1.00
		40	7.29	0.716	1.02
		80	7.63	0.729	1.04
		100	7.78	0.736	1.05
		200	8.38	0.756	1.08
		300	8.69	0.769	1.10
		400	8.80	0.773	1.10
		500	8.82	0.772	1.10
		600	8.81	0.771	1.10
		800	8.75	0.769	1.10
		1000	8.70	0.768	1.10
100	2.96	1	6.94	0.693	1.00
		20	7.06	0.696	1.00
		40	7.18	0.700	1.01
		60	7.29	0.703	1.01
		80	7.40	0.711	1.03
		100	7.50	0.708	1.02
		200	7.95	0.723	1.04
		300	8.27	0.732	1.06
		400	8.47	0.739	1.07
		500	8.57	0.744	1.07
		600	8.61	0.745	1.08
		800	8.64	0.747	1.08
		1000	8.71	0.756	1.09

Therefore the Prandtl number ratio is a function of the reduced pressure, the reduced temperature, and the molal heat capacity of the separate gases at atmospheric pressure.

Although it has just been shown that the Prandtl number ratio is not a function of reduced temperature and reduced pressure alone, an approximate correlation was prepared on this basis. It indicates the magnitude of the variations in the Prandtl number with pressure.

Values of MC_p were calculated from the correlation by Watson and Smith for several gases, and the ratio C_p/C_{p_1} was determined. Prandtl number ratios were then evaluated from the predicted viscosity and thermal conductivity ratios, and are shown in Figure 6 as a function of reduced pressure at several constant values of reduced temperature. Figure 6 is of limited utility as a generalized correlation since it does not indicate the variation with MC_{p_1}, and also because the Watson and Smith correlation predict values of $MC_p - MC_{p_1}$ which may be as much as 50% in error at some points.

At temperatures just above the critical, the Prandtl number increases considerably with increase in pressure but at somewhat higher temperatures, the effect of pressure on $C_p\mu/k$ is slight.

The Prandtl number ratio may be predicted for a given gas with greater certainty than by using Figure 6. This method consists of predicting the three ratios μ/μ_1, k/k_1, and C_p/C_{p_1} (calculated from the correlations of $MC_p - MC_{p_1}$ and the experimental value of MC_{p_1}) from the separate correlations, and combining these to give the desired Prandtl number ratio. This method takes account of the dependence of the latter ratio on MC_{p_1} which Figure 6 does not.

NOMENCLATURE

A = $\frac{1}{b\rho x} + 0.8 + 0.7614 b\rho x$
a = constant
b = actual volume of molecules
B = $\frac{1}{b\rho x} + 1.2 + 0.7574 b\rho x$
C = constant
C_p = specific heat at constant pressure
C_v = specific heat at constant volume
g = constant
k = thermal conductivity at given pressure and temperature
k_1 = thermal conductivity at 1 atmosphere and temperature of k
M = molecular weight
P = pressure, atmospheres
P_r = reduced pressure = P/P_c, where P_c is critical pressure
R = gas constant, (cc.)(atm.)/° K./mole
r = pressure residual, atmospheres
s = constant
T = absolute temperature, ° K.
T_r = reduced temperature = T/T_c, where T_c is critical temperature
v = specific volume, cc./gram
x = molecular collision probability factor
ρ = density, grams/cc.
μ = viscosity at given pressure and temperature
μ_1 = viscosity at 1 atmosphere and temperature of μ

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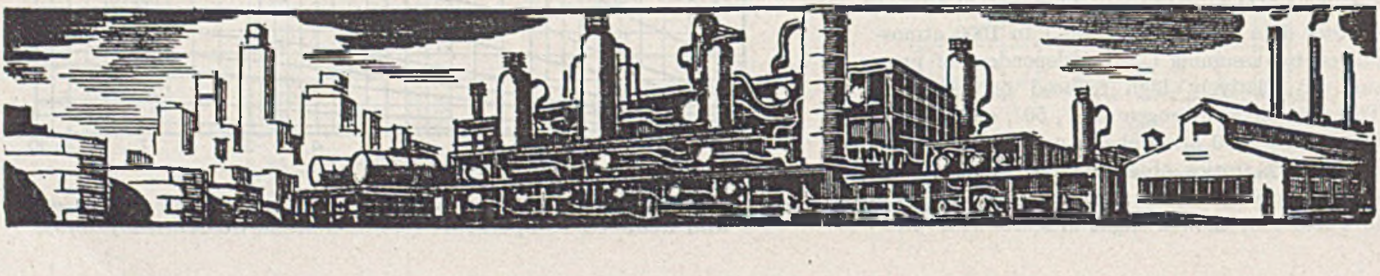

Circulating HTS as a Pilot Plant Heat Transfer Medium

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This paper covers the actual experience gained in the operation of an oil-fired pilot plant furnace for heating HTS. The salt mixture, containing 50% sodium nitrite and 50% potassium nitrate, is pumped through a standard vertical, fire-tube type boiler made of steel. A heat transfer rate of 1200 to 2000 B.t.u./hour/square foot of boiler surface is obtained when the unit is operated at 600° to 850° F. salt temperature, giving a capacity of 200,000 to 400,000 B.t.u./hour for a boiler having a total heating surface of 203 square feet. The fuel efficiency is 50 to 55% without the use of economizers or waste heat boilers. The unit has been operated for a total of 178 runs, equivalent to about 1500 hours. No unusual safety hazards were encountered. The pilot plant provides a convenient source of heat for general use in semiworks operations where the temperature required is above that provided by high pressure steam. In operation the unit is versatile, and standard types of air-operated temperature and pressure control instruments may be used to control the oil burner or to control a salt feed valve to an autoclave. It is believed that information on a heating system of this size may be of general interest to the chemical industry.

THE extensive use of heat transfer salt (HTS) as a heat transfer liquid in Houdry catalytic cracking plants is well known (*3*). HTS has also been used in the Thermofor kiln, developed by the Socony-Vacuum Oil Company (*2*), and to a lesser degree in the chemical industry. Because of the wide usefulness of this salt mixture in the high temperature field, a comprehensive paper was published in 1940 (*1*) giving the general characteristics of HTS plus a considerable amount of data on specific gravity of the liquid from 300° to 1000° F., specific heat of the liquid and solid, latent heat of fusion, viscosity of the liquid from 300° to 820° F., and coefficients of heat transfer from 600° to 1000° F. and at velocities up to 6 feet per second. A commonly used HTS mixture contains about 50% sodium nitrite and 50% potassium nitrate by weight and melts at 282° F. The salt is thermally stable and is noncorrosive to steel up to 850° F. At higher temperatures the salt gradually decomposes with increase in freezing point, and stainless steel is used to reduce corrosion.

In 1942 a pilot plant furnace was designed and installed at this laboratory to provide operating experience and for general use in heating various kinds of semiworks equipment. Our results with this unit may be of interest to others in the chemical industry.

The arrangement of the equipment is shown schematically in Figure 1. A storage tank is fitted with a steam coil (150 pounds per square inch gage) for maintaining the salt in the

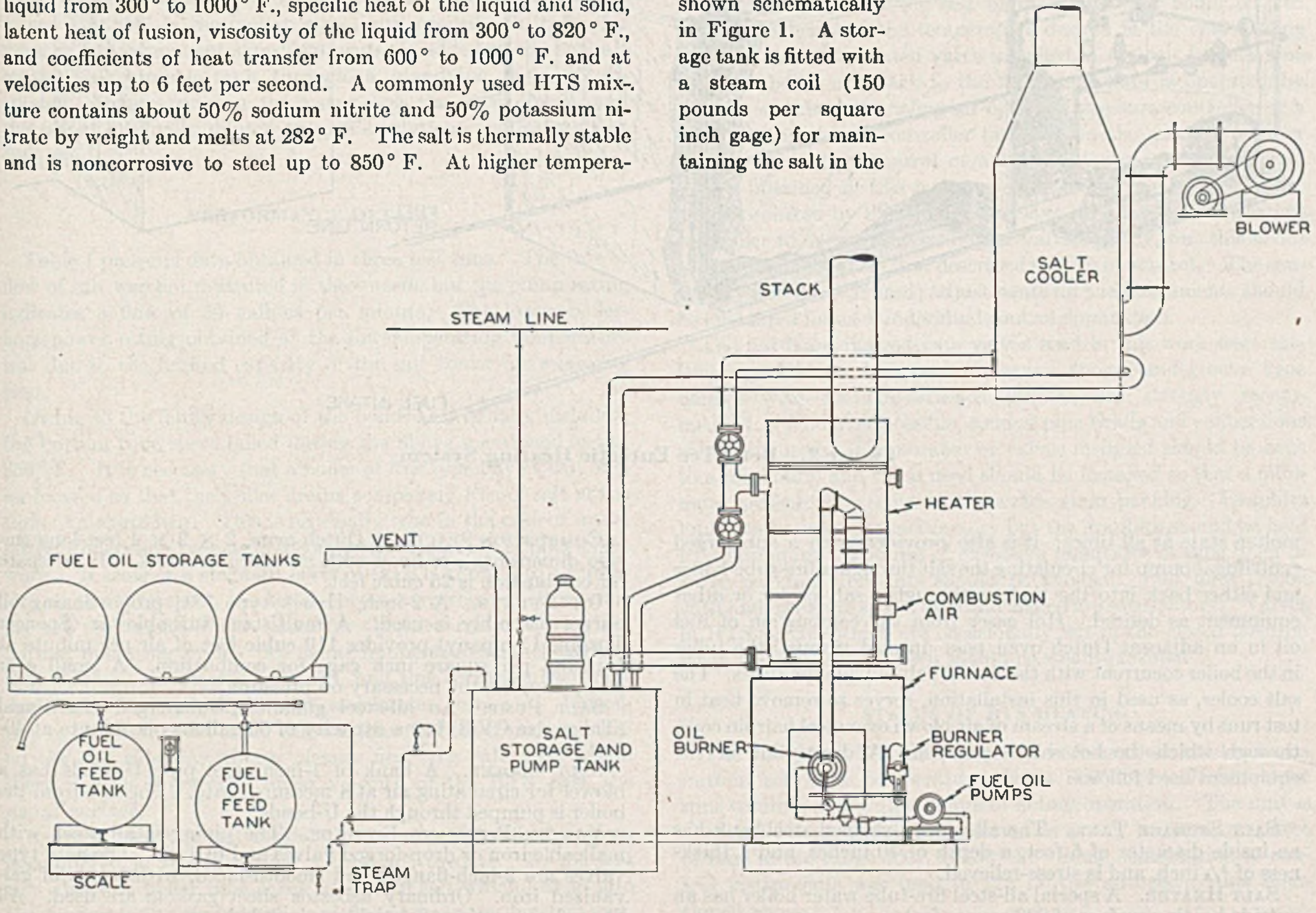

Figure 1. Arrangement of Heat Transfer Salt Equipment

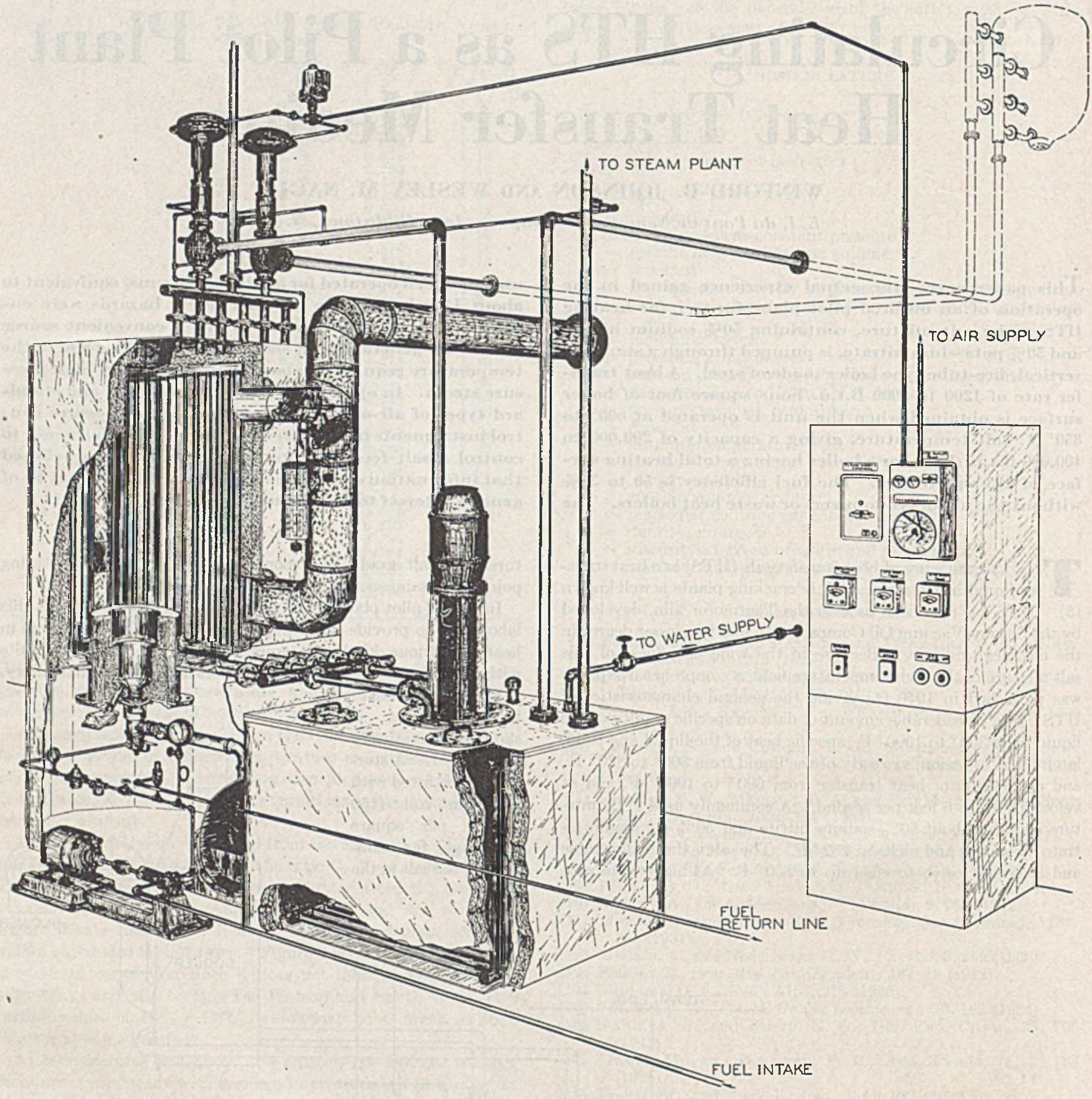

Figure 2. Beth-Tec Eutectic Heating System

molten state at all times; it is also provided with a submerged centrifugal pump for circulating the salt through a fire-tube boiler and either back into the tank or through a salt cooler or other equipment as desired. Hot gases from the combustion of fuel oil in an adjacent Dutch oven pass upward through the tubes in the boiler cocurrent with the flow of salt outside the tubes. The salt cooler, as used in this installation, serves to remove heat in test runs by means of a stream of air blown over steel hairpin coils, through which the hot salt is pumped. A description of the equipment used follows:

Salt Storage Tank. The all-welded vertical steel tank has an inside diameter of 5 feet, a depth of 40 inches, and a thickness of $^{3}/_{8}$ inch, and is stress-relieved.

Salt Heater. A special all-steel fire-tube water boiler has an outside heating surface of 203 square feet.

Combustion Space. A Dutch oven, 2 × 2 × 4 feet long (inside dimensions), is lined with standard firebrick. Total space for combustion is 25 cubic feet.

Oil Burner. A 2-inch, Hauck type 781, proportioning oil burner assembly is used. A multistage turboblower (Spencer Turbine Company) provides 110 cubic feet of air per minute at 1 pound per square inch gage for combustion. A small gear pump supplies the necessary oil pressure.

Salt Pump. An all-steel glandless, submerged centrifugal (Taber size CV-3) has a capacity of 50 gallons per minute at 40-foot head.

Salt Cooler. A bank of 1-inch steel pipe U-bends has a blower for circulating air at a measured rate. The salt from the boiler is pumped through the U-bends.

Valves, Pipe, and Fittings. The piping is all steel, with malleable iron or drop-forged valves and fittings. The gate type valves are 2-inch-flanged and smooth-faced, with hoods of galvanized iron. Ordinary asbestos sheet gaskets are used. All flanged connections are tightened while hot.

Instruments. The salt temperature at the boiler exit is controlled by a recording-controlling electric pyrometer which operates an electric reversing motor to give high-low control of the Hauck oil burner. An over-temperature cutoff is installed at the bottom of the boiler to shut off the unit whenever the temperature exceeds an arbitrarily set maximum operating temperature.

Electrical Circuits and Safety Equipment. A Mercoid switch, attached to a butterfly valve in the combustion air duct to the burner, is used to close a solenoid valve in the oil line in case of failure of the combustion air blower. In addition, the 220-volt circuit (including the motors on the combustion air blower and the salt pump) is interlocked through a relay so that any electrical failure shuts down the unit. A remote, manually operated control switch is provided to kill the entire circuit when desired.

Procedure. As HTS is a strong oxidizing agent, it is important to clean the entire system of all wood, paper, or organic material of any kind, before the salt is introduced. The system is washed out with a solution of 25 pounds trisodium phosphate or its equivalent in 100 gallons of water. When the system is clean, sufficient water is added to cover the steam coil. In this case the melting of the HTS as it is charged is greatly expedited. When all of the salt has been added and the evolution of water vapor has substantially ceased, circulation of the salt through the boiler may be started. Heating of the salt must be very gradual as it is likely to foam at 450° to 500° F. when the last of the water is being removed. Usually the oil fire is lighted a few minutes before the circulation of salt is started through the boiler. The stream of salt leaving the boiler is returned through a by-pass to the pump tank until the entire system is heated to the desired operating temperature. The salt by-pass valve may then be adjusted to give any desired degree of flow to the vessel to be heated.

When the unit is shut down temporarily, the oil burner is shut off and the hot salt allowed to flow by gravity into the pump tank where it is held in the molten state until needed. In case of a more or less permanent shutdown, water is added to the hot salt in the salt storage tank through a standpipe of small diameter. By evaporation the water cools the mass of salt, and the salt is gradually diluted to give a solution containing about 40% solids.

PERFORMANCE DETAILS

Table I presents data obtained in three test runs. The rate of flow of salt was not measured in these tests, but the pump rating indicates a flow of 50 gallons per minute. The lower boiler-horsepower rating obtained at the lower operating temperature was due to the limited capacity of the salt cooler for removing heat.

Owing to the faulty design of the boiler as originally installed, the bottom tube sheet failed during the above mentioned test at 850° F. It is necessary that a boiler of this type have a salt outlet located so that the boiler drains completely free of salt at the time of a shutdown. This is especially true in the case of intermittent operation such as is encountered commonly in pilot plant work. If scale or a stagnant layer of HTS is allowed to accumulate on the tube sheet, the latter becomes overheated either during the preheating of the boiler for the next run or during the normal operating cycle. At metal temperatures much greater than 900° F. the steel is corroded, and this corrosion then produces more scale which, in turn, accelerates corrosion. Inspection of the pilot plant boiler showed that the heat transfer surface on the salt side was always cleaner near the salt inlet where there was an appreciable linear velocity of the HTS past the metal surface.

Safety. No unusual incident pertaining to safety has been encountered in the operation of this unit to date. In the test run when the boiler tube sheet failed, the salt which leaked into the firebox led to no indication of fire or pressure development. The salt appeared to sublime, and part of it went up the stack with the flue gas. The following general precautions are observed:

Table I. Performance Data

Run No.	I	II	III
HTS operating temperature, ° F.	575	575	850
Oil rate, lb./hr.	24	21	41
Heat input based on high heating value of oil, B.t.u./hr.	459,500	409,400	793,900
Heat removed in cooler, B.t.u./hr.	236,400	223,300	413,800
Thermal efficiency, %	51.5	54.5	52.0
Boiler horsepower developed	7.1	6.7	12.4
Heat flux in boiler, B.t.u./hr./sq. ft.	1165	1100	2040
Excess air in furnace, %	217	128	106

1. A 4 × 4 inch dam separates the area where molten salt is handled from the operating floor area.
2. Forged steel or stainless valves and fittings are used, not cast iron.
3. All valves and flanges are hooded or guarded.
4. A minimum number of valves is used. If possible these valves are left in the open position at the time of a shutdown.
5. All equipment is well insulated.
6. All temperature measurements are taken by means of remote recording or indicating instruments.
7. Combustible matter is kept away from the salt.
8. Aluminum, magnesium, and iron filings or mixtures of these materials are kept away from HTS.

INSTRUMENTATION AND PIPING

The salt temperature at the boiler exit is easily controlled within a range of 5° to 10° F. by using the high-low reversing motor operated by the on-off electrical pyrometer controller. In the case of an autoclave which is heated by HTS supplied from this unit, it is possible to control automatically the flow of salt to the autoclave. This is done by using the on-off electric pyrometer to control the salt temperature at a point 50° to 100° F. higher than the temperature desired in the vessel being heated. An air-operated valve installed in the salt by-pass line from the boiler exit back to the salt pump tank is operated by either a standard throttling air-operated pressure controller or a similar temperature controller installed on the autoclave being heated. Excellent control of autoclave temperature and pressure is obtained in this manner. The on-off electric pyrometer can be omitted by use of the autoclave pressure or temperature controller to operate the oil burner valve directly, but this is not so satisfactory as the first described system of control. The sensitivity and reset (if used) adjustments for the instruments should be evaluated for each individual control application.

The flat-faced flanged gate valves used in this work were satisfactory, but for long, severe service tongue-and-groove type flanges with metallic-asbestos gaskets are strongly recommended. Wherever possible, welded pipe bends and connections should be used. The number of valves installed should be kept to a minimum, and those used should be installed so that a minimum pressure is exerted on the valve stem packing. Graphite lubricated asbestos is satisfactory but the graphite should be held to a minimum. The use of excessive quantities of pipe dope or valve packing lubricants should be avoided. Salt lines traced with high pressure steam pipe and lagged are satisfactory. Valves in HTS service which are occasionally left in the closed position when the unit is shut down should be steam-jacketed.

STATUS OF HTS HEATING

The pilot plant HTS unit described here has been used in intermittent service at temperatures below 800° F. in 178 autoclave runs totaling about 1500 hours of actual operation. The unit is operated by a technician and serves as a very convenient source of heat in the range 400° to 850° F. Some combination of control instruments was used in 125 of the autoclave runs mentioned above.

HTS heating has the following advantages: There is no appreciable vapor pressure. The degree of heating is easily controlled. The coefficient of heat transfer is good; the low temperature difference required is an advantage in the design of equipment to operate at high temperature and high pressure. The possibility of toxic fumes or vapors is remote.

A standard model HTS heating plant having a capacity of 500,000 B.t.u. per hour will soon be available from the Bethlehem Foundry and Machine Company. One of these units will be installed in a du Pont laboratory and another in the Chemical Engineering Laboratory of Lehigh University. The du Pont Company collaborated in the design of this HTS furnace which will be known as the Beth-Tec eutectic heating system. This commercial unit (Figure 2) consists of a vertical water-tube type of boiler which, based on our work, should give a minimum of difficulty due to accumulation of scale and dirt on any part of the heat transfer surface. Initial units are to be fabricated from carbon steel and should be suitable for working temperatures up to 850° F. The Beth-Tec unit is designed to give safe, dependable, and reliable service.

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TRIOXANE AS A SOURCE OF FORMALDEHYDE

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Trioxane, the relatively stable, cyclic polymer of formaldehyde, possesses unique properties which give it value as a special form of formaldehyde for use in chemical syntheses. Since its use as a source of formaldehyde is dependent upon the rate at which it can be depolymerized, a study of trioxane depolymerization has been made in aqueous and nonaqueous solvents. Results demonstrate that depolymerization is a first-order reaction. In aqueous solutions relatively high concentrations of strong acids are required, whereas much smaller concentrations are equally effective in nonaqueous media. The kinetics of phenol-trioxane reactions have been studied. A study of synthetic reactions indicates that trioxane is of value in chloromethylations, production of formals, condensations with phenols and amides, and the Mannich synthesis.

THE unique properties of trioxane, the cyclic trimer of formaldehyde, were briefly summarized by Walker and Carlisle (*7*). This polymer is quite unlike aqueous formaldehyde or the hydrated polymer, paraformaldehyde, since it is a colorless crystalline compound melting at 61–62° C. and boiling without decomposition at 115° C. It has a pleasant chloroformlike odor and is readily soluble in common organic solvents. In the molten state it is an excellent solvent. Recent physiological tests (*1*) have shown that it does not appear highly toxic to rats when given by mouth or when inhaled. Patch tests show that there does not appear to be much risk of its causing dermatitis in humans.

One of the most obvious uses for trioxane is as a special source of formaldehyde in chemical reactions. For this purpose it possesses four advantages over aqueous formaldehyde and paraformaldehyde: (1) It is soluble in most organic solvents and reagents. (2) Its rate of reaction as formaldehyde can be controlled by the use of acid depolymerization catalysts. (3) It is a completely anhydrous form of formaldehyde. (4) It has a pleasant, nonirritating odor and, therefore, does not create special ventilating problems. Therefore, although trioxane is more expensive than present commercial forms of formaldehyde, it has value for uses in which these forms cannot be readily employed or prove less efficient. Since utilization of trioxane for this purpose requires a thorough knowledge of the conditions under which it may be converted to formaldehyde, a study was made of its rate of depolymerization in various solvents and with various acidic catalysts.

DEPOLYMERIZATION IN AQUEOUS SOLUTION

Trioxane is stable in neutral and alkaline solutions but is depolymerized by strong acids. To determine the rate of depolymerization, this reaction was followed by keeping acidified 3% trioxane solutions in a constant temperature bath and titrating samples at intervals for free formaldehyde by the iodometric method (*5*). Since the acid concentration does not change during the reaction, good first-order rate constants were obtained, an indication that the reaction velocity at any given temperature and acidity is a function only of the trioxane concentration. This agrees with the work of Skrabal, Stockmair, and Schreiner (*3*), who determined constants for trioxane depolymerization at 35°, 45°, and 55° C. by 0.5 *M* toluenesulfonic acid.

First-order constants were calculated from experimental data by the following equation:

$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

where a = initial trioxane concentration
x = amount depolymerized in time t
k = first-order rate constant

Table I shows the data for a typical reaction. Constant k varies with acid strength and temperature. A series of constants was determined for varying sulfuric acid concentrations at 20°, 40°, 70°, and 95° C. using 3% trioxane. The results are shown in Figure 1, where the logarithm of the first-order constants is plotted against the normality of the acid used. For solutions containing 12 and 20% trioxane, the rate of depolymerization was found to be substantially identical to that obtained for the 3% solution. However, with higher concentrations the rate increased rapidly. The percentage of trioxane depolymerized in one hour at 75° C. for solutions which had a normality of 1 with respect to hydrochloric acid for a 20% trioxane solution was 23%. For solutions containing 40 and 60% trioxane, depolymerization was 40 and 65%, respectively. Pure trioxane was more than 90% depolymerized under the same conditions, but in this case the monomeric formaldehyde polymerized rapidly to polyoxymethylene. These findings indicate a deviation from first-order kinetics for highly concentrated trioxane solutions.

The time necessary for the depolymerization of any given percentage of the trioxane may be readily calculated with the following equation, where t_x is the time necessary for the depolymerization of x% trioxane:

$$t_x = \frac{1}{k} \ln \frac{100}{100 - x}$$

Table II gives the time required for depolymerization of 10, 50, 75, and 99% of the trioxane at various temperatures and acidities as calculated from the first-order rate constants taken from the curves of Figure 1.

Experiments were also carried out to show the catalytic effect of different acids. As Table III shows, hydrochloric acid is more active than sulfuric acid of the same normality; the difference becoming greater at higher acidities. Phosphoric acid is less active even when it is considered as a monobasic acid. A value based on Skrabal's work is included in Table III for comparison.

By use of the Arrhenius equation, the activation energy for the reaction was found to be 26 ± 3 kg.-cal. per mole.

TABLE I. DEPOLYMERIZATION OF 3% TRIOXANE IN 3.84 *N* SULFURIC ACID AT 40° C.

Time, Sec.	Concn., Grams/100 Cc. CH_2O, x	Concn., Grams/100 Cc. Trioxane, $a - x$	$k \times 10^4$ for Interval 0 to t, Sec.$^{-1}$
0	0.000	3.000	
7,200	0.073	2.927	3.42
16,200	0.175	2.825	3.95
77,400	0.691	2.309	3.38
165,600	1.292	1.708	3.62
443,000	2.42	0.58	3.71
702,000	2.76	0.24	3.60

TABLE II. RATE OF TRIOXANE DEPOLYMERIZATION AT VARIOUS TEMPERATURES WITH SULFURIC ACID AS CATALYST

Normality of H_2SO_4	Time of Liberation of Following Percentage Formaldehyde 10%	50%	75%	99%
	Depolymerization at 20° C.			
8	12.3 hr.	3.4 days	6.8 days	22.5 days
12	55 min.	6.1 hr.	12.2 hr.	40 hr.
16	4.4 min.	29 min.	58 min.	190 min.
20	20 sec.	22 min.	4.4 min.	14.5 min.
	Depolymerization at 40° C.			
1	3.0 days	21 days	42 days	137 days
2	29 hr.	8.0 days	16 days	53 days
4	6.5 hr.	1.78 days	3.6 days	11.8 days
8	31 min.	3.5 hr.	7.0 hr.	23 hr.
12	3.6 min.	24 min.	48 min.	160 min.
16	25 sec.	2.8 min.	5.6 min.	18.3 min.
	Depolymerization at 70° C.			
0.5	41 hr.	1.13 days	2.3 days	7.5 days
1	20 hr.	13.4 hr.	27 hr.	3.8 days
2	7.9 hr.	5.3 hr.	10.6 hr.	35 hr.
4	10.1 min.	1.13 hr.	2.3 hr.	7.5 hr.
8	66 sec.	7.3 min.	14.6 min.	48 min.
12	10.7 sec.	71 sec.	2.4 min.	7.8 min.
	Depolymerization at 95° C.			
0.1	11.3 days	75 days	150 days	500 days
0.25	33 min.	3.6 hr.	7.2 hr.	24 hr.
0.5	17.3 min.	1.8 hr.	3.7 hr.	12.8 hr.
1	7.4 min.	49 min.	1.6 hr.	5.4 hr.
2	2.4 min.	15.6 min.	31 min.	103 min.
4	45 sec.	5 min.	10 min.	33 min.
8	11.6 sec.	77 sec.	2.6 min.	8.5 min.

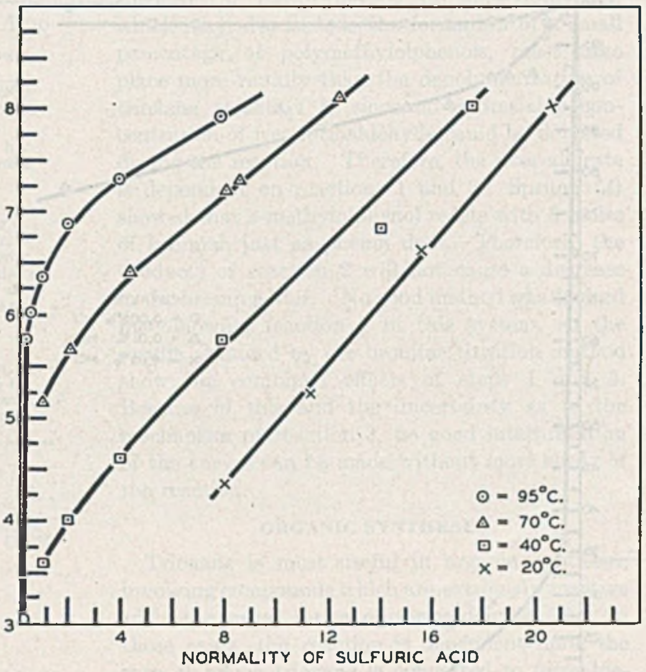

Figure 1. Effect of Sulfuric Acid Concentration on Rate of Trioxane Depolymerization

DEPOLYMERIZATION IN GLACIAL ACETIC ACID

The rates of depolymerization of trioxane in glacial acetic acid using sulfuric acid as a catalyst were determined by the same method used for the aqueous reactions. However, in acetic acid solutions, the free formaldehyde concentration never reached the theoretical end value because some of it was converted to polyoxymethylene acetates which do not show up as formaldehyde in the analysis used. This effect was greater for the higher concentrations of sulfuric acid. As this caused the values obtained for the constant to drop rapidly toward the end of the reaction, the figure obtained during the initial period was taken as the true constant. Therefore, these constants are not so accurate as those obtained for aqueous depolymerization. The results show that sulfuric acid is a much more effective catalyst in acetic acid than in water; the reaction with a given acid concentration was of the order of a thousand times faster in the former solvent. At 95° C. depolymerization proceeded at a measurable rate in glacial acetic acid with no added catalyst. Experiments with zinc chloride showed that this catalyst is much less effective than sulfuric acid.

Table IV gives the first-order constants obtained for these reactions and lists the time necessary for depolymerizing certain fractions of the trioxane as calculated from the reaction constants.

DEPOLYMERIZATION IN OTHER ORGANIC SOLVENTS

As a preliminary to this study, the solubility of trioxane in a few organic solvents was determined as follows for temperatures below the melting point of trioxane:

Solvent	Trioxane Soly., Grams/100 G. Soln. 25° C.	35° C.	45° C.
Acetic acid	40	52	..
Benzene	37	49	62
Toluene	..	41	58
Trichloroethylene	23	35	47

Formaldehyde itself is nearly insoluble in solvents like toluene and trichloroethylene. Therefore, when trioxane is depolymerized in these solvents, most of the liberated formaldehyde polymerizes rapidly to paraformaldehyde or polyoxymethylene which collects on any cool surface in the reaction vessel. To measure

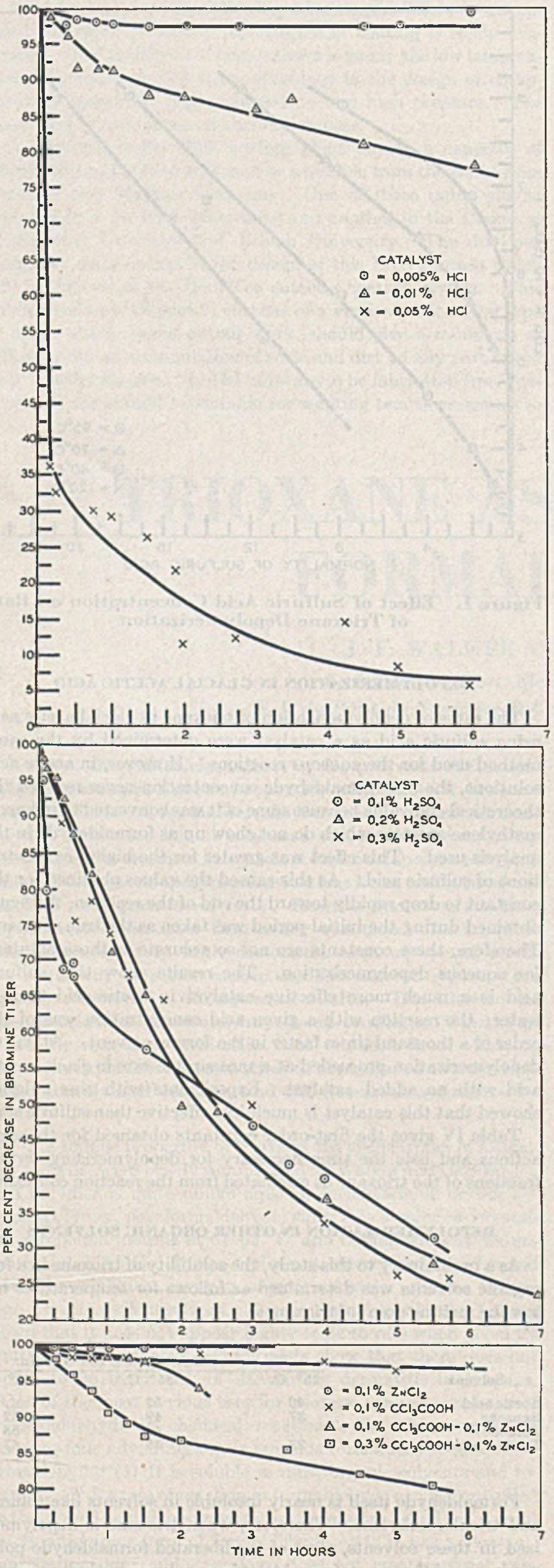

Figure 2. Effect of Various Catalysts on Reaction of Phenol and Trioxane at 75° C.

Table III. Effect of Different Acids on Aqueous Trioxane Depolymerization at 40° C.

Acid Concn.	Log k + 10[a] H_2SO_4	HCl	H_3PO_4
0.95 N	3.60	4.00	...
3.95 N	4.68	5.10	...
7.75 N	5.68	6.85	...
7.50 M	...	...	5.21

[a] Log k + 10 for unit acidity = 3.65. This value was obtained by interpolation from Skrabal, Stockmair, and Schreiner's values for 35° and 45° C.

depolymerization in these solutions, it was necessary to determine both the small amount of dissolved formaldehyde and the amount which had polymerized. The sodium sulfite method (*5*) was used for this determination.

The first-order rate constant for depolymerization of 3% trioxane in toluene solution catalyzed by 0.95 N trichloroacetic acid at C. 75° was found to be about 2×10^{-6} sec.$^{-1}$. The constant appeared to be dropping during the course of the reaction, but, as in the case of the reaction in acetic acid, this was probably due to side reactions which decreased the acidity of the solution and lowered the concentration of free formaldehyde by converting it to derivatives or polymers.

A series of tests was made to compare the effects of different catalysts in trichloroethylene and toluene solution. Samples were heated at 75° C. for 2 hours and then titrated. The most rapid depolymerization was obtained with a mixture of trichloroacetic acid and zinc chloride. The rates obtainable with mineral acids are limited by the solubility of the acids in the solvents used. Zinc chloride, apparently, did not accelerate the sulfuric acid–catalyzed reaction, but some of the liberated formaldehyde may have reacted with the toluene since zinc chloride is a good catalyst for the reaction of aromatic hydrocarbons with formaldehyde. Ferric chloride by itself was more effective than either zinc chloride or aluminum chloride, probably because it is a little more soluble. Ferric chloride and zinc chloride in combination with acetic acid catalyze the depolymerization at a moderate rate, but no quantitative data were obtained for these combinations. An experiment was tried with stannic chloride in each solvent, but black, resinous products separated at the bottom of the reaction mixture so that no rate measurements could be made. With all the catalysts tried, depolymerization took place more rapidly in toluene than in trichloroethylene. Table V lists the results.

The depolymerization of trioxane in alcohols was studied briefly but because formaldehyde reacts with the alcohol as fast as trioxane is depolymerized, no quantitative data were obtained. In acetone solution some free formaldehyde is liberated, but a large proportion reacts with the solvent to form condensation products.

REACTION WITH PHENOL

Phenol is very soluble in trioxane; a mixture of 1 mole of phenol with trioxane equivalent to 1 or 2 moles of formaldehyde is liquid at room temperature. Solution takes place with pronounced absorption of heat on mixing the crystalline reagents. When acid catalysts are added to these phenol-trioxane solutions, resins are formed. The rate of reaction and the nature of the resinous product depend on the amount of catalyst used. The resin formation can be stopped at any desired point by neutralizing the catalyst.

Addition of 0.2% hydrochloric or sulfuric acid initiated an exothermic reaction at room temperature. When this mixture was allowed to warm itself, the reaction accelerated gradually until the temperature reached 70–80° C. Then the mixture boiled violently, the temperature rising to 180° C. in 20–30 seconds. The product was a light pink, brittle resin. If external cooling was applied so that the temperature did not rise above 40–50° C., a

Table IV. Rate of Trioxane Depolymerization in Glacial Acetic Acid

Catalyst	Molar Concn.	k, Sec.$^{-1}$	Time of Depolymerization of Following Percentage Trioxane: 10%	50%	75%	99%
			Depolymerization at 40° C.			
H_2SO_4	0.5	8×10^{-4}	2 min	14 min.	28 min.	1.4 hr.
H_2SO_4	1	2×10^{-3}	1 min.	6 min.	12 min.	38 min.
			Depolymerization at 70° C.			
H_2SO_4	0.025	2×10^{-4}	10 min.	1 hr.	2 hr.	6 hr.
H_2SO_4	0.052	4×10^{-4}	5 min.	30 min.	1 hr.	3 hr.
H_2SO_4	0.27	3×10^{-3}	35 sec.	4 min.	8 min.	25 min.
$ZnCl_2$	0.075(1%)	5×10^{-6}	6 hr.	1.6 days	3 days	10 days
$ZnCl_2$	0.15(2%)	3.5×10^{-5}	50 min.	6 hr.	11 hr.	1.5 days
$ZnCl_2$	0.30(4%)	5.6×10^{-5}	30 min.	3 hr.	7 hr.	1 day
			Depolymerization at 95° C.			
None	...	2.4×10^{-4}	7 min.	45 min.	1.5 hr.	5 hr.
H_2SO_4	0.014	8×10^{-4}	2 min.	14 min.	28 min.	1.4 hr.
H_2SO_4	0.027	1.5×10^{-3}	1.2 min.	8 min.	16 min.	50 min.
H_2SO_4	0.063	3×10^{-3}	35 sec.	4 min.	8 min.	25 min.

Table V. Decomposition of 3% Trioxane in Toluene and in Trichloroethylene

Solvent	Catalyst	Concentration	Depolymerization in 2 Hr. at 75° C., %
Toluene	H_2SO_4	0.01 M^a	26
	$H_2SO_4 + ZnCl_2$	0.008 M^a + 0.045 M^b	23
	HCl	0.1 M^a	30
	Trichloroacetic acid	1.0 M^a	10
	Trichloroacetic acid + $ZnCl_2$	1.0 + 0.0015 M^b	45
	Dichloroacetic acid	1.0 M^b	3
	Toluenesulfonic acid	0.006 M^b	2
	$FeCl_3$	<0.1%^{b}	22
	$ZnCl_2$	<<0.1%^{b}	1
	$AlCl_3$	<<0.1%^{b}	0
Trichloroethylene	H_2SO_4	0.003 M^a	9
	HCl	0.04 M^a	10
	Trichloroacetic acid	1.0 M^a	3
	Dichloroacetic acid	1.0 M^a	0.5
	Toluenesulfonic acid	0.006 M^b	0.8
	$FeCl_3$	<0.1%^{b}	17
	$ZnCl_2$	<<0.1%^{b}	0
	$AlCl_3$	<<0.1%^{b}	0

[a] Solutions saturated with catalyst at 75° C.

[b] Solutions saturated with catalyst at room temperature.

viscous liquid resin resulted which slowly hardened on standing at room temperature. If the depolymerization of the trioxane were the only rate-controlling factor in this reaction, the nature of the phenol used should have little effect on the rate. However, this is not the case. When 0.5 mole of resorcinol was used in place of half of the phenol, only 0.03% hydrochloric acid was needed to start an exothermic reaction compared to the 0.2% used with pure phenol.

The reaction was followed quantitatively by determining the rate at which water-insoluble resin was formed in the presence of various acid catalysts at 75° C. This method is similar to that used by Nordlander (*2*) in following phenol-formaldehyde reactions. Reaction samples were analyzed by extracting with water and titrating the aqueous extract with bromine in acetic acid. The decrease in bromine titer as the reaction progresses gives a rough measure of the quantity of insoluble resin formed.

Figure 2 shows the results of these reactions graphically. Hydrochloric acid is the most active of the catalysts tried; in addition to the experiments shown, one was started using 0.1% hydrochloric acid but resinification was too rapid for any rate measurements. The curves obtained with sulfuric acid show an unexpected phenomenon. With 0.1% acid the reaction starts much faster than with 0.2 or 0.3%. However, after 2 hours less resin has been produced than with the larger quantities of acid.

The catalytic effect of the trichloroacetic acid–zinc chloride combination is much less than that of the mineral acids.

Three types of reaction take place during the phenol-trioxane condensation:

$$(CH_2O)_3 \longrightarrow 3CH_2O \qquad (1)$$

$$C_6H_5OH + CH_2O \longrightarrow C_6H_4OH(CH_2OH) \qquad (2)$$

$$C_6H_4OH(CH_2OH) \longrightarrow \text{resins} \qquad (3)$$

Reaction 2, the formation of methylolphenol, which may also include the formation of a small percentage of polymethylolphenols, must take place more rapidly than the depolymerization of trioxane (reaction 1) since no appreciable concentration of free formaldehyde could be detected during the reaction. Therefore, the over-all rate is dependent on reactions 1 and 3. Sprung (*4*) showed that *o*-methylolphenol reacts with 3 moles of bromine just as phenol does. Therefore, the products of reaction 2 will not cause a decrease in the bromine titer. No good method was devised for following reaction 1 in this system, so the results obtained by the bromine titration method show the combined effects of steps 1 and 3. Because of this and the uncertainty as to the mechanism of reaction 3, no good interpretation of the curves can be made without more study of the reaction.

ORGANIC SYNTHESES

Trioxane is most useful in organic syntheses involving compounds which are extremely reactive with the usual forms of formaldehyde (*6*). In these cases, the reaction is dependent upon the rate at which trioxane is converted to formaldehyde. Since this rate is determined by the catalyst concentration, conditions are ideal for chemical control. The solubility and compatibility of trioxane with organic reagents give a homogeneous medium in which unreacted trioxane functions as a subsidiary solvent. Reactions involving compounds which react slowly with formaldehyde are less satisfactory since the monomeric formaldehyde may polymerize to polyoxymethylene before reaction if the reaction medium does not function as a formaldehyde solvent. The condensation of toluene with formaldehyde to form ditolylmethane is an example of the latter type. Anisole, on the contrary, reacts rapidly so that dianisylmethane can be readily prepared by reaction with trioxane.

Trioxane was found to give excellent results in a number of chloromethylation reactions involving alcohols and aromatic hydrocarbons. A 93% yield of octyl chloromethyl ether was obtained by passing anhydrous hydrogen chloride into a solution of trioxane in octyl alcohol. It can also be used advantageously in the preparation of formals by reaction with alcohols and glycols.

Trioxane can be employed successfully in the Mannich synthesis. A synthesis of this type involving piperidine hydrochloride and acetophenone gave good results without addition of a solvent; trioxane has sufficient solvent action itself to form a clear initial solution. As reaction progressed, the mixture solidified to the solid reaction product, phenyl β-piperidinoethyl ketone hydrochloride. Reaction of trioxane with amides is illustrated by the precipitation of polymethyleneurea when hydrochloric acid is added to a molten solution of urea in trioxane.

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CRUDE RUBBER PREPARATION

Sheet Production by Continuous Coagulation of Hevea Latex

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When fresh Hevea latex is acidified to pH 4.5 to 4.9, as in standard estate practice, an elapsed time of 1 to 6 hours is required for satisfactory coagulum formation. By the use of coalescence accelerators the time required for coagulum formation can be controlled. For instance, it can be reduced to 1 minute or so, or even be eliminated altogether in the case of the most active agents. Representative of this type of material are the straight-chain saturated fatty acids, especially those of ten to fourteen carbon atoms, certain phenols, and some of the higher fatty alcohols. The former are added as soluble salts to fresh latex, which is then fed continuously together with a stream of coagulant onto a properly shaped conveyer belt discharging the coagulum continuously into a sheeting battery. Machined wet sheet can be produced within 3 minutes or so after acidification of treated latex.

THE widespread use of dilute acid as the principal coagulant for Hevea latex in the rubber plantation industry is due to a suggestion of Biffen (*3*), who, during an investigation of the type of smoke used in the Brazilian method of rubber preparation, found acetic acid to be the chief constituent of the aqueous condensate.

The reaction of fresh Hevea latex to the addition of dilute acids is quite different from that of ammonia-preserved latex as received in this country. (In this discussion the term "fresh latex" denotes latex not more than 12 hours old, counting from the time of tapping the tree.) When ammonia-preserved latex is acidified, coagulation is essentially instantaneous at the spot on the latex surface where the dilute acid falls. But in the case of fresh latex, flocculation occurs, and the mix, although thickened, can still be stirred with gentle action to distribute the coagulant adequately throughout the entire batch. More than an hour later these flocs begin to fuse into a solid coagulum, but it is not until some hours' standing, usually overnight in Malayan practice, that this coagulum is strong enough to withstand without undue deformation the handling attendant on machining it into wet sheet—the process of putting the slabs of coagulated latex through a series of close-set rolls (sheeting battery) to squeeze out rubber-free serum.

Tapping a Rubber Tree in Malaya with a Jebong or Drawing Knife

Where the daily output of rubber amounts to only a few pounds, as is the case with many small holders (operators of less than 100 acres of rubber trees), coagulation is carried out in individual pans of about 1 Imperial gallon capacity yielding 1.5 pounds of rubber sheet (dry basis). Where large volumes of latex are to be converted, as in estate practice, coagulation is run in rectangular tanks of 200 to 220 Imperial gallons capacity, a standard size being 10 feet long, 3 feet wide, and 15 inches deep (Figure 1). Inside these tanks along their length, vertical slots are cut every 1.5 inches so that, after the acid coagulant is mixed with the diluted latex, solid separating sheets or partitions may be inserted. The acidified latex which subsequently coagulates is thus effectively shaped in slabs convenient for handling. Upwards of eighty of these partitions per standard tank must be inserted, removed, and kept clean every time a coagulation is run. On some very large estates the method of fitting the partitions in the coagulation tanks is modified so that only the opposite ends of alternate partitions touch the sides of the tank. With this system the coagulum forms in serpentine fashion in each tank. On removal of the partitions the coagulum can be withdrawn as a continuous ribbon and fed into a suitable sheeting battery. The process is continuous only in so far as the machining of coagulum from an individual tank is concerned. The rate of coagulum formation is not accelerated over that of the usual practice.

After a visit to Malaya in 1939, Stevens (*17*) commented that the method of sheet rubber production had not changed basically since the days of the pioneers, and suggested that a process of continuous

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coagulation and sheet formation should be available where large volumes of latex are converted into sheet rubber. In recent years patents have been issued describing rubber production by continuous coagulation methods applicable to fresh Hevea latex (*18, 25*) and to synthetic latices (*4, 15, 22*) including the salt-acid coagulation method (*24*).

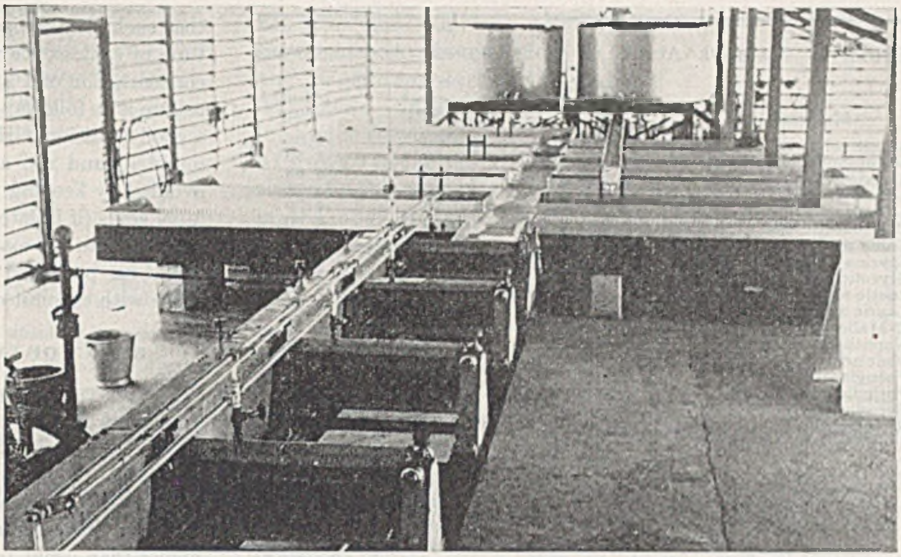

Figure 1. Malayan Sheet Factory

Background, bulking tanks; center, coagulating tanks; foreground, sheeting battery

COAGULATION OF HEVEA LATEX

The importance of coagulation phenomena from theoretical as well as practical viewpoints is evident on even casual examination of literature published since the turn of the present century.

Pertinent to the present discussion is an interesting chain of studies started by Whitby's observation (*23*) that fresh latex which has been sterilized by heating does not form a solid coagulum or clot on acidification with the usual amount of acetic acid (to approximately pH 4.6 to 4.8). The latex particles merely flocculate and cream upward but do not coalesce (*19*) into a clot even after 1 or 2 days' standing. (The term "coalescence" is used in this discussion in the same way de Vries employed it—namely, "the transition of a loose mass of flocs into a fixed gel.") Eaton and Grantham (*6*) observed that some latex which they had heat-sterilized in an autoclave did form a clot on acidification, but Barrowcliff (*2*) pointed out that as a result of their heating method, it is probable the temperature of the latex itself never reached that of the surrounding steam. The latter investigator, without the use of pressure equipment, prepared a modified latex similar to Whitby's by slowly pouring fresh latex into an equal volume of water at 90° C. with subsequent cooling to room temperature. Latex so treated (Barrowcliff latex) lost its ability to coalesce on acidification. He also observed, however, that the addition of a few drops of fresh latex to a small volume of Barrowcliff latex restored this ability. Whitby (*23*) had suggested that the heating destroyed a specific enzyme essential to coagulation, and Barrowcliff's inoculation technique lent support to this view. Campbell's experiments (*5*) led to a similar conclusion. Eaton and Grantham (*6*), on the other hand, attributed the natural spontaneous coagulation of latex to bacterial action rather than to a specific enzyme, and it is noteworthy that acidified Barrowcliff latex will form a clot under tropical conditions after standing exposed to the air for upwards of a week.

De Vries and Beumée-Nieuwland (*20*) modified Barrowcliff's method to give a more dilute latex, B liquid, and found it possible to obtain from it a natural coalescence agent in this way (*21*). B liquid[3] was inoculated with a few drops of fresh latex and then acidified to form a clot. The resulting coagulum, when dry, was soaked in dilute aqueous sodium carbonate. The extract so obtained could be used, interchangeably with fresh latex, as a coalescence agent for B liquid. It is of interest to note that, with a given coagulum, successful extraction of coalescence agent could not be repeated indefinitely. Conceivably, the sodium carbonate reacted with a portion of any free fatty acids present in the coagulum to form sodium soaps, and these were the active agents.

Van Harpen (*7*) has provided an exhaustive review up to 1930 of natural and synthetic agents capable of causing coalescence or clot formation in acidified B liquid. The treatise includes a series of reagents first used by that author, notably the ammonium soaps of oleic, palmitic, and stearic acids, and the ammonia-soluble portion as well as the alcohol-soluble portion of the acetone extract of crepe rubber, the latter being particularly active. Until the work discussed below was undertaken, no investigator appears to have applied coalescence accelerators together with adequate control of pH to the coagulation of fresh Hevea latex, either from the standpoint of theoretical interest or as a practical attempt to devise processes for continuous sheet production.

COALESCENCE ACCELERATORS IN FRESH LATEX

The problem of accelerating the rate of coagulation of fresh latex was first attacked empirically (Table I). The various acids to be tested for coalescence activity were dissolved in ammonia and added to the latex diluted to a dry rubber content (D.R.C.) of 2%; this was then acidified with 2% acetic acid. The general procedure of coagulation used in this study was carried out as follows:

Method of Coagulation. 300 ml. of fresh latex were added to 300 ml. of tap water containing the coalescence agent, and this was then poured into 4000 ml. of tap water containing 80 ml. of 2% acetic acid with stirring.

Time to coalesce was taken as the interval between addition of the latex and the time at which the flocculates actually began to form a continuous clot when the surface was moved with a spatula. Time to firm up was read when the coagulum no longer adhered to wetted fingers when slipped beneath the coagulum. The pH was determined by glass electrode, and coagulation was carried out at 2% dry rubber content.

When the latex flocs began to stick together to form a continuous clot, time was taken. This end point was a good deal more definite than might be predicted by one who has not observed it. Readings could be reproduced within ±10% of the elapsed time, and even less on many occasions. With the preferred coalescence agents, a variation of ±10% in the time actually amounts to only ±3 to 6 seconds.

The data in Table I show that, of the materials tried, the soap-forming fatty acids possess greatest activity. While the untreated latex requires about 3/4 hour for clot formation, addition of approximately 2% of the active fatty acids as soaps may reduce this time to only a few seconds.

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[3] Boil 9 volumes of water, add 1 volume of fresh latex, boil 3 minutes, hold at 100° C. for 5 minutes, and then cool to room temperature. The product is similar to Barrowcliff latex in reaction to acid and to inoculation with fresh latex.

TABLE I. VARIOUS ACIDS AS COALESCENCE ACCELERATORS

Material	Quantity[a] per 100 G. Rubber	Time of Coalescence[b], Min.:Sec.	pH of Serum
Adipic acid	1.5	>3:00	4.33
o-Aminophenol sulfonic acid	1.9	>3:00	4.50
Azelaic acid	1.9	>3:00	4.68
n-Butyric acid	0.9	>3:00	4.71
n-Capric acid	1.7	0:10	4.70
Chloroacetic acid	0.9	>3:00	4.50
Gallic acid	1.7	>3:00	4.36
Glycine	0.8	>3:00	4.60
Glycolic acid	0.8	>3:00	4.25
Lactic acid	0.9	>3:00	4.60
Lauric acid	2.0	0:40	4.78
dl-Malic acid	1.3	>3:00	4.11
Naphthenic acid	1.3	3:00	4.75
Oleic acid	2.8	0:20	4.77
Phenylacetic acid	1.4	>3:00	4.58
Phthalic acid	1.7	>3:00	4.50
Pyruvic acid	0.9	>3:00	4.69
Ricinoleic acid	3.0	0:01	4.87
Succinic acid	1.2	>3:00	4.40
Control			
Coconut fatty acids (1% on rubber)	...	1:20	4.75
Fresh latex	None	About 45:00	4.70

[a] Coalescence agents added to latex, on the basis of 0.01 molar equivalent per 100 grams of rubber, dissolved in 20% aqueous ammonia (about 0.75 ml.) per 100 grams rubber.

[b] Coalescence times of 3 minutes or less were regarded as preferable.

TABLE II. COALESCENCE AGENTS SHOWING FAST ACCELERATION

Coalescence Accelerator	% by Wt. on Rubber	Time Required to Coalesce, min.:sec.	Time Required to Firm up, min.:sec.	pH of Serum
None (control)	..	30:00	60:00	4.62
β-Naphthol[a]	0.5	0:45	2:45	4.90
	1.0	0:45	2:00	5.0
Lauric acid[a]	0.5	2:45	4:15	4.65
	1.0	0:55	2:15	4.81
	1.5	0:40	2:00	4.83
Stearic acid[a]	0.5	9:15	15:00	4.70
	1.0	7:30	12:00	4.79
	1.5	2:15	5:00	4.81
Lux soap flakes	None (control)	25:00	38:00	4.67
	0.10	17:30	22:00	4.72
	0.25	5:45	8:30	4.85
	0.50	2:45	3:00	4.84
	1.00	1:00	2:15	4.85
	1.50	0:40	2:15	4.94
Ricinoleic acid[b]	0.25	1:00	...	..
	0.50	0:20	...	..
	1.00	0:02	...	..
	2.00	0:01	...	..
	3.00	0:01	...	..

[a] Added to latex as ammonium salts.

[b] Added to latex as sodium soap.

COALESCENCE AGENTS OF HIGH ACTIVITY

Some of the reagents showing very fast acceleration are set forth in Table II. The pH of the serum must be adequately controlled just as it should be in good estate practice where clean-cut coagulation with clear (not milky) serum is the rule. This means the pH of coagulation should be less than 5, preferably in the range of pH 4.6 to 4.9. A small increase in acid is required to neutralize the alkalinity contributed by the coalescence agent as added. Particular reference is directed to the remarkable activity of ricinoleic acid. This material used in the range of 1 to 3% on the rubber causes instantaneous local coagulation where the acetic acid solution (as coagulant) strikes the latex. Such coagulations gave milky serums because the coagulant could not be uniformly stirred in; but the coagulations using 0.5 and 0.25% of this agent on the rubber were satisfactory in this respect.

LOCALLY MADE SOAPS AS ACCELERATORS

Malaya is a large producer of both coconut oil and palm oil, the cheapest sources of fatty acids available in that locality. Their utility was investigated. The mixed fatty acids of each of these oils were isolated and, as sodium soaps, were tried as coalescence accelerators. In another case the entire saponification mixture was employed for the same purpose. The coagulant in these tests was 2% acetic acid. Results recorded in Table III show that such locally made soaps are entirely satisfactory in reducing time of coalescence to about 1 minute when they are used at a concentration of 1% (fatty acid basis) on the rubber. The procedure is as follows: Stir hot caustic solution into hot oil to effect a good emulsion. Heat gradually to 120° C. (this takes 30 to 60 minutes) and use as 1% solution. Gelling during dilution is avoided by keeping the soap solution at 60° to 70° C. Yield of fatty acids (if isolated) is 75 to 75.5 grams from 80 grams of palm oil. Coconut oil soap was prepared in the same way.

Rubber produced with palm oil soap had less odor than that made with coconut oil soap.

EFFECT OF VARIABLES ON RATE OF COALESCENCE

CONCENTRATION OF COALESCENCE AGENT. These variations are shown in Table IV for whole coconut oil sodium soap alone as well as for mixtures of this with sodium ricinoleate. As little as 0.25% of the former reduces time of coalescence to one third that of the untreated latex which, in this series, is already more sensitive than ordinarily encountered (probably because of a higher-than-usual bacteria count). Increased amounts of coalescence agent in the latex progressively decrease the time of coalescence. Hence, the rate of coagulation can be varied over a wide range (*a*) by choice of coalescence agent of suitable activity and (*b*) by the amount of this agent used in the latex. The inclusion of 1% or so of fatty acid during the preparation of rubber for general purpose compounding is regarded as beneficial rather than detrimental.

INORGANIC IONS. Addition of barium, calcium, lead, magnesium, and zinc as acetates (1% each on the rubber) to the coagulant accelerated the rate of coalescence of fresh untreated latex, coagulation being run at 2% D.R.C. As shown in Table V, calcium, magnesium, and barium were active, the calcium especially so. In the presence of coconut oil soap, however, only the calcium ion shows enhanced activity.

CALCIUM SALTS. As was shown in the preceding paragraph, the presence of calcium ions during coagulation with acetic acid

TABLE III. COMPARISON OF CRUDE LAURIC AND PALMITIC ACIDS, WHOLE COCONUT OIL, AND WHOLE PALM OIL AS SOAPS

Coalescence Accelerator	% by Wt. on Rubber	$^1/_1$ *N* H_2SO_4[a], Ml.	D.R.C. at Coagulation	Time to Coalesce, min.:sec.	Time to Firm up, min.:sec.	pH of Serum
Coconut oil fatty acids	1	None	2	0:53	1:47	4.83
Palm oil fatty acids	1	None	2	1:15	2:10	4.80
Whole coconut oil soap	1	None	2	0:50	..	4.90
Whole palm oil soap[b]	1	6	2	1:05	2:10	4.79
Whole palm oil soap[b]	1	7	2	0:47	1:35	4.78

[a] To neutralize excess NaOH in the whole soap.

[b] Red unbleached Malayan palm oil, 80 grams heated to 100° C.; NaOH (includes 50% excess), 18 grams heated to 100° C.; water, 36 grams heated to 100° C.

TABLE IV. EFFECT OF VARYING SOAP CONCENTRATION ON RATE OF COALESCENCE[a]

Kind of Soap	% Added on Rubber	Time of Coalescence, Min.:Sec.	pH of Serum
None	..	23:00	4.84
Coconut oil	0.25	7:20	4.70
Coconut oil	0.50	2:30	4.80
Coconut oil	0.75	1:30	4.82
Coconut oil	1.00	0:50	4.90
Coconut oil	2.00	0:20	..
Coconut oil Ricinoleic acid	0.50 0.05	0:45	..
Coconut oil Ricinoleic acid	0.50 0.10	0:30	..
Coconut oil Ricinoleic acid	1.00 0.05	0:15	..
Coconut oil Ricinoleic acid	1.00 0.10	0:11	..

[a] D.R.C., 2% at coagulation; coagulant, acetic acid; coalescence agents, sodium soaps.

TABLE V. EFFECT OF SEVERAL IONS ON RATE OF COALESCENCE[a]

	Without Coalescence Agent		With Coalescence Agent[c]	
Ion[b]	Time of coalescence, min.:sec.	pH of serum	Time of coalescence, min.:sec.	pH of serum
None (control)	50:00	4.50	0:40	4.51
Barium	4:25	4.10	0:40	4.21
Calcium	1:45	4.40	0:13	4.41
Lead	17:30	4.21	1:26	4.72
Magnesium	9:30	4.31	0:55	4.63
Zinc	17:00	4.06	3:00	4.23

[a] Acetic acid coagulation run at 2% D.R.C. as follows: 300 ml. field latex, 4200 ml. dilution water, and 100 ml. 1% sodium soap (if used) added to latex and mixed, then 80 ml. of 2% acetic acid added. Salts when used were added to the acid prior to coagulation.

[b] Added as acetate (1% by weight on the rubber) dissolved in acetic acid coagulant.

[c] 1 part of coconut fatty acids as sodium soap per 100 parts rubber by weight added to latex before coagulation.

TABLE VI. EFFECT OF CALCIUM SALTS ON RATE OF COALESCENCE

		Without Coalescence Agent		With Coalescence Agent	
Salt Used	% on Rubber	Coalescence, min.:sec.	pH of serum[a]	Coalescence, min.:sec.	pH of serum[a]
None	..	32:00	4.73	1:05	4.81
Calcium acetate	0.25	24:00	4.80	0:50	4.88
	0.50	18:00	4.86	0:31	4.90
	1.00	14:00	5.00	0:22	4.96
Calcium chloride	0.25	19:40	4.70	0:40	4.80
	0.50	14:23	4.70	0:35	4.80
	1.00	11:20	4.69	0:15	4.73

[a] Within 1 hour of adding coagulant. Use of chloride has less effect on final pH of serum. Procedure of coagulation (at 2% D.R.C.) is the same as in Table V, but pH values of serum in Table VI series are higher than those in Table V series.

TABLE VII. USE OF PHENOLS[a] AS COALESCENCE AGENTS

		Without $CaCl_2$		With $CaCl_2$[b]	
Agent Used	% on Rubber	Coalescence, min.:sec.	pH of serum	Coalescence, min.:sec.	pH of serum
None	...	50:00	4.50	..	..
Soap[c]	1	1:10	4.58	0:25	4.59
Quinosol	1	7:00	4.51	1:50	4.58
p-Chloro-*m*-cresol	1	1:00	4.60	0:25	4.69
m- and *p*-Cresol	1	4:55	4.64	1:15	4.68
β-Naphthol	1	1:00	4.58	0:25	4.62
p-Chlorophenol	1	3:00	4.61	1:05	4.69
Pentachlorophenol	1	1:00	4.61	0:30	4.67
Resorcinol	1	13:00	4.61	3:00	4.65

[a] Phenols as fungicides could be combined with soap as coalescence agents.

[b] 1% by weight on the rubber.

[c] Sodium soap of coconut oil fatty acids.

speeds up the rate of coalescence of both the untreated fresh latex and identical latex containing coconut oil soap (1% on the rubber). Broadly speaking, the effect where both agents are present appears to be additive. These data are given in Table VI.

TEMPERATURE. In an isolated experiment using 1% stearic acid (added as the sodium soap) on the rubber as coalescence agent, coalescence occurred at 48° C. in one third to one fourth the time required at 29° C. when aliquots of identical latex were acidified with the same volume of acetic acid.

COALESCENCE AGENTS

PHENOLS. Certain phenols, notably *p*-chloro-*m*-cresol, β-naphthol, and pentachlorophenol, are just as active in promoting coalescence as is coconut oil soap (Table VII). They were dissolved as sodium salts in water before addition to the fresh latex. As with the coconut oil soap, their activity is enhanced in the presence of calcium ion during coagulation. Small amounts of these active phenols could be mixed with the soap-treated latex to act in the capacities of preservative for latex and finished rubber, and coalescence agent during coagulation.

HIGHER ALCOHOLS. Two of the higher alcohols, *n*-octyl and capryl alcohols, were found to be active in promoting coalescence at concentrations of 1 and 2% on the rubber content of the latex. At 2% concentration the capryl alcohol had activity comparable to that shown by lauric acid. In this instance the latex used was not fresh but had been aged 6 days in the presence of 0.2% NH_3. Judging by the slowness of coagulation shown by this latex in the absence of added coalescence agents, it would seem that little if any hydrolysis of the fats or lipoids naturally present (with resulting ammonium soap formation) had occurred. Table VIII shows the results obtained.

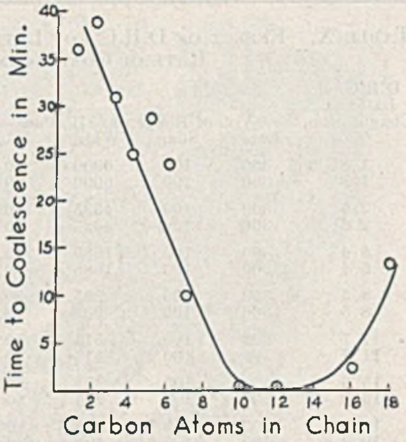

Figure 2. Effect of Number of Carbon Atoms in Chain on Activity of Saturated Straight-Chain Fatty Acids as Coalescence Agents

RELATIVE ACTIVITY OF FATTY ACIDS

Coalescence activity of an homologous series of saturated straight-chain fatty acids was investigated. The results, although fragmentary because of lack of material, are extremely interesting. The data set forth in Table IX are plotted in Figure 2 as time of coalescence (activity) against number of carbon atoms in the chain. There is a progressive increase in activity as chain length increases to 10 or 12 carbon atoms, and a decrease in activity as the number rises beyond this point. This peak of activity in the region of 10 to 12 carbon atoms calls to mind instances of such an effect encountered in other investigations—for example, that of Smith and Boone (*16*), who compounded this

TABLE VIII. OCTYL AND CAPRYL ALCOHOLS AS COALESCENCE AGENTS[a]

		Coagulant/100 G. Rubber			
Coalescence Agent	% on Rubber	10% sulfuric acid, ml.	10% acetic acid, ml.	Time of Coalescence, Min.:Sec.	pH of Serum
None	..	13.6	..	94:00	4.77
None	..	7.5	12.0	90:00	4.76
None	..	..	30.0	83:00	4.78
Crude lauric acid[b]	1	16.0	..	0:60	4.75
Crude lauric acid	1	10.0	12.0	3:10	4.82
Crude lauric acid	1	..	36.0	1:45	4.72
Octyl alcohol[c]	1	8.0	12.0	16:15	4.8
Octyl alcohol	2	8.0	12.0	8:30	4.8
Capryl alcohol[c]	1	8.0	12.0	13:00	4.8
Capryl alcohol	2	8.0	12.0	1:35	4.8

[a] Latex ammoniated to 0.2% NH_3 and aged 6 days before coagulation; coagulation run at 4% D.R.C.

[b] Crude lauric acid added to latex as sodium soap; coalescence accelerated control.

[c] Octyl and capryl alcohols were first emulsified separately in water, using 1% Aquarex D (mostly sodium lauryl sulfate) on the alcohol, and thereafter added to the latex before acidification.

TABLE IX. SATURATED STRAIGHT-CHAIN FATTY ACIDS AS COALESCENCE AGENTS[a]

Fatty Acid	Quantity[b] per 100 Grams of Rubber	Time of Coalescence, Min.:Sec.
Formic	0.5	36:00
Acetic	0.6	39:00
Propionic	0.7	31:20
Butyric	0.9	25:00
Valeric	1.0	29:00
Caproic	1.2	24:00
Heptanoic	1.3	10:00
Capric	1.7	0:12
Lauric	2.0	0:15
Palmitic	2.6	2:30
Stearic	2.8	13:30

[a] Coagulation at 2% D.R.C. with 2% aqueous acetic acid at pH 4.6–4.8.

[b] Coalescence agent added to latex before coagulation, in 0.01 molar quantities on 100 grams of rubber, dissolved in a minimum of aqueous ammonia.

Table X. Effect of D.R.C.[a] of Latex at Coagulation on Rate of Coalescence[b]

D.R.C. of Latex at Coagulation, %	Vol. of Reagents, Ml./Pan: Latex	Soap	Water	Acid	Time of Coalescence, Min.:Sec.	pH of Serum
1.8	300	100	6000	80	0:40	4.79
1.8	300	100	6000	80	0:40	4.77
2.6	300	100	4025	80	0:30	4.82
2.6	300	100	4025	80	0:34	4.83
5.4	300	100	1685	80	0:25	4.58
5.4	300	100	1685	80	0:27	4.60
8.5	300	100	905	80	0:35	4.70
8.5	300	100	905	80	0:25	4.69
11.7	300	100	515	80	0:42	4.55
11.7	300	100	515	80	0:35	4.54
15.6	300	100	271	80	0:25	4.59
15.6	300	100	271	80	0:30	4.53
19.3	300	100	125	80	0:25	4.60
19.3	300	100	125	80	0:20	4.51
23.7	300	100	15	80	0:24	4.52
23.7	300	100	15	80	0:20	4.50
2.0	Control, no coalescence agent				42:00	4.73

[a] Dry rubber content of latex as received, 39.04%.

[b] Coalescence accelerator, sodium soap of coconut fatty acids added as a 1% aqueous solution to the latex; coagulant, acetic acid added as 2% aqueous solution.

same series of fatty acids in a vulcanizable rubber stock. Tensile strengths for the vulcanized rubber rose to a maximum as the fatty-acid chain length increased to the region of about 10 carbon atoms and thereafter gradually declined. Below this point the acids containing an odd number of carbon atoms in their chains showed highest activation effect; above this point the even-numbered chains assumed pre-eminence.

Translating this into practice from the standpoint of adequate coalescence activity as well as of low cost, the use of coconut oil soap for latex pretreatment is clearly indicated.

EFFECT OF DRY RUBBER CONTENT OF LATEX

On Rate of Coalescence. The change in rate of coagulation (in the presence of coalescence accelerators) as the latex is diluted from about 25% D.R.C. down to 2% is not so striking as might be imagined. Although the time is halved at the higher concentration, coagulation in no case in this series required so much as 60 seconds (Table X). The real difference, practically speaking, is not in the time but rather in the strength of the clots; those made at the higher concentrations were much stronger and easier to handle during machining.

Table XI. Effect of Added Fatty Acids on Acetone Extract

Rubber Type	D.R.C. at Coagulation, %	Fatty Acid Used	Acetone Extract: Per cent	Acetone Extract: Mg. KOH/100 g. rubber[a]	Added Fatty Acid Retained, %
Latex L-499 + 0.2% NH_3, Coagulated with Acetic Acid 3 Days after Being Received					
T.S.R. washed	2	None	2.10 2.09	175 176	Control
C.S.R. washed	2	1% coconut (calcd. as lauric)	2.75 2.74	336 330	57
C.S.R. washed	2	1% c.p. capric	2.53 2.56	280 278	32
Latex L-500 Coagulated with Acetic Acid Same Day as Received					
T.S.R. washed	2	None	2.02 2.02	79 81	Control
C.S.R. washed	2	1% coconut (calcd. as lauric)	Flask broke 2.83	... 294	76
Pale crepe	15	None	2.16 2.23	74 72	Control

[a] Acetone extract dissolved in 20 ml. methyl alcohol and titrated with 0.084 N KOH using phenolphthalein indicator; 1 ml. of 0.084 N KOH required to neutralize acid in blank containing 20 ml. methyl alcohol.

On Acetone Extract. The fatty acids used as coalescence accelerators (and added as soaps in the latex pretreatment) reappear in the acetone extract of the rubber after the drying of the sheet. The acetone extract of such rubber (continuous sheet rubber, C.S.R.) is higher than that of the controls (thin sheet rubber, T.S.R., and standard crepe), and the free fatty acid content of such rubber is also higher; but the fatty acids are not recovered quantitatively (Table XI). In the case of coconut fatty acids (calculated as lauric acid) only about 50 to 75% of the added fatty acid (compared with the control) is retained by the rubber. In the case of capric acid, only one third of the added amount was retained. Although the particular sheets described here received a special washing treatment in water, the loss of fatty acid is not more significant than that experienced in the standard practice of washing a coagulum on a mill in the making of pale crepe, as will be seen on comparison of the acid number of T.S.R. and pale crepe controls made from latex L-500.

ACTION OF COALESCENCE ACCELERATORS ON CENTRIFUGE CONCENTRATES

Centrifuged concentrates (1 day old and containing 0.16% NH_3) responded normally to coconut oil soap as coalescence agent. A limited number of trials with the skim fractions (using 1% coconut oil soap based on the D.R.C. followed by acidification to pH 4.8 to 4.9) produced flocculated mixtures rather than a continuous sheet. At the time, there was no particular reason to do further work with the skim fraction. It may be that intensified effort and the use of very active agents, such as ricinoleic acid, in higher concentrations could convert centrifugal skim into continuous sheet by this process.

THEORY OF COAGULATION

As a result of these experiments and a general experience with coagulation of Hevea latex, the conclusion is reached that the essential feature of clot formation is fusion of the latex particles in a manner entirely analogous to the adhesion of two clean surfaces of unvulcanized rubber. [The experiments of Seifriz (*14*) with Hevea and Cryptostegia latex led him to the same or essentially the same conclusion.] As in the latter case it would not seem essential that the surfaces be completely clean to permit at least spotty fusion, but it would follow that, other factors being constant, the more complete the fusion, the stronger the clot would be.

In the ionic type of coagulation the important factors are believed to be: (*a*) neutralization of the electric charge on the surface of the particle (*11*); (*b*) dehydration of adsorbed surface layer (*11*); (*c*) clearing of the surface of the particle; and (*d*) fusion of the latex particles.

This is regarded as the sequence of events in the case of acetic acid coagulation of fresh latex. As the dehydration (*b*) and clearing of the surface (*c*) are time factors, the induction period preceding coalescence would be of appreciable duration, as is found in actual practice.

The function of coalescence agents is regarded as primarily that of clearing the surface of the particle by preferential adsorption. When, for example, soap is added to the fresh latex, displacement of adsorbed serum material occurs because of adsorption of the soap molecules. On acidification, the soap molecules are converted into rubber-soluble fatty acids. This function of cleaning the surface of the latex particles here ascribed to the coalescence agent, although arrived at independently, is essentially that of the enzyme rennet in the coagulation of milk as viewed by Schryver (*13*) in his studies thirty-odd years ago.

The absence of coalescence phenomena when either Barrowcliff latex or B liquid are acidified can be clarified by assuming that the heat treatment (to which these latices are subjected during preparation) coagulates the adsorbed serum material on the surface of the latex particles. This in effect encloses each particle in an envelope. When acidified, such latices do not coalesce because the surfaces of the particles are not clean. Addition of the coalescence agent by preferential adsorption displaces this film, and, on acidification under such conditions, coalescence ensues. It need not be assumed, as was mentioned before, that the particle surfaces be completely cleared.

Coalescence of Barrowcliff latex and B liquid can also be induced by the introduction of relatively small amounts of fresh latex. Van Harpen (*8*) calculates that the ratio of the rubber in fresh latex to that of the rubber in B liquid is in the range of 1:2000 to 1:20,000. At first sight it is difficult to see how such small amounts can be effective. However, if the matter is viewed from the standpoint of surface area or the number of fresh latex particles added during the inoculation, the case becomes more understandable. Hauser (*9*), using Henri's data (*10*), calculates that there are about 200,000,000 particles in 1 ml. of latex of 35% D.R.C. (This value, determined before the advent of ultraviolet and electron microscopy, is probably low.) An ordinary drop (0.05 ml.) should therefore carry at least 10,000,000 particles as well as an undetermined number of microorganisms. The inoculation technique could therefore induce coalescence in Barrowcliff latex or B liquid by an entrapping action in which the added fresh latex coagulates after acidification and the resulting network encloses the particles of B liquid forming a weak coagulum. (Microorganisms, introduced in the fresh latex droplets used in the inoculation of B liquid, can conceivably, through fermentative action, clear a portion of the surface of the rubber particles in the B liquid. This would increase the chances for fusion into a clot.)

In the case of coagulation of latex by pressure, as by rubbing a drop between the fingers, only points *c* and *d* appear involved. Pressure overcomes the repulsion set up by electric surface charges, forces a displacement of the adsorbed serum material—in effect clearing the surfaces of the latex particle—and forces fusion of the particles into a clot.

CONTINUOUS SHEET RUBBER PRODUCTION

An arrangement for the continuous processing of field latex into sheet rubber appears to offer the advantages of improved uniformity of product and reduction in factory floor space for a given output of rubber. These apparent advantages may become real in the case of large block estates preferring to use a central factory, or in case of the amalgamation of the latex output of smaller estates; the latter method has been suggested from time to time, as, for example, by Ascoli (*1*).

In dealing with the problem of continuous production of sheet rubber from Hevea latex, at least six points arise for consideration. These are: (*a*) continuous feeding of streams of latex and coagulant in proper proportions; (*b*) control of the induction period preceding coagulation by accelerating the rate of coalescence of the flocculated rubber particles; (*c*) formation of the coagulating latex into a ribbon and means of its transportation to the sheeting battery; (*d*) continuous machining of the ribbon into wet sheet; (*e*) drying the wet sheet; and (*f*) packing the dried rubber.

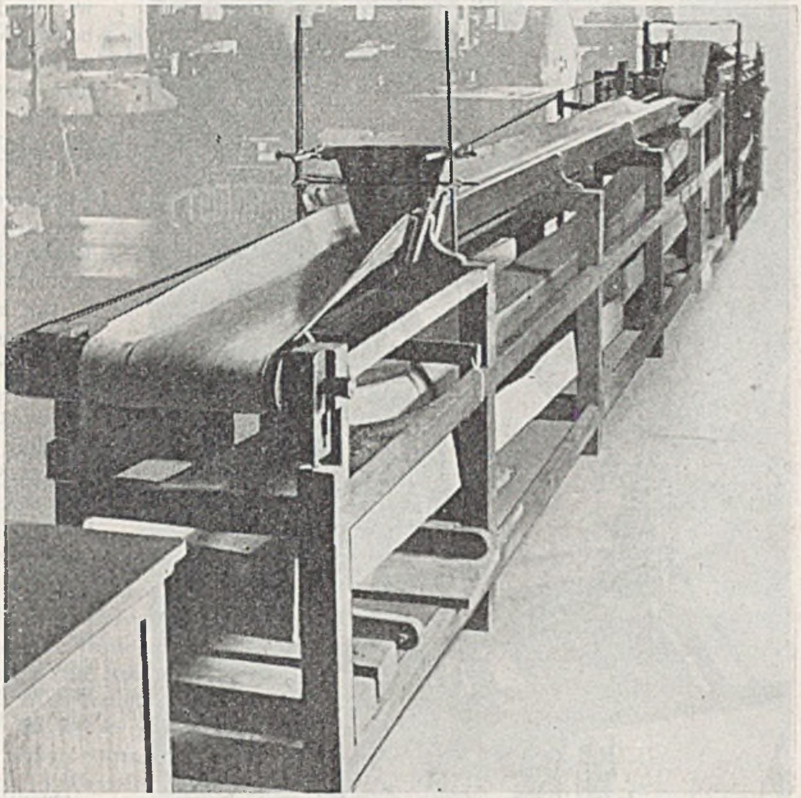

Figure 3. Continuous Sheet Rubber Machine with Coagulum Conveyer Trough in Foreground

Continuous Feed. Once the idea presents itself of continuously feeding latex and coagulant into a containing vessel to form a ribbon of coagulum, the actual proportioning of the liquids offers no real difficulty. An acceptable method is the use of rotameters, one for the latex and one for the coagulant stream, fed from bulking tanks by gravity or under low air pressure. The outlets should be arranged to set up turbulent flow to ensure adequate mixing of the coagulant with the latex.

Control of Induction Period. This step, in company with continuous feed, is essential to the success of the method. Control of coagulation rate is accomplished by addition of coalescence agents to the latex prior to its admixture with coagulant, as has been described in foregoing sections of the discussion. It is entirely possible to obtain adequate acceleration of coagulation by addition of the coalescence agent to the acidified latex, but pretreatment of the field latex is the preferred and simpler method. Also preferred is the adjustment of the rate to give a firm coagulum in about 1 minute after admixture of the treated latex and coagulant. For general-purpose rubber, this rate may be obtained by the addition to the field latex of 1% of coconut oil soap alone or together with a smaller amount of one of the phenolic materials (Table VII) as a fungicide. Although the coagulation may be made instantaneous, as by the use of ricinoleic acid (Table II), it is not desirable to do so because of the difficulty then encountered of uniformly mixing in the coagulant.

Experimental Machine. The simplest method of forming the coagulum into a continuous ribbon is to flow the coagulating latex mixture down a trough, but this is not a positive method. There is a tendency for the flocculated latex and the freshly set coagulum to adhere to the sides of the trough and cause undesirable accretions which impede smooth flow. This is especially true in cases where coagulation is run with low D.R.C. latex. The difficulty may be minimized by keeping the sides of the trough wet with water or by lining the trough with a very smooth surface which is readily wetted by water.

The best method, however, is to run the coagulation on a horizontally moving conveyer belt (Figure 3). The outside surface of an endless conveyer belt (about 8 inches wide in this case) is

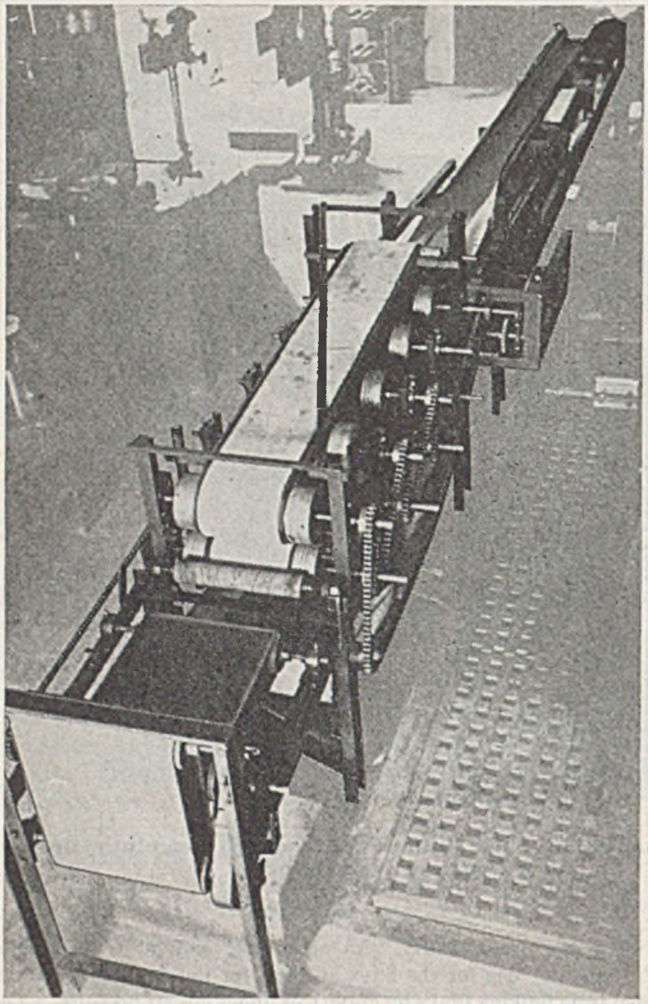

Figure 4. Continuous Sheet Rubber Machine with Sheeting Battery in Foreground

covered with a flexible sheet of vulcanized rubber which projects 5 or 6 inches beyond the edges of the conveyer belt. At the ends of the machine this special belt moves flat over driven rolls and from there is passed down a trough having sloping sides. When the belt enters the trough section, the rubber flanges are bent upward to form a moving rubber lining. One end of this trough section is sealed by a thin rubber sac shaped to the cross section of the trough. Contact with the sides of the trough is maintained by inflating the sac with air or with a liquid, such as calcium chloride brine. The sac is prevented from bulging under inflation pressure by flat metal plates on either side. Alternately, the seal may be made by feeding the conveyer belt into the trough section at an angle. This particular machine had a trough section about 12 feet long, and the belt moved at the rate of 6 feet per minute. For large scale production this rate would be increased several times.

In operation, a movable dam was placed in the trough section just beyond the rubber sac. Streams of treated latex and coagulant were proportioned into the space so formed. When the space was filled to the depth required, the machine was started. After a travel of about 6 feet the latex first added began to coagulate. This solid coagulum formed the seal at the exit end of the trough; at that time the removable dam, no longer required, could be lifted out, and a continuous ribbon of coagulum emerged.

Machining the Coagulum. This ribbon of coagulum was fed into a continuous sheeting battery where excess serum was squeezed out. Figure 4 shows the battery actually used in the experimental machine. The continuous ribbon of coagulum was gradually squeezed between two cloth-covered conveyer belts supported by a series of rolls. This type of compressing machine was used because of interest in coagulation of latex at high dilution. Continuous sheeting batteries were commercially available before the war and doubtless could be adapted to handle this type of coagulum when made from latex of about 15 to 25% D.R.C.

Drying Wet Sheet. This problem has received considerable attention in the past, and more recently by Piddlesden (*12*) of the Rubber Research Institute. Continuous drying of natural-rubber wet sheet is probably feasible if the sheet is thin enough. In this laboratory, wet sheet with a thickness of about 0.015 inch, made by a filtration process and seemingly more porous than machine coagula, has been dried in 8 to 12 minutes at 105° C. The method of continuously preparing and mechanically transporting coagula as here described is ideally suited to the handling of thin sheet as feed stock for continuous driers.

Packing. This matter, like that of drying wet sheet, has in the past received more than a modicum of attention. Thin sheet prepared by a continuous method could be rolled into cylinders, or, better (for stacking), folded and cut into rectangular blocks, as is done with thin sheet at the synthetic rubber plant designed by The B. F. Goodrich Company at Louisville. There seems to be merit in the idea of preparing parcels of a shape and size that can be easily handled by one man. This is the experience of the synthetic rubber industry and of manufacturers who use that product.

SUMMARY

Quantitative experiments in controlling the rate of coagulation of fresh Hevea latex are described, and the results have been applied in a process for the continuous preparation of sheet rubber on a laboratory scale. As with most continuous processes, this method is more applicable where large, rather than small, volumes of latex must be worked up. Its apparent advantages reside in a possible improvement in uniformity of product and a reduction in factory floor space for a given output of rubber.

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Nutritive Value of Canned Foods

EFFECT OF COMMERCIAL CANNING OPERATIONS ON THE ASCORBIC ACID, THIAMINE, RIBOFLAVIN, AND NIACIN CONTENTS OF VEGETABLES[1]

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In the preparation and canning of asparagus, peas, green beans, and lima beans, the blanching operation has an adverse effect on the retention of water-soluble vitamins. After blanching in hot water these products retained 44–94, 36–99, and 59–103% of their raw-product ascorbic acid, thiamine, and riboflavin contents, respectively. Analagous figures for steam blanching were 39–93, 32–88, and 63–103%. Green beans and lima beans retained 60–100% of their original niacin after hot-water blanching and 77–100% after steam blanching. Additional amounts of thiamine were destroyed in the processing operation, whereas the three other vitamins were not seriously affected by processing. Values for over-all retentions of ascorbic acid, thiamine, riboflavin, and niacin were 39–121, 31–88, 63–103, and 77–100%, respectively.

THE rapidly developing realization among food industries of the importance of protecting the natural nutritional values of their products has greatly stimulated interest in research along these lines. Consequently there has been a steady increase in information regarding the effects of commercial operations on the nutritional quality of processed foods. In general, the canning industry has kept abreast of this trend, but the data available concerning the effects of commercial operations on canned vegetables are still quite limited. Harris *et al.* (*9*) studied the over-all effects of experimental canning on the retention of thiamine in several vegetables and reported the following thiamine retentions: asparagus, 65–90%; lima beans, 32–60%; cut green beans, 83%; cut wax beans, 60%; peas (not blanched), 77–92%; sliced beets, 92%; spinach, 18–44%; diced carrots, 76%; squash, 32–39%; tomatoes, 76–90%. Experimentally and commercially canned asparagus from a single lot of raw product retained approximately the same amounts of thiamine.

King and Tressler (*12*) discussed the problem of vitamin C retention in the canning of foods and pointed out that, although neutral vegetables such as asparagus, peas, green beans, and kale frequently undergo losses of ascorbic acid in canning to the extent of 40–60%, precautionary measures with regard to oxidation and solution will reduce such losses. For example, even such highly disintegrated products as neutral baby foods often retain 35–65% of the original antiscorbutic value.

Adams (*1*) is of the opinion that some thiamine may be lost by leaching, particularly during blanching, and that further loss due to destruction is to be expected from the sterilization process. In reference to ascorbic acid this author says, "Blanching accounts for heavier losses than any other canning operation, leaching being the chief cause; only a small proportion of the vitamin C is destroyed by oxidation." For the control of ascorbic acid losses due to processing, he recommends thorough heat exhausting and keeping can head space at a minimum. Adams, Horner, and Stanworth (*2*) observed that peas, green stringless beans, and leafy vegetables which have a large surface area show the greatest losses; most of the leaching occurs during the first 2 minutes of the blanching operation. These types of vegetables generally lose 25–55% of their ascorbic acid at this stage and root vegetables only 10–20%.

Farrell and Fellers (*5*) found that experimentally canned green beans retained 22–25% of their ascorbic acid, 83% of their thiamine, and 97% of their riboflavin. The low retention of ascorbic acid may have been due partially to the excessive head space indicated by the fill-in weights reported by these workers. Similar retentions were found whether the beans were packed in tin or glass containers. Fellers, Esselen, Maclinn, and Dunker (*7*) reported that spinach retained 35–40% of its ascorbic acid content in canning and that asparagus, peas, lima beans, and spinach retained 71, 66, 25, and 87% of their thiamine and 78, 100, 73, and 38% of their riboflavin, respectively.

Fellers, Esselen, and Fitzgerald (*6*) reported over-all retentions of thiamine and riboflavin for some commercially canned vegetables. Asparagus, peas, lima beans, and spinach retained 72, 60, 28, and 71% of their thiamine and 98, 100, 70, and 45% of their riboflavin, respectively.

Fincke (*8*) compared the effects of various times and temperatures of blanching on the thiamine content of peas and found that there was an increasing loss of thiamine with longer times and higher temperatures.

Mayfield and Richardson (*16*) observed that home-canned cut green beans retained about 60% of their thiamine content when stored for 6 months and prepared for serving. Under the same conditions only 15 to 20% of the vitamin C remained.

Langley, Richardson, and Andes (*14*) observed that canned carrots lost only a small amount of thiamine but a large amount of vitamin C.

Clifcorn and Heberlein (*4*) published an extensive report on the retention of thiamine in commercially canned vegetables. They found that the most serious losses of thiamine occurred in the blanching and processing operations. Retentions of thiamine during commercial blanching of asparagus, green beans, lima beans, and peas ranged from 64–100% and, during commercial processing, from 58–79%. Over-all thiamine retentions ranged from 31–89% with an average over-all retention of 57%. The thiamine content of canned vegetables was found to be significantly affected by grade and size of the raw products and by the segment of the stalk canned in the case of asparagus.

In order to obtain more complete information on the subject, it was decided to investigate further the retention of water-soluble

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[1] This is the fourteenth of a series of papers dealing with the general subject "Nutritive Value of Canned Foods." Other articles have appeared in *The Journal of Nutrition*, *Journal of the American Dietetic Association*, *Food Research*, ANALYTICAL EDITION OF INDUSTRIAL AND ENGINEERING CHEMISTRY (August and November 1945), and INDUSTRIAL AND ENGINEERING CHEMISTRY (December 1945 and August 1946).

vitamins in commercially canned vegetables. Since ascorbic acid, thiamine, riboflavin, and niacin are the water-soluble factors most frequently found lacking in human dietaries and of the greatest concern to the Food and Nutrition Board of the National Research Council, plans were made for the inclusion of these factors in the study. Furthermore, it was felt that a simultaneous study of the effects of canning on several nutrients might give a better picture of changes undergone by the vegetables than would the study of any one nutrient. Because of differences in stability to various influences it seemed that, in addition to their own nutritional significance, these compounds might give some indication as to the relative extent of changes due to oxidation, extraction, heat, or light. All four of these vitamins are water-soluble. Each has a characteristic weakness, with the exception of niacin, to conditions encountered in commercial canning operations. Ascorbic acid is sensitive to oxidation, thiamine to high temperatures, and riboflavin to light. Consequently it was hoped that a comparison of the retentions of the four vitamins after each operation might give some indication as to the relative influence of each of these conditions.

Table I. Retention of Vitamins in Commercially Canned Peas

	Vitamin Content, Mg./100 G. Dry Wt.			Retention, %			Dry Matter, %	
Sampling Station	Ascorbic acid	Thiamine[a]	Riboflavin	Ascorbic acid	Thiamine	Riboflavin	Ascorbic acid samples	Thiamine and riboflavin samples
Cannery No. 3, Alaska peas, No. 2 cans								
Ungraded, raw	136.7	1.10	0.47	..	..	..	24.60	29.20
No. 3 sieve								
Raw	122.0	1.23	0.53	100	100	100	25.50	26.10
Blanched (3 min. at 190–200° F.)	...	1.08	0.42	..	88	79	...	28.10
Blanched (3 min. at 170° F.)	79.7	..	..	65	..	..	24.00	...
Filled (no brine)	97.5	0.94	0.38	80	76	72	15.29 (1.51)[b]	29.10
Processed (25 min. at 245° F.)	97.5	0.68	0.42	80	55	79	15.29 (1.51)	17.42 (1.51)
No. 4 sieve								
Raw	93.7	1.06	0.45	100	100	100	28.90	30.60
Blanched (3 min. at 190–200° F.)	74.2	0.98	0.33	79	92	73	29.40	33.70
Filled	76.8	0.88	0.30	82	83	67	17.28 (1.62)	33.00
Processed (25 min. at 245° F.)	76.8	0.68	0.32	82	64	71	17.28 (1.62)	17.66 (1.62)
Cannery No. 4, Alaska peas, No. 10 cans								
Ungraded, raw	148.0	1.08	0.60	..	..	..	23.60	24.10
No. 3 sieve								
Raw	141.0	1.16	0.66	100	100	100	23.70	20.50
Blanched (5–6¹/₂ min. at 190–200° F.)	...	0.95	0.52	..	82	78	...	24.60
Blanched (4¹/₂–5 min. at 170–175° F.)	93.7	..	..	66	..	..	25.10	...
Filled	106.0	0.89	0.43	75	77	65	13.79 (1.81)	19.90
Processed (55 min. at 240° F.)	107.0	0.51	0.50	76	44	76	13.79 (1.81)	14.49 (1.81)
No. 5. sieve								
Raw	...	1.05	0.59	..	100	100	...	25.20
Blanched (5–6¹/₂ min. at 190–200° F.)	...	0.93	0.46	..	88	78	...	26.80
Filled	...	0.81	0.46	..	77	78	...	24.20
Processed (55 min. at 240° F.)	...	0.52	0.49	..	49	83	...	15.13 (1.81)
No. 4 sieve								
Raw	114.3	..	..	100	..	..	27.60	...
Blanched (4¹/₂–5 min. at 170–175° F.)	73.3	..	..	64	..	..	28.50	...
Filled	87	..	..	76	..	..	14.99 (1.81)	...
Processed	92	..	..	80	..	..	14.99 (1.81)	...
Cannery No. 5, Alaska peas, No. 2 cans								
Ungraded, raw	132.7	1.06	0.36	..	..	..	21.10	35.00
No. 3 sieve								
Raw	142.0	1.04	0.44	100	100	100	22.20	32.40
Blanched (4¹/₂–5 min. at 190–195° F.)	...	0.92	0.32	..	88	73	...	36.90
Blanched (3 min. at 200–205° F.)	90.6	..	..	64	..	..	24.10	...
Filled	121	0.82	0.30	85	79	68	12.10 (2.90)	36.37
Processed (25 min. at 245° F.)	120	0.63	0.37	85	60	84	12.10 (2.90)	16.52 (2.90)
No. 4 sieve								
Raw	98.4	1.00	0.35	100	100	100	27.10	36.90
Blanched (4¹/₂–5 min. at 190–195° F.)	...	0.93	0.31	..	93	89	...	37.50
Blanched (3 min. at 200–205° F.)	66.8	..	..	68	..	..	31.30	...
Filled	88	0.93	0.30	89	93	86	14.50 (2.90)	37.80
Processed (25 min. at 245° F.)	91	0.55	0.36	93	55	103	14.50 (2.90)	17.20 (2.90)
Cannery No. 6 peas, sweets, No. 2 cans								
Ungraded[c]								
Raw	127.0	1.53	0.61	100	100	100	18.30	22.90
Blanched (6 min. at 200° F.)	79.8	1.47	0.51	63	96	84	20.30	24.90
Quality graded[d], floaters	75.7	1.47	0.53	..	..	..	20.50	20.50
Floaters, at filler	85	1.43	0.51	100	100	100	11.30 (2.00)	20.50
Floaters, processed (40 min. at 245° F.)	92	1.03	0.60	108[e]	68[e]	117[e]	11.30 (2.00)	11.8 (2.00)
Quality graded[d], sinkers	64.3	1.33	0.46	..	..	..	25.20	25.00
Sinkers, at filler	63	1.28	0.45	100	100	100	15.20 (2.00)	25.72
Sinkers, processed (50 min. at 245° F.)	74	0.92	0.53	116[e]	72[e]	115[e]	15.20 (2.00)	14.10 (2.00)
Cannery No. 7 peas, sweets, No. 10 cans								
Ungraded, raw	...	1.65	0.61	..	..	..	...	24.37
No. 5 sieve								
Raw	...	1.66	0.61	..	..	..	...	24.70
Into blanch	...	1.54	0.63	..	100	100	...	24.70
Blanched (8 min. at 175° F.)	...	1.36	0.47	..	88	75	...	25.70
At filler	...	1.28	0.45	..	83	71	...	25.50
Processed (55 min. at 240° F.)	...	1.08	0.53	..	70	84	...	14.14 (2.00)
Cannery No. 8, peas, sweets, No. 2 cans								
Ungraded, raw	152.5	1.76	0.59	..	..	..	17.50	27.00
Quality graded[d], fancy	152.0	1.60	0.55	..	..	..	16.80	29.70
Quality graded, extra standard	112.3	1.83	0.59	..	..	..	21.30	27.00
Quality graded, standard	88.2	1.68	0.55	..	..	..	22.90	29.70
Extra standard, No. 4 sieve								
Raw	143.5	1.71	0.60	100	100	100	16.60	26.70
Blanched (6 min. at 190–200° F.)	111.0	1.48	0.40	77	87	67	16.20	26.70
Filler	102.0	1.42	0.38	71	83	63	10.00 (2.20)	28.30
Processed (35 min. at 240° F.)	102.0	0.92	0.43	71	54	72	10.00 (2.20)	16.76 (2.20)
Extra standard, No. 5 sieve								
Raw	139.5	1.64	0.61	100	100	100	18.40	26.40
Blanched (6 min. at 190–200° F.)	118.2	1.45	0.44	85	88	72	16.30	29.10
Filler	108.0	1.36	0.38	77	83	62	10.20 (2.20)	28.30
Processed (35 min. at 240° F.)	108.7	0.85	0.44	78	52	72	10.20 (2.20)	16.95 (2.20)
Cannery No. 9, peas, sweets, No. 2 cans[f]								
Ungraded, raw	126.2	2.19	0.59	..	..	..	21.00	24.40
No. 4 sieve								
Raw	156.0	2.33	0.64	100	100	100	18.60	22.00
Blanched (6–7 min. at 190–200° F.)	...	1.84	0.44	..	79	69	...	24.60
Blanched (2 min. at 185° F.)	116.0	..	..	74	..	..	18.70	...
Filler	128.0	1.87	0.41	82	80	64	15.60 (4.50)	23.40
Processed (25 min. at 245° F.)	128.0	1.37	0.53	82	59	83	15.60 (4.50)	16.47 (4.50)
No. 5 sieve								
Raw	131.0	2.12	0.59	100	100	100	20.20	24.60
Blanched (6–7 min. at 190–200° F.)	...	1.75	0.37	..	82	63	...	27.30
Blanched (2 min. at 185° F.)	101.0	..	..	77	..	..	20.20	...
Filler	105.0	1.71	0.38	80	81	64	12.00 (2.50)	26.40
Processed (25 min. at 245° F.)	105.0	1.11	0.42	80	52	71	12.00 (2.50)	15.52 (2.50)

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[a] All thiamine values expressed as thiamine hydrochloride.

[b] Figures in parentheses indicate amount of solids introduced with the brine, expressed as per cent of the original fresh weight of the sample.

[c] Not separated into sieve sizes; No. 3 field grade on basis of tenderometer measurements.

[d] 34–35° Salometer brine used for quality separation of peas at cannery No. 6; 45° Salometer brine used for quality separation of lima beans at cannery No. 16. Concentration of brine used for separation of peas at cannery No. 8 is not known.

[e] Per cent of filler-sample content retained after processing.

[f] No. 4 sieve peas, vacuum-packed.

CANNING PROCEDURES

This work was conducted during the summers of 1943 and 1944 in canning plants located in Wisconsin, Illinois, and Michigan. Although the same general canning operations are widely used for any one product, there is considerable variation in the details of application. Differences in the number and kinds of cleaning operations, time, temperature, and type of blanch, the use or absence of quality grading, and time and temperature of the sterilization process are the most common variations. Such modifications may be necessitated by the condition of the raw product or the type of equipment used, or may be required in order to develop some particular characteristics desired in the canned product. The personal experiences and opinions of each packer exert a further influence. Although many of these details probably merit further study, the amount of work involved has compelled the authors to limit the investigation to surveys of operations in two plants packing green asparagus, four packing sweet peas, and three each for green beans, Alaska peas, yellow whole kernel corn, and lima beans. Ascorbic acid, thiamine, and riboflavin retentions were investigated for all of these products. The studies on niacin retention were restricted to corn, green beans, and lima beans.

At each plant records were made of the sequence of operations, and a sampling schedule was prepared to include those that seemed to be critical operations. Selected uniform lots of raw product of known field and harvesting history were then passed through the canneries' regular operations. Such lots of raw product were selected with regard to uniformity and total quantity so as to facilitate sampling and, at the same time, provide sufficient material so that operations could proceed at their usual rate. Consequently the size of the lot selected varied with the capacity of the canning line under observation and with the number of grades and sizes into which the raw product was separated for canning. For asparagus surveys 300- to 600-pound lots were canned. The lots of peas and lima beans weighed 600 to 1200 pounds. For the work on green beans lots of 400 to 800 pounds were used. Loads of the unhusked corn weighing 1 to 2 tons were selected for work on that product.

As each lot of product passed through the canning line, small samples were taken at intervals at each of the predetermined sampling stations. All samples taken at each station were combined and mixed. A total of approximately 10 pounds was collected at each station before the filling operation. At the filler six brined and closed, but unprocessed, cans were collected from each lot, with the exception of the asparagus samples and part of the pea samples, which were collected at the filler without brine. Twelve cans were taken from the processed product. Six of the processed cans were used for vitamin analyses. The others were submitted to the Continental Can Company for food inspection and moisture analyses. Corrections for added sugar and salt, determined from the brine formulas and the weight of brine filled into the cans, were subsequently subtracted from the per cent dry weight of filler and processed samples.

SAMPLE TESTING

From each of the samples taken before the filling operation, 200 grams were weighed into a No. 2 can. One hundred grams of water were added, and the cans were closed and processed. The can contents were subsequently analyzed for dry matter. Multiplication of these dry matter figures by 1.5 gave the dry matter content of the original material. Another 300-gram sample was weighed out for ascorbic acid determination immediately after collection of the material and placed in the bowl of a Waring Blendor. An equal volume of stabilizing solution was added, and nitrogen was bubbled through the liquid for about 1 minute before the Blendor was started and through the resulting slurry throughout the blending period. Two to three minutes of blending resulted in satisfactory disintegration of the material, except in the case of green beans, which required approximately 5 minutes of blending for satisfactory results. Twenty- to thirty-gram samples were weighed out from the resulting slurry, diluted to 250 ml. with an aqueous stabilizing solution containing 3% metaphosphoric acid (sticks) and 8% acetic acid, and filtered through paper. Duplicate aliquots of the filtrate were titrated with 0.02% aqueous sodium 2,6-dichlorobenzenone-indophenol dye solution buffered with sodium bicarbonate to pH 8.0 to 8.5.

All titrations were completed within an hour of the time that the sample was collected. With asparagus satisfactory results were obtained when the ascorbic acid slurry was prepared with an aqueous stabilizing solution containing 3% metaphosphoric acid and 8% acetic acid. When this was tried with peas, serious discrepancies were found in the ascorbic acid values because of rapid oxidation of the vitamin in the unblanched samples. Stern (*19*) encountered similar difficulties which he overcame by increasing the metaphosphoric acid concentration to 6% in the stabilizing solution. When our solution was modified accordingly, satisfactory results were obtained.

A third portion weighing 200 grams was blended with an equal weight of 0.2 *N* sulfuric acid and 2–3 ml. of chloroform. The slurry was poured into a glass-topped pint jar and covered with 5 ml. of toluene. The acidified slurries were refrigerated, taken to the laboratory, and stored in cardboard boxes at 4° C. Subsequently they were used for the thiamine, riboflavin, and niacin analyses. Thiamine was determined by the thiochrome method of Hennessy (*10*) as modified by Ives, Wagner, Elvehjem, and Strong (*11*). Riboflavin was determined by the method of Snell and Strong (*17*) and niacin by the method of Snell and Wright (*18*), using the modified medium of Krehl, Strong, and Elvehjem (*13*). Duplicate assays were run for each of these vitamins.

For vitamin analyses of the unprocessed cans collected at the filling machine and of the processed samples, six cans were opened in each instance. The total liquid and solid contents were measured; aliquots of each were recombined and blended with equal weights of metaphosphoric acid–acetic acid solution or 0.2 *N* sulfuric acid for the determination of ascorbic acid and the members of the B complex studied.

RESULTS AND DISCUSSION OF ASSAYS

The results of the assays for the entire investigation are listed in Tables I and II. All of the assay values were calculated to a dry weight basis. The per cent of dry matter in all samples is included in the tables to allow calculation of the values to the original basis. The values for filler and processed samples given in the tables were corrected for added sugar and salt by subtraction of the brine solids. The brine corrections are based on the composition of the brines used and the amounts added to the canned products. For calculation of the vitamin contents of filler and processed samples to original basis the corrected per cent dry weight should be used. Per cent retentions were calculated on the basis of the starting material wherever the sequence of canning operations made it practical. In those instances where the starting sample was separated into a number of sizes and grades, per cent retentions for each size and grade investigated were calculated on the basis of the raw material after separation rather than the ungraded lots. Canneries No. 6 and 16 are exceptions to this procedure; in those plants the product was quality-graded by brine separation after blanching. Therefore only the per cent retentions after blanching and the per cent of the filler-sample vitamin content retained after processing were calculated.

Because of the difficulties encountered in 1943 with ascorbic acid determinations on peas, that part of the work was repeated in the summer of 1944. Therefore, the values reported for ascorbic acid retention in the canning of peas were determined on different lots of material than were the values for thiamine and riboflavin retention. In some instances the blanching procedure used in 1944 differed from that used in 1943 and is listed accordingly. The extent to which the commercial operations studied affected the ascorbic acid, thiamine, riboflavin, and niacin contents varied considerably from one product to another. There is also some difference in the per cent retentions for a given product from one cannery to another.

The variations apparently were the result of characteristics of each product—differences of size, maturity, and grade of individual lots, and modifications of the canning operations. The percentage of original vitamin content of the raw foods retained after blanching in hot-water blanchers was found to be:

Vitamin	Asparagus	Alaska Peas	Sweet Peas	Green Beans	Lima Beans
Ascorbic acid	89–94	64–79	63–85	44–83	54–83
Thiamine	93–99	82–93	79–96	72–89	36–77
Riboflavin	86–103	73–89	63–84	70–93	59–92
Niacin	....	...	...	60–100	68–98

Smaller, more tender peas and lima beans retained less of the vitamins than did more mature sizes and grades.

In general, blanching had a more adverse effect on the retention of nutrients than did any other operation. Since appreciable amounts of all four of these water-soluble vitamins are lost at this point, it appears that extraction is an important factor. Ascorbic acid tends to be lost to a greater extent than others, and it seems reasonable to conclude that oxidation also occurred. Lima beans suffered the greatest loss of thiamine, and green beans showed the poorest retention of ascorbic acid in this respect. Blanched peas, green beans, and lima beans retained approximately the same proportions of their raw-product riboflavin contents. Some of these variations may be due to the different range of time and temperature used for different vegetables. Asparagus was outstanding for its high retention of vitamins after blanching. Clifcorn and Heberlein (*4*) observed that asparagus loses relatively little thiamine in commercial blanching and felt that it was due to the low ratio of surface area to mass in this product, as compared to peas, green beans, and lima beans; and to the comparatively mild blanching conditions used for asparagus. Distribution of the vitamins within the vegetables may also affect their retentions.

There was a tendency toward a slight decrease of all of the vitamins between the blanching and filling operations, presumably because of the use of cold-water rinses after blanching and from the drainage of fluids from the blanched product. Oxidation of ascorbic acid and light destruction of riboflavin may have also contributed to these losses.

It is difficult to evaluate closely the effects on peas and lima beans of quality separation by cold brine solutions, because the proportions of floaters and sinkers obtained from the ungraded products were not determined. However, it appears that the operation has less effect on raw products than on blanched products.

Yellow whole kernel corn retained 65–82% of its ascorbic acid, 69–113% of its thiamine, 70–93% of its riboflavin, and 74–91% of its niacin at the time it was filled into the cans.

TABLE II. RETENTION OF VITAMINS IN GREEN ASPARAGUS, GREEN BEANS,

Sampling Station	Vitamin Content, Mg./100 G. Dry Wt. Ascorbic acid	Thiamine[a]	Riboflavin	Niacin	Retention, % Ascorbic acid	Thiamine	Riboflavin	Niacin	Dry Matter, %
			GREEN ASPARAGUS						
Cannery No. 1, No. 2 cans									
Raw, snapped, and washed	...	1.78	1.87	..	..	...	...	..	8.55
Cut and sorted	565.0	1.85	1.85	..	100	100	100	..	9.00
Blanched (6 min. at 190° F.) and rinsed	504.0	1.72	1.91	..	89	93	103	..	8.40
Filled (no brine)	508.0	1.68	1.81	..	90	91	98	..	8.10
Processed (25 min. at 240° F.)	467	1.49	1.91	..	83	84	89	..	5.60 (0.46)[b]
Cannery No. 2, No. 2 cans									
Cut, unwashed	410.0	1.92	2.15	..	..	...	...	..	8.70
Washed	415.0	1.92	2.39	..	100	100	100	..	8.10
Blanched (4 min. at 150° F.)	368.0	1.82	2.05	..	89	95	86	..	9.00
Filled (no brine)	320.0	1.93	2.20	..	77	100	92	..	8.50
Processed (15 min. at 248° F.)	345.0	1.34	2.24	..	83	70	95	..	6.07 (0.63)
Blanched (1½ min. at 167° F.)	390.0	1.91	2.16	..	94	99	90	..	8.5
Procesed (15 min. at 248° F.), hand filled	384.0	1.35	2.33	..	93	70	99	..	5.32 (0.63)
			GREEN BEANS						
Cannery No. 10, No. 2 cans									
Snipped beans	183.0	0.68	1.33	5.74	100	100	100	100	10.80
Cut, before blanch	193.0	0.72	1.32	5.60	105	106	99	98	9.67
Blanched (4½ min. at 180° F.), washed	136.0	0.59	1.21	4.20	74	87	91	73	10.50
Filled and brined	152.0	0.76	1.43	5.00	83	111	107	87	5.43 (1.17)
Processed (28 min. at 240° F.)	110.0	0.55	1.36	5.00	60	81	102	87	5.43 (1.17)
Cannery No. 11, No. 2 cans									
Rough-graded	111.0	0.92	1.59	4.10	..	..	..	..	9.52
No. 3 sieve									
Raw	120.0	0.94	1.21	4.06	100	100	100	100	9.60
Blanched (4–5 min. at 180–190° F.)	78.5	0.80	1.06	3.92	65	85	88	96	10.20
Filled and brined	86.7	0.91	1.19	4.04	67	97	98	99	4.70 (0.70)
Processed (20 min. at 240° F.)	64.2	0.83	1.27	3.92	53	88	105	97	4.70 (0.70)
No. 4 sieve									
Snipped	167.0	1.05	1.46	5.85	..	..	..	..	8.20
Cut	129.0	0.87	1.20	4.63	100	100	100	100	9.30
Blanched (4–5 min. at 180–190° F.)	107.0	0.75	1.12	4.28	83	86	93	93	8.40
Filled and brined	88.9	0.72	1.14	4.40	69	83	95	95	5.00 (0.70)
Processed (20 min. at 240° F.)	88.0	0.50	1.14	4.00	68	57	95	87	5.00 (0.70)
Cannery No. 12									
No. 2 cans, No. 3 sieve									
Snipped	146.0	0.86	1.38	6.13	100	100	100	100	8.70
Blanched (4½ min. at 186° F.)	79.0	0.62	1.25	3.68	54	72	91	60	10.60
Filled and brined	85.0	0.93	1.56	4.62	58	108	113	75	4.60
Processed (20 min. at 240° F.)	60.2	0.75	1.47	4.90	41	88	106	80	4.60 (0.90)
No. 10 cans, No. 4 sieve									
Snipped	211.0	0.83	0.17	4.38	..	..	..	..	8.70
Cut	202.0	0.85	1.56	4.73	100	100	100	100	8.25
Blanched (4½ min. at 178° F.)	88.5	0.76	1.09	4.76	44	89	70	100	8.40
Filled and brined	67.3	0.71	1.05	4.58	33	83	67	97	4.85 (0.80)
Processed (38 min. at 240° F.)	79.3	0.65	1.09	4.62	39	76	70	98	4.85 (0.80)
			YELLOW WHOLE KERNEL CORN						
Cannery No. 13, No. 2 cans									
From cutter	35.2	0.55	0.44	6.10	100	100	100	100	28.30
From cleaner	31.4	0.43	0.42	5.57	89	78	96	91	29.50
Filled and brined	32.4	0.45	0.45	5.58	92	82	102	91	18.10 (3.30)
Processed (50 min. at 240° F.)	42.5	0.17	0.42	5.87	121	31	96	96	18.10 (3.30)
Cannery No. 14									
No. 2 cans									
From cutter	41.7	0.47	0.42	5.78	100	100	100	100	29.70
From cleaner	39.1	0.49	0.39	5.82	94	105	93	101	28.90
Filled and brined[c]	32.0	0.45	0.41	5.45	77	96	98	94	20.50 (0.80)
Processed (55 min. at 240° F.)	39.0	0.16	0.40	5.27	94	38	95	91	20.58 (0.80)
No. 10 cans									
From cutter	45.2	0.60	0.53	5.35	100	100	100	100	23.20
From cleaner	42.2	0.56	0.48	5.43	93	93	91	101	24.30
Filled[c]	32.3	0.50	0.50	4.93	71	84	94	92	25.60
Brined and exhausted	30.9	0.58	0.39	5.38	68	97	73	100	17.55 (0.80)
Processed (90 min. at 240° F.)	41.2	0.20	0.36	5.02	91	33	68	94	17.55 (0.80)
Cannery No. 15, No. 2 cans									
From cutter	41.8	0.46	0.41	6.75	100	100	100	100	30.27
From cleaner	39.7	0.50	0.40	6.40	95	109	98	95	28.77
Filled and brined	34.3	...	0.39	5.85	82	..	95	86	16.38 (4.20)
Processed (50 min. at 240° F.)	45.0	0.22	0.40	5.80	107	48	98	86	16.38 (4.20)

The percentage of the original vitamin content of the raw foods retained after processing in steam-pressure retorts was found to be:

Vitamin	Asparagus	Alaska Peas	Sweet Peas	Green Beans	Corn	Lima Beans
Ascorbic acid	83–93	75–93	71–82	39–68	91–121	60–84
Thiamine	70–84	44–64	52–70	57–88	31–48	32–60
Riboflavin	89–99	71–103	71–84	70–106	68–98	63–97
Niacin	...	....	...	80–98	86–96	77–100

Since the per cent retentions after processing for canneries 6 and 16 were calculated on the basis of the sample taken at the filler rather than the raw product, they were not included in these ranges. The given ranges of per cent retention after blanching and after processing are in good agreement with most of the present literature. However, the over-all ascorbic acid retentions tend to be greater than values reported for experimental canning. This may be partly due to the promptness with which commercially canned foods are generally filled into the cans, brined, and closed after blanching.

Processing increased the ascorbic acid values for corn. These increases were 13–32% of the ascorbic acid values obtained on the corresponding filled, brined, unprocessed samples. McHenry and Graham (*15*) suggested that heating might cause such increases in reducing power through the liberation of ascorbic acid from a bound form. However, that explanation is open to question. Wokes, Organ, Duncan, and Jacoby (*20*) pointed out that apparent vitamin C can be produced in a number of foods by heating.

Processing markedly reduced the thiamine contents of all products. Corn and lima beans were most seriously affected in this respect, presumably because of the long processing times used. Processing, in general, had negligible effects on riboflavin and niacin. Small decreases of ascorbic acid were noted in some instances.

YELLOW WHOLE KERNEL CORN, AND LIMA BEANS

Sampling Station	Vitamin Content, Mg./100 G. Dry Wt.				Retention, %				
	Ascorbic acid	Thiamine[a]	Riboflavin	Niacin	Ascorbic acid	Thiamine	Riboflavin	Niacin	Dry Matter, %
				LIMA BEANS					
Cannery No. 16, No. 2 cans									
Ungraded	59.0	0.53	0.33	4.74	..	..	..	..	39.70
Small size, raw	57.5	0.53	0.33	4.50	100	100	100	100	39.17
Small size, blanched (10 min. at 190° F.)	41.2	0.30	0.23	3.49	72	57	70	78	36.69
Quality-graded[d]									
Floaters	61.7	0.18	0.25	3.48	..	..	..	..	32.20
Floaters, filled and brined	45.9	0.18	0.24	2.96	100	100	100	100	25.20 (0.90)
Floaters, processed (45 min. at 240° F.)	44.8	0.12	0.25	2.32	98[d]	67[d]	104[d]	78	25.20 (0.90)
Sinkers	30.1	0.29	0.20	3.18	..	..	..	..	40.26
Sinkers, filled and brined	24.9	0.31	0.20	3.11	100	100	100	100	23.00 (0.90)
Sinkers, processed (45 min. at 240° F.)	26.3	0.21	0.19	2.57	105[e]	67[e]	95[e]	83[e]	23.00 (0.90)
Second run									
Tiny, raw	50.3	0.54	0.38	3.76	..	..	..	..	42.60
Small, raw	65.4	0.57	0.39	3.93	..	..	..	..	36.70
Medium, raw	46.7	0.41	0.39	3.37	100	100	100	100	41.70
Medium, blanched (10 min. at 190° F.)	28.8	0.24	0.23	3.16	62	58	59	94	39.18
Medium, quality separation[d]									
Floaters	44.0	0.19	0.23	2.97	..	..	..	..	35.70
Floaters, filled and brined	40.7	0.26	0.24	2.97	100	100	100	100	20.80 (0.9)
Floaters, processed (45 min. at 240° F.)	43.5	0.13	0.24	3.02	106[d]	48[d]	100[d]	102[d]	20.80 (0.9)
Sinkers	31.2	0.31	0.23	2.82	..	..	..	..	37.50
Sinkers, filled and brined	31.4	0.34	0.24	2.73	100	100	100	100	21.30 (0.9)
Sinkers, processed (45 min. at 240° F.)	34.2	0.19	0.23	2.93	108[e]	54[e]	96[e]	107[e]	21.30 (0.9)
Cannery No. 17, No. 2 cans									
No. 3 sieve									
Raw	51.6	0.30	0.27	3.83	100	100	100	100	43.80
Blanched (5 min. at 190° F.)	42.7	0.13	0.20	3.07	83	43	74	80	36.50
Filled and brined	42.9	0.15	0.25	3.10	83	50	93	81	20.90 (1.2)
Processed (18 min. at 250° F.)	38.3	0.13	0.25	2.94	74	43	93	77	20.90 (1.2)
No. 2 sieve									
Raw	66.3	0.40	0.35	4.38	100	100	100	100	38.40
Blanched (5 min. at 190° F.)	40.0	0.23	0.22	3.26	60	58	63	74	36.80
Filled and brined	49.8	0.18	0.25	3.74	66	45	71	87	20.69 (1.20)
Processed (18 min. at 250° F.)	45.0	0.13	0.22	3.77	60	32	63	88	20.69 (1.20)
No. 1 sieve (mixed floaters and sinkers)	125.0	0.62	0.64	7.15	..	..	..	..	28.00
Floaters									
Raw	139.0	0.63	0.61	6.35	100	100	100	100	26.30
Blanched (5 min. at 190° F.)	102.5	0.23	0.56	4.30	74	36	92	68	24.20
Filled and brined	113.0	0.31	0.65	5.25	81	49	103	83	14.34 (1.20)
Processed (18 min. at 250° F.)	117.0	0.26	0.61	4.85	84	41	97	77	14.34 (1.20)
Cannery No. 18, No. 2 cans									
Ungraded, washed	56.0	1.24	0.39	3.99	..	..	..	..	36.13
No. 3 sieve									
Inspected	73.7	0.65	0.40	4.05	100	100	100	100	32.60
Blanched (4 min. at 190° F.)	40.2	0.38	0.29	2.82	54	58	73	70	32.60
Filled and brined	55.0	0.39	0.31	3.42	75	60	77	85	17.00 (0.7)
Processed (35 min. at 240° F.)	52.7	0.32	0.31	3.18	72	48	77	78	17.00 (0.7)
No. 5 sieve									
Inspected	46.3	0.48	0.33	3.47	100	100	100	100	36.96
Blanched (4 min. at 190° F.)	33.9	0.37	0.24	3.39	73	77	73	98	35.41
Filled and brined	34.8	0.38	0.26	3.50	77	79	79	101	18.40 (0.70)
Processed (35 min. at 240° F.)	34.8	0.29	0.25	3.38	77	60	76	100	18.40 (0.70)

[a] All thiamine values expressed as thiamine hydrochloride.

[b] Figures in parentheses indicate amount of solids introduced with the brine, expressed as per cent of the original fresh weight of the sample.

[c] Hydraulic lift employed using hot water. Equivalent blanch 1/4 minute at 130–140° F.

[d] 34–35° Salometer brine used for quality separation of peas at cannery No. 6; 45° Salometer brine used for quality separation of lima beans at cannery No. 16. Concentration of brine used for quality separation of peas at cannery No. 8 is not known.

[e] Per cent of filler-sample content retained after processing.

SUMMARY

Studies on the preparation and canning of asparagus, peas, green beans, and lima beans indicate that the blanching operation has an adverse effect on the retention of water-soluble vitamins. When blanched in hot-water blanchers, these products retained 44–94% of the raw-product ascorbic acid content, 36–99% of the raw-product thiamine content, and 59–103% of the raw-product riboflavin content. Blanched green beans and lima beans retained 60–100% of the raw-product niacin content. The retention of these vitamins was affected by the size, maturity, and grade of the raw products, the characteristics of different products, and differences in blanching procedures. The highest retentions of ascorbic acid, thiamine, and riboflavin occurred in asparagus. Lima beans had the lowest thiamine retention after blanching, and green beans the poorest ascorbic acid retentions. Riboflavin retention in blanched peas, green beans, and lima beans was about the same in all three products. Although yellow whole kernel corn was not blanched, the cleaning operations resulted in the loss of small amounts of the water-soluble vitamins.

Additional amounts of thiamine were destroyed in the processing operation. Because of prolonged processing times, lima beans and corn lose more thiamine at this step than do the other products. Ascorbic acid, riboflavin, and niacin retentions are not seriously affected by the processing operation. Values for over-all retentions of ascorbic acid, thiamine, riboflavin, and niacin ranged from 39–121, 31–88, 63–106, and 77–100%, respectively.

Heat processing increases the capacity of corn to reduce the indophenol dye. It is questionable whether the increases are due to ascorbic acid.

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(*Nutritive Value of Canned Foods*)

EFFECTS OF BLANCHING ON THE RETENTION OF ASCORBIC ACID, THIAMINE, AND NIACIN IN VEGETABLES[1]

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A study of the effect of variations in blanching conditions on the retention of ascorbic acid, thiamine, and niacin in vegetables indicated that high temperature–short time blanches in general permit a better retention than do long-time blanches at either high or low temperatures. Very low ascorbic acid retentions were observed in green beans blanched at 160° F. Lima beans canned without blanching showed a high vitamin retention but were inferior in flavor to blanched samples.

As a result of the increasing interest of the canning industry in the preservation of natural nutritive values of canned foods, attention has been directed to the effects of commercial canning operations on the retention of vitamins. Much of the recent literature on the problem has been discussed by Clifcorn and Heberlein (*1*) and by Wagner, Strong, and Elvehjem (*2*). These authors observed that commercial blanching practices greatly affected the retention of water-soluble vitamins in the canning of vegetables.

In order to obtain further information on this subject, it was decided to conduct a series of experimental blanches on peas, green beans, and lima beans using commercial equipment. Since the study was intended to be of an exploratory nature, an effort was made to investigate as many variables as the time and available equipment would permit. Blanching times and temperatures representing the extremes of commercial practice were used in order to accentuate differences.

Portions of the vegetables from each experimental blanch were canned and processed, so that the effects of each blanching procedure on the vitamin content and quality of the final canned product could be determined.

The experimental studies reported here were carried out in commercial canning plants in the midwest. The necessary arrangements were made through the services of the American Can Company and the Continental Can Company.

BLANCHING TESTS

With the exception of the steam blanches all of the experiments were conducted with commercial, rotary hot-water blanchers (Tables I to VII). The effects of variations in blanching times and temperatures and in size or grade of the raw products were the major considerations. Some data are also reported on the relative effects of cutting green beans (Table V) and of quality-grading peas by brine separation before and after blanching, respectively (Table III).

Steam blanching equipment was not available in the plants visited for this work. In order to obtain some data on the comparative effects of steam and water blanching on green beans and lima beans, samples of the raw products were suspended in retorts on screens or in perforated lug boxes placed in retort crates. These samples were subjected to flowing steam at atmospheric pressure and temperatures of 210–212° F. for 4- to 10-minute intervals. At the end of the blanching period they were removed, hand-filled into No. 2 cans, brined, closed, and processed (Tables VI and VII).

The possibility of canning lima beans without blanching was given some consideration. Washed, unblanched lima beans were hand-filled into No. 2 cans, brined, closed, and processed for comparison with processed cans of blanched lima beans (Table VII).

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[1] This is the fifteenth of a series of papers dealing with the general subject "Nutritive Values of Canned Foods."

The general procedure was to select uniform lots of raw product for each experiment and divide them into portions according to the number of blanches involved. The lots of raw product selected for each experiment were of such size as to yield portions of 50 to 100 pounds for each blanch.

Numerous small samples were taken from the original lot of raw product and from each blanched lot. In each instance the small portions were combined and mixed, and resulted in total samples of 5 to 10 pounds of material, which was used for the preparation of aliquots for the determination of moisture, ascorbic acid, thiamine, and niacin. The methods used for the preparation of the analytical samples and for the determination of ascorbic acid, thiamine, and niacin were the same as previously described by Wagner, Strong, and Elvehjem (2), except that acetic acid was omitted from the stabilizing solutions for ascorbic acid, and 0.5 *N* instead of 0.2 *N* sulfuric acid was used for the preparation of the slurry for thiamine and niacin assays. Moisture determinations were made on all raw and blanched samples by the laboratories of the Continental Can Company.

TABLE I. EFFECTS OF SIEVE SIZE AND BLANCHING CONDITIONS ON RETENTION OF VITAMINS IN PEAS

		Mg./100 Grams Dry Wt.						Per Cent Retained							
Blanch	Sieve Size	Ascorbic acid		Thiamine[a]		Niacin		Ascorbic acid		Thiamine[a]		Niacin		Dry Matter, %	
		Bl.[b]	Pr.[c]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
Raw product	1, 2, 3	136		1.94		10.80		100		100		100		20.4	
	4	103		1.85		10.80		100		100		100		22.3	
	5, 6	87		1.73		11.45		100		100		100		24.4	
2.5 min. at 170–180° F.	1, 2, 3	117	...	1.80	1.20	9.12	8.63	86	...	93	62	84	80	18.4	10.7 (2.4)
	4	88.5	...	1.57	1.11	9.15	8.52	86	...	85	60	85	79	22.7	13.2 (2.4)
	5, 6	87.3	...	1.65	1.27	11.20	10.13	100	...	95	73	98	88	22.5	13.0 (2.4)
2.5 min. at 200° F.	1, 2, 3	124	...	1.73	1.36	8.45	8.30	91	...	89	70	78	77	17.5	10.1 (2.4)
	4	106	...	1.83	1.16	9.42	8.95	103	...	99	63	87	83	20.8	12.0 (2.4)
	5, 6	87.3	...	1.70	1.13	9.75	9.42	100	...	98	65	85	82	24.2	14.0 (2.4)
8 min. at 170–180° F.	1, 2, 3	89.0	...	1.28	1.08	7.22	6.80	65	...	66	56	67	63	17.2	10.0 (2.4)
	4	70.2	...	1.49	0.97	6.78	7.18	68	...	80	52	63	67	22.1	12.8 (2.4)
	4, 6	66.0	...	1.21	0.98	7.28	7.30	76	...	70	57	64	64	25.8	14.8 (2.4)
8 min. at 200° F.	1, 2, 3	86.5	...	1.39	1.16	7.80	7.60	64	...	72	60	72	70	17.2	10.0 (2.4)
	4	75.5	...	1.47	1.12	7.78	7.13	73	...	79	60	72	66	21.3	12.3 (2.4)
	5, 6	66.0	...	1.37	1.05	7.33	7.64	76	...	79	61	64	67	26.2	15.2 (2.4)

[a] Expressed as thiamine hydrochloride.
[b] Bl. = blanched.
[c] Pr. = processed.

TABLE II. EFFECTS OF MATURITY AND OF BLANCHING CONDITIONS ON RETENTION OF VITAMINS IN PEAS

		Mg./100 Grams Dry Wt.						Per Cent Retained							
Blanch	Field Grade[a]	Ascorbic acid		Thiamine[b]		Niacin		Ascorbic acid		Thiamine		Niacin		Dry Matter, %	
		Bl.[c]	Pr.[d]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
Raw product	3	177.5		1.65		10.37		100		100		100		19.3	
	7	116.0		1.34		8.56		100		100		100		23.8	
3 min. at 172° F.	3	109.0	108.3	1.57	0.99	9.95	9.58	61	61	95	60	96	92	20.1	12.5 (2.00)
	7	74.3	80.5	1.38	0.79	9.02	7.38	64	69	103	59	105	86	24.4	14.9 (2.00)
3 min. at 200–208° F.	3	93.4	106.3	1.43	0.93	7.16	7.50	53	60	87	56	69	72	21.2	12.8 (2.00)
	7	82.6	77.5	1.29	0.76	6.92	6.72	71	69	96	57	81	79	27.2	15.5 (2.00)
9 min. at 172° F.	3	87.6	86.8	1.43	0.88	8.08	6.55	49	49	87	53	78	63	19.3	12.2 (2.00)
	7	66.3	71.0	1.09	0.76	6.43	6.53	57	61	81	57	75	76	24.3	14.1 (2.00)
9 min. at 200–205° F.	3	85.0	94.5	1.32	0.87	..	7.13	48	53	80	53	..	69	19.9	11.2 (2.00)
	7	68.6	67.0	1.02	0.66	..	5.75	59	58	76	49	..	67	26.1	14.6 (2.00)

[a] As determined by tenderometer measurements.
[b] Expressed as thiamine hydrochloride.
[c] Bl. = blanched.
[d] Pr. = processed.

The remaining material from each blanched lot was filled into cans, brined, closed, and processed. Twelve processed cans were taken from each lot, and the remainder were held in reserve. Six of the twelve cans were submitted to the laboratories of the Continental Can Company or the American Can Company for food inspection and moisture determinations. The other six cans were opened, and samples prepared for the vitamin determinations.

PEAS. In the experiment outlined in Table I the peas were washed and separated into sieve sizes. The No. 1, 2, and 3 sieve peas were recombined; the No. 4 peas were handled separately; and the No. 5 and 6 sizes were recombined. Portions of each group were then blanched according to conditions in Table I.

In another experiment two lots of peas were selected, one classified as No. 3 field grade and a more mature lot classified as No. 7 field grade on the basis of tenderometer measurements. The tenderometer reading was less than 105 on the No. 3 lot and more than 150 on the No. 7. Portions of the two lots were blanched according to conditions listed in Table II.

For the study of the comparative effects of quality grading by brine separation before and after blanching, single lots of peas weighing 400 to 500 pounds were used. Half of each lot was run through the regular sequence of operations in a canning line in which the peas were quality-graded after blanching. The other half of the raw peas was caught in lug boxes at the washing machines and carried directly to the quality grader. The raw sinkers and floaters obtained were then blanched separately, filled into cans, brined, closed, and processed. Samples were taken at the points indicated in Table III.

GREEN BEANS. The lots of raw products were collected at the graders or cutters, mixed, and then divided into 50- to 100-pound portions for blanching (Tables IV, V, and VI).

TABLE III. VITAMIN CONTENT OF PEAS QUALITY-GRADED[a] BEFORE OR AFTER BLANCHING

	Mg./100 Grams Dry Wt.			
	Ascorbic acid	Thiamine[b]	Niacin	Dry Matter, %
Ungraded[c], raw	127.0	1.61	13.33	18.3
Blanched before quality grading				
Ungraded, blanched	79.8	1.28	9.47	20.3
Quality graded, floaters	75.7	1.29	8.10	20.5
Processed, floaters	92.0	0.75	9.20	11.3 (2.00)
Quality graded, sinkers	64.3	1.17	9.40	25.2
Processed, sinkers	73.6	0.65	9.40	15.2 (2.00)
Blanched after quality grading				
Raw, floaters	99.0	1.35	11.08	21.3
Blanched, floaters	75.2	1.26	8.10	21.0
Processed, floaters	80.0	0.76	7.08	12.7 (2.00)
Raw, sinkers	88.8	1.23	11.65	21.5
Blanched, sinkers	75.2	1.06	8.75	21.0
Processed, sinkers	76.6	0.69	7.20	13.3 (2.00)

[a] Quality-graded with brine of 34 to 35° Salometer.
[b] Expressed as thiamine hydrochloride.
[c] These peas were ungraded for size—that is, pod run. They were classified No. 3 field quality on the basis of tenderometer measurements.

Table IV. Effects of Blanching Conditions and Product Variation on Retention of Vitamins in Green Beans

		Mg./100 Grams Dry Wt.						Per Cent Retained							
Blanch	Sieve Size	Ascorbic acid		Thiamine[a]		Niacin		Ascorbic acid		Thiamine		Niacin		Dry Matter, %	
Raw, whole	3	140.0		0.99		4.57		100		100		100		9.7	
Raw, cut	4	155.0		0.95		4.95		100		100		100		9.7	
		Bl.[b]	Pr.[c]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
2 min. at 160° F.	3	...	58.0	0.96	0.71	4.38	5.60	..	41	97	72	96	122	9.6	4.3 (0.8)
	4	68.6	79.0	0.91	0.72	5.25	5.63	44	51	96	76	106	114	9.9	5.3 (0.8)
2 min. at 210° F.	3	108	86.5	0.94	0.67	4.45	4.70	77	62	95	68	97	103	9.0	5.1 (0.8)
	4	108	80.9	0.90	0.46	4.83	5.40	69	52	95	48	98	109	8.7	5.2 (0.8)
6 min. at 160° F.	3	57.2	52.4	0.97	0.75	4.40	3.92	41	37	98	76	96	86	9.1	4.6 (0.8)
	4	88.4	64.8	1.00	0.63	5.42	5.56	57	42	105	66	109	112	9.6	5.4 (0.8)
6 min. at 210° F.	3	84.0	73.2	0.94	0.59	4.08	3.85	60	52	95	60	89	84	8.8	5.2 (0.8)
	4	114.0	77.8	0.91	0.55	4.42	5.93	74	50	96	58	89	120	8.6	5.4 (0.8)
Raw, whole	3	129.0		0.99		4.83		100		100		100		9.1	
2 min. at 160° F.	3	44.8	..	0.92	..	4.67	..	35	..	93	..	97	...	9.0	...
2 min. at 185° F.	3	126.0	..	0.89	..	4.94	..	98	..	90	..	102	...	8.9	...

[a] Expressed as thiamine hydrochloride.
[b] Bl. = blanched.
[c] Pr. = processed.

Table V. Vitamin Retention in Green Beans of Sieve Size 4, Cut before and after Blanching

	Mg./100 Grams Dry Wt.						Per Cent Retained							
Blanch	Ascorbic acid		Thiamine[a]		Niacin		Ascorbic acid		Thiamine		Niacin		Dry Matter, %	
Raw, whole	143.0		1.08		5.38		100		100		100		11.4	
	Bl.[b]	Pr.[c]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
4.5 min. at 160° F. and then cut	132.0	74.2	0.98	0.85	5.25	5.27	91	52	91	78	98	98	9.9	5.8 (0.7)
Cut, then blanched 4.5 min. at 160° F.	120.0	78.5	0.98	0.74	5.20	5.62	84	55	91	68	97	104	10.0	5.7 (0.7)

[a] Expressed as thiamine hydrochloride.
[b] Bl. = blanched.
[c] Pr. = processed.

Table VI. Effect of Steam Blanching and Hot-Water Blanching on Vitamin Retention in Green Beans

		Mg./100 Grams Dry Wt.						Per Cent Retained							
Blanch	Sieve size	Ascorbic acid		Thiamine[a]		Niacin		Ascorbic acid		Thiamine		Niacin		Dry Matter, %	
Raw, cut (blend)	1, 2, 3	130		0.57		5.28		100		100		100		9.5	
		Bl.[b]	Pr.[c]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
Steam, 4 min.	1, 2, 3	80.0	79.0	0.54	0.46	5.20	5.63	61	61	95	81	98	107	10.0	5.7 (1.2)
Steam, 10 min.	1, 2, 3	74.3	73.3	0.51	0.42	4.90	3.93	57	56	89	74	93	74	10.2	5.6 (1.2)
Water, 4.5 min. at 190–200° F.	1, 2, 3	..	84.5	..	0.41	..	3.67	..	65	..	72	..	69	..	4.9 (1.2)

[a] Expressed as thiamine hydrochloride.
[b] Bl. = blanched.
[c] Pr. = processed.

Lima Beans. Lots of lima beans were obtained at the plant intakes where they were classified as greens (extra standard quality), and green and white blend (standard quality). Table VII presents the data obtained.

All vitamin values were calculated to a dry weight basis. The values given for processed samples represent the total contents of the cans. The results were corrected for the sugar and salt content of the brine. The dry matter percentages given in the tables for processed samples are corrected values. The figures in parentheses are the corrections which were subtracted from the percentages of dry matter found by analysis to obtain the corrected values. The results are also expressed on the basis of per cent retention of the original content, except in the quality grading experiment. In that experiment the exact proportion of sinkers and floaters obtained from the ungraded product was not determined. However, the vitamin contents of the blanched, quality-graded peas obtained by the two procedures were compared directly.

RESULTS WITH PEAS

In the blanching of peas it was found that, within the temperature (170-205° F.) and time (2.5 to 9 minutes) ranges used, ascorbic acid, thiamine, and niacin retentions decreased with longer times. The higher blanching temperatures had no consistent effect on the retention of thiamine, but tended to increase the retention of ascorbic acid and lower the retention of niacin. Within these ranges differences of time had a greater effect than differences of temperature. The more mature peas tended to retain a greater per cent of the vitamins than the smaller, more tender peas. In one lot of peas (Table I) about equal percentages of the three vitamins were retained during blanching. Two other lots (Table II) retained a greater percentage of thiamine and niacin than of ascorbic acid.

The differences in vitamin content between peas blanched before quality grading and those blanched after quality grading (Table III) were very small and probably not significant.

RESULTS WITH GREEN BEANS

The results obtained on the hot-water blanching experiments with green beans were more complex. A greater range of temperatures (160-210° F.) was used than for peas, but there was less variation of the time factor (2 to 6 minutes). When whole No. 3 sieve green beans and No. 4 sieve cut green beans were blanched 2 or 6 minutes at 160° or 210° F., the retention of ascorbic acid was poorer at the lower temperature, whereas the retention of thiamine was not greatly affected by the variations in blanching conditions, and the retention of niacin was slightly less in beans blanched at the higher temperature for the longer time. No. 3 whole green beans blanched at 185° F. for 2 minutes retained a greater percentage of ascorbic acid than did similar beans blanched at 160° or 210° F. Since the more drastic blanching conditions resulted in a better retention of ascorbic acid than was obtained in any sample blanched at 160° F., it appears that the lower temperature favors oxidation losses. Losses due to extraction would be greater at the higher temperature. It may be that enzymatic activity is not completely destroyed at 160° F.

The effects of size are somewhat obscured in the experiments on green beans because the large sizes were cut and the smaller sizes were not. Green beans that were cut before blanching retained less ascorbic acid than those cut after blanching, but no difference was found in the retention of thiamine and niacin (Table V). Processed cans of green beans that had been steam-blanched for 4 or 10 minutes retained approximately the same percentage of the vitamins as did processed green beans that had been blanched in hot water for 4.5 minutes. The steam-blanched samples were too soft, and they were dark and off flavor because of the presence of foreign substances that would ordinarily be removed by water blanching. Obviously shorter steam-blanching times should be tried.

Table VII. Effect of Experimental Blanching Procedures on Vitamin Retention in Lima Beans

Blanch	Grade	Mg./100 Grams Dry Wt.						Per Cent Retained						Dry Matter, %	
		Ascorbic acid		Thiamine[a]		Niacin		Ascorbic acid		Thiamine[a]		Niacin			
							Series A								
Raw	Blend[b]	43		0.39		2.83		100		100		100		36.8	
Raw	Green[c]	76.2		0.42		3.27		100		100		100		33.0	
		Bl.[d]	Pr.[e]	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.	Bl.	Pr.
2.5 min. at 170° F.	Blend	37.8	33.5	0.26	0.21	2.93	3.12	88	78	67	54	104	110	36.8	19.7 (0.9)
	Green	52.2	57.5	0.23	0.22	3.25	3.22	69	75	55	52	99	99	34.5	18.6 (0.9)
2.5 min. at 180° F.	Blend	38.6	33.8	0.26	0.19	2.77	2.46	90	79	67	49	98	87	37.5	20.7 (0.9)
2.5 min. at 190° F.	Blend	34.7	35.8	0.26	0.17	2.55	2.15	81	83	67	44	90	76	36.0	20.1 (0.9)
	Green	54.6	60.5	0.25	0.21	2.48	2.26	72	79	60	50	76	69	33.8	18.5 (0.9)
4.5 min. at 170° F.	Blend	36.4	37.2	0.24	0.19	2.50	2.39	85	86	61	49	88	84	36.8	20.1 (0.9)
4.5 min. at 190° F.	Blend	33.5	30.3	0.24	0.19	2.39	2.34	78	70	61	49	84	83	36.8	20.7 (0.9)
Raw	Blend	46.2		0.34		2.88		100		100		100		36.8	
Canned without blanching	Blend	..	48.7	..	0.24	..	2.42	..	106	..	71	...	84	..	20.1 (0.9)
							Series B								
Raw	Green[c]	90		0.43		4.59		100		100		100		30.4	
Raw	Blend[b]	59.4		0.37		3.67		100		100		100		39.4	
3.5 min. at 170° F.	Green	74.5	63.2	0.21	0.17	4.03	3.91	83	70	49	40	88	85	32.8	18.4 (0.9)
	Blend	53.7	50.5	0.19	0.19	3.25	3.56	90	85	51	51	88	97	29.4	21.4 (0.9)
3.5 min. at 190° F.	Green	71.8	56.2	0.22	0.15	3.47	2.76	80	62	51	35	76	60	33.4	21.7 (0.9)
	Blend	58.2	61.0	0.21	0.20	3.09	3.18	98	103	57	54	84	87	37.5	17.6 (0.9)
8.2 min. at 170° F.	Green	56.8	54.8	0.18	0.14	3.23	2.78	63	61	42	33	70	60	33.4	18.6 (0.9)
	Blend	45.7	46.4	...	0.16	...	2.65	77	78	..	43	...	72	37.2	21.1 (0.9)
8.2 min. at 190° F.	Green	56.5	46.8	0.20	0.12	2.33	2.02	63	52	46	28	51	44	32.6	21.8 (0.9)
	Blend	47.2	47.9	0.19	0.11	2.15	2.25	80	81	51	30	58	61	35.4	19.6 (0.9
Steam, 5 min.	Blend	51.4	54.5	0.33	0.23	2.66	2.40	87	92	89	62	72	65	39.0	22.8 (0.9
Steam, 8 min.	Blend	58.4	52.6	0.33	0.24	2.35	2.63	98	86	89	65	64	72	34.4	21.6 (0.9
Canned without blanching	Green	..	108.0	..	0.35	..	4.45	..	120	..	81	...	97	..	18.0 (0.9)
	Blend	..	62.2	..	0.27	..	3.14	..	105	..	73	...	86	..	22.9 (0.9)

[a] Expressed as thiamine hydrochloride.
[b] Mixture of green and white beans of standard quality.
[c] Green beans, extra standard quality.
[d] Bl. = blanched.
[e] Pr. = processed.

RESULTS WITH LIMA BEANS

Within the temperature (170–190° F.) and time (2.5–8.2 minutes) ranges for the hot water blanching experiments with lima beans the effect of increasing the blanching time was greater than that of increasing the temperature, although niacin retentions were lower at the higher temperatures. The differences between the effects of blanching for 2.5 and 4.5 minutes (series A) were very small within this temperature range. A greater contrast is found between beans blanched for 3.5 and 8.2 minutes (series B).

The adverse effect of hot-water blanches on the thiamine content of lima beans is evident. This effect has been reported previously by Clifcorn and Heberlein (*1*) and by Wagner, Strong, and Elvehjem (*2*). Lima beans blanched with flowing steam for 5 and 8 minutes retained approximately the same levels of ascorbic acid and niacin as did lima beans blanched with hot water, but the retention of thiamine was considerably higher.

Lima beans canned without blanching retained all of their ascorbic acid content and more of their thiamine than did samples that were canned after blanching.

It would be difficult to correlate the quality of the processed samples with the vitamin content of the blanched samples, because changes in one canning operation often require compensatory changes in other operations to produce a satisfactory product. For example, steam-blanched green beans were not so clean as they would have been after a hot-water blanch. In another instance cans of experimentally blanched peas were found to contain insufficient salt because the brine available had been adjusted for peas which had picked up salt in the quality graders. These particular samples had not been through the brine separation and consequently had a lower salt content.

Because of these difficulties and because the blanching conditions were extremes of commercial practice rather than average practice, the canned samples from the experimental blanches tended to be of a lower quality than commercial packs. Unblanched processed samples of lima beans were inferior in flavor to blanched lima beans and had cloudy brines. The steam-blanched lima beans were also of inferior quality.

SUMMARY

There was a decreased retention of ascorbic acid, thiamine, and niacin in the blanching of peas with increasing times.

Low ascorbic acid retentions were observed in green beans blanched at 160° F. With that exception the vitamin retentions in green beans decreased with increasing times and temperatures.

Steam-blanched green beans retained approximately the same proportions of their vitamin content as did water-blanched green beans.

The relative effects of time and temperature variations in the hot-water blanching of lima beans were similar to those found in peas. However, lower retentions of thiamine were observed in lima beans than in green beans and peas. Steam-blanched lima beans retained considerably more thiamine than water-blanched beans.

Lima beans canned without blanching retained a large proportion of their ascorbic acid, thiamine, and niacin contents but were inferior in flavor to the blanched samples.

The percentage of the raw product vitamin content retained in peas, green beans, and lima beans after hot-water blanching fell in the following ranges: ascorbic acid, 48–103, 35–98, and 63–98; thiamine, 66–103, 90–105, and 42–67; and niacin, 63–105, 89–109, and 51–104, respectively. High temperature–short time blanches in general permit a better retention of the three vitamins than do long-time blanches at either high or low temperatures.

ACKNOWLEDGMENT

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(Nutritive Value of Canned Foods)

EFFECT OF TIME AND TEMPERATURE OF STORAGE ON VITAMIN CONTENT OF COMMERCIALLY CANNED FRUITS AND FRUIT JUICES (STORED 12 MONTHS)[1]

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The effect of 4, 8, and 12 months' storage at 50°, 65°, and 80° F. on the ascorbic acid, carotene, niacin, riboflavin, and thiamine content of seventeen lots of canned fruits and fruit juices has been studied. Comparisons were also made as to the effect of a year's storage, in nine warehouses located in cities throughout the United States, on the ascorbic acid and thiamine content of tomatoes and orange juice. The canned foods, held under constant temperature conditions, at 50° F. showed no significant losses in ascorbic acid, thiamine, or carotene. Tomatoes showed a significant loss in niacin after 8 months of storage regardless of the temperature employed. In general, storage at 65° F. also resulted in good retention of the vitamins studied. The fruit and fruit juices stored at 80° F. showed definite losses in ascorbic acid and thiamine after 8 months, which increased with 12-month storage at this temperature. The retention of ascorbic acid and thiamine in canned foods stored for 12 months in nine warehouses in different localities decreased as the yearly average temperature increased. The retentions of ascorbic acid varied from 78% at New Orleans average temperature 77° F. to 100% in New York average temperature 58° F. The retentions of thiamine varied from 87% at Tampa average temperature 77° F. to 97% in New York.

A NUMBER of studies on the nutritive value of canned fruits and vegetables have been reported in the last few years. The results point out that canned foods are important sources of the essential food nutrients. Since, however, the unstable character of several of the vitamins suggests the possibility of appreciable losses during storage, definite information is needed as to the effect of time and temperature on these nutrients. A few studies of limited scope on the effect of such variables in storage conditions on vitamin retention in commercially canned foods have been published. These data show that both time and temperature affect the retention of ascorbic acid (*7, 15, 22, 26*) and that temperature has a limited effect on carotene retention but a marked effect on thiamine (*7*).

To widen the scope of information on this subject a more extensive investigation was planned of the effect of time and temperature of storage on the retention of ascorbic acid, carotene, niacin, riboflavin, and thiamine in commercially canned fruit and vegetable products. This paper presents the results obtained from the first year's storage and examination of certain of the more acid—pH below 4.5—fruit products. It includes the data obtained by periodic assays for the vitamins mentioned on seventeen lots of canned foods stored at three constant temperatures, as well as 1-year assays on three foods stored in nine warehouses located in areas having varied climatic conditions. In addition, periodic assays are reported of a preliminary experiment on the ascorbic acid in two grapefruit juice samples stored at three other constant temperatures for 18 months.

EXPERIMENTAL CONDITIONS

TEMPERATURES. The three constant temperatures chosen for the main project were 50°, 65°, and 80° F. These temperatures were considered to cover the range of yearly average temperatures of warehouses located in varied areas throughout the United States. Moreover, the lowest temperature, 50° F., was believed to offer a possibility of practical attainment from the standpoint of economy if results should indicate that cooler storage is warranted. Through the cooperation of the National Canners Association–Can Manufacturers Institute Nutrition Research Committee three constant temperature storage chambers were constructed at the laboratory for use in this experiment. Temperature records were kept on these chambers using the readings of two thermometers in each, one placed above the canned foods, the other at a low level. The warehouses used for storage of the other group of experimental samples were located in New Orleans, La., Tampa, Fla., Tempe, Ariz., Yuba City and Oakland, Calif., Washington, D. C., St. Louis, Mo., Rochelle, Ill., and New York, N. Y. In these warehouses daily maximum and minimum temperatures were recorded. The samples for the earlier, more limited experiment were stored in a refrigerator, a room-temperature storeroom, and an incubator, with average temperatures maintained at approximately 45°, 70°, and 98° F., respectively.

TIME. In addition to the initial analyses on the samples for controlled-temperature storage, assays for the five vitamins were made after 4-, 8-, and 12-month storage intervals, and one additional assay for ascorbic acid was made after the first 2- to 4-week storage. For the warehouse-stored samples, assays for two vitamins, ascorbic acid and thiamin, were made only after 12 months. For the preliminary experiment with grapefruit juice held at 45°, 70°, and 98° F., ascorbic acid assays were made at intervals of 0.5, 4, 8, 12, and 18 months.

CANNED FOODS. The canned food products stored at constant temperatures and analyzed at intervals were: three lots of grapefruit juice, one each from California, Florida, and Texas; one lot of Florida grapefruit segments; two lots of orange juice, one each from California and Florida; two lots of halved peaches, one clingstone and one freestone variety, both western-grown; two lots of Hawaiian pineapple juice; one lot of Hawaiian sliced pineapple; three lots of tomato juice, one each from canneries in the eastern, western, and midwestern production areas; and three lots of whole tomatoes, one each from the same areas. The warehouse-stored samples included one lot of California orange juice and two lots of western whole tomatoes. The samples used in the preliminary study were two lots of Texas grapefruit juice.

All samples were of fancy or extra standard quality. The lots of cans for this storage study were obtained during a period when each cannery was operating on a uniform lot of raw stock in the

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[1] This is the twenty-second of a series of papers dealing with the general subject "Nutritive Value of Canned Foods."

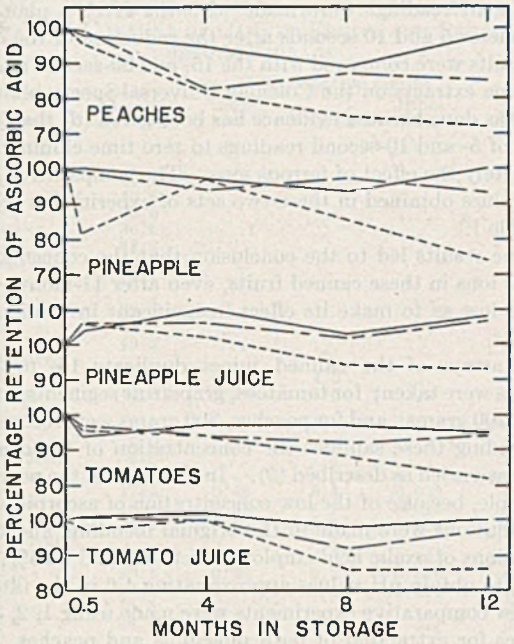

Figure 1. Effect of Storage Time on Ascorbic Acid in Tomato, Pineapple, and Peach Samples

———— 50° F.
—·—·— 65° F.
- - - - - 80° F.

regular course of commercial production of retail-sized cans. In general the cans in each lot were numbered consecutively in order of filling and closing, and were processed in one retort at the same time. There were 144 cans in the lots of samples used for controlled-temperature storage and 360 in those used for controlled-temperature storage and warehouse storage. Immediately after cooling they were cased and shipped.

Those shipped to the laboratory were promptly assorted; six cans were used for the initial assays, and the others were placed in storage under experimental conditions. The assortment was made according to the planned schedule in reference to can numbers; six cans were allowed for each storage period and temperature. These groups were arranged in such a way that no one assay would be made on a composite sample of cans coming from the canning line in close sequence. In this way it was hoped that representative sampling for each treatment would be ensured as nearly as possible. Those cans to be stored in warehouses in the different cities were sent directly there, and, after approximately 1 year, one or two 6-can samples of each food were withdrawn from storage at each warehouse and sent to the laboratory for the scheduled assays.

Assays. Not all five vitamins were determined for each of the foods. The retention of ascorbic acid was followed for all seventeen samples, and that of thiamine for all except the grapefruit segments and freestone peach. The carotene and niacin contents were determined for peaches, tomatoes, and tomato juice, and riboflavin for tomatoes and tomato juice only.

Preparation of Samples. The procedure of preparing samples for withdrawal of the aliquots used for assays was the same as that described by Hinman, Higgins, and Halliday (*9*). For niacin and riboflavin assays the aliquots were taken from the same type of blended mixtures as were those prepared for thiamine determinations.

ASSAY METHODS

Carotene. The method used combined the extraction method of Moore and Ely (*18*) and the chromatographic technique of Wall and Kelly (*27*) with slight modifications as used in some assays by Hinman *et al.* (*9*).

The carotene concentrations were evaluated with a Coleman Universal spectrophotometer using a wave length of 455 millimicrons and a 20 × 40 mm. optically ground glass cuvette.

Since no saponification step was included and since Mackinney (*17*) stated that some peaches contain xanthophyll esters which, like the carotenes, are weakly absorbed, the question arose concerning the accuracy of the carotene values of the peach samples. Comparative determinations were therefore made on samples from both lots of peaches to study the effect of saponification by blending the sample for 5 minutes with 12% alcoholic potassium hydroxide (*13*). The lower values obtained for carotene after saponification indicated that the presence of xanthophyll esters in the unsaponified extracts gave falsely high carotene values; that in the case of the clingstone variety the values were approximately doubled by the presence of these esters; and that in the case of the freestone variety the very low pigment value previously obtained was entirely accounted for as xanthophyll esters. In this last case, storage effect on carotene alone would not have been measurable, and even in the case of the clingstone peach the storage changes were so small that they would have been more or less completely masked by experimental errors in the isolation of carotene.

Niacin. The assay method of Snell and Wright (*25*) was used with the modified medium of Krehl, Strong, and Elvehjem (*14*) changed as follows: The biotin was increased twentyfold and the pyridoxine was doubled. The samples were set up in duplicate at five levels.

In making digests, 16 grams of the tomato juices and tomatoes and 25 grams of peaches were autoclaved with 1 *N* hydrochloric acid in a volume of approximately 200 ml. Since others (*12*) had reported using 1 *N* sodium hydroxide for hydrolyzing samples, a comparison was made between acid and alkaline hydrolysis for each food analyzed. In each case the acid-hydrolyzed sample gave slightly higher (7–12%) results.

As a check on the assay, standard recoveries were determined on each run for each different type of food material. Only such values were accepted as agreed within 10% on three to five levels and for which the standard recovery was found to fall between 90 and 110% at three to five levels.

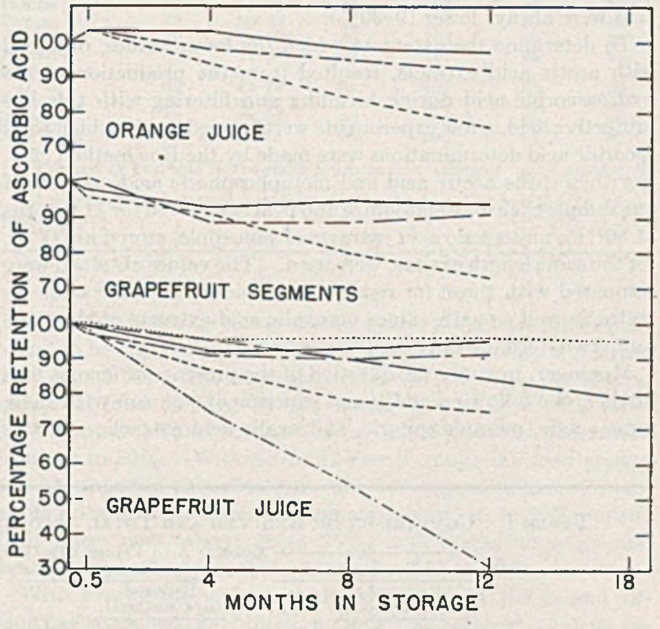

Figure 2. Effect of Storage Time on Ascorbic Acid in Grapefruit and Orange Samples

. . . . 45° F.
———— 50° F.
— - — - 65° F.
— — — 70° F.
- - - - - - 80° F.
—·—·— 98° F.

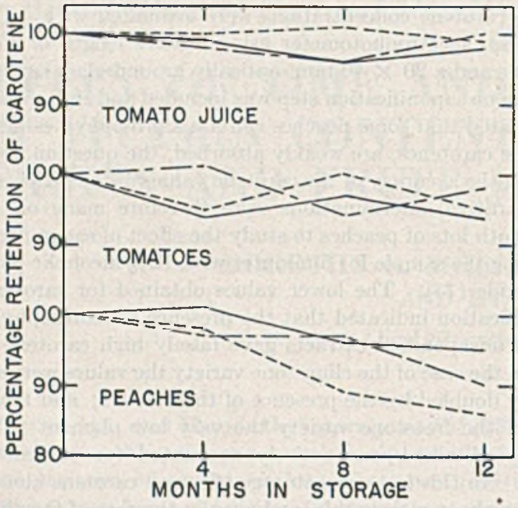

Figure 3. Effect of Storage Time on Carotene

———— 50° F.
—·—·—· 65° F.
- - - - - - - 80° F.

Reduced Ascorbic Acid. The photoelectric measurement was used for the reduction of 9 ml. of indophenol dye by 1 ml. of unbuffered acid-extracted sample (*5*), as applied to vegetables and fruits by Loeffler and Ponting (*16*) employing oxalic acid (*20*).

However, it was known that ferrous ions reduce the dye in the presence of metaphosphoric acid (*6, 11, 28*) and presumably would also in oxalic acid in which the oxidized ferrioxalate complex forms; also, the possibility existed that the ferrous ions might accumulate in stored canned foods. Consequently it was considered necessary to learn whether the reduction of the dye by those ions was being included in experimentally significant amounts. To do so, parallel determinations were made with 8% acetic acid (*6*) on the samples which were assayed after 4 and 8 months of storage. On the whole, the values obtained with acetic acid were lower by less than 10%, although in about one eighth of the cases they were identical or slightly higher. With the peach samples, however, the values obtained with acetic acid were always lower (9–30%).

To determine the extent to which the lower values, obtained with acetic acid extracts, resulted from the production of dehydroascorbic acid during blending and filtering with this less protective acid, a few experiments were carried out in which total ascorbic acid determinations were made by the Roe method (*21*). For these tests acetic acid and metaphosphoric acid extracts of one sample each of tomato juice and peaches, stored for 11 months at 80° F., and acetic acid extracts of pineapple, stored at 50° F. for the same length of time, were used. The values obtained were compared with those for reduced ascorbic acid on the same filtrates as well as with values on oxalic acid extracts of the same samples determined by the dye method.

Moreover, to study the question of the presence of ferrous ions further, the following additional experiment was run with these same acetic, metaphosphoric, and oxalic acid extracts. In this experiment readings were made with the Evelyn photoelectric colorimeter 5 and 10 seconds after the reduction of the dye, and the results were compared with the 15- and 30-second readings of the same extracts on the Coleman Universal Spectrophotometer. This was done because evidence has been given (*6*) that extrapolation of 5- and 10-second readings to zero time eliminated more completely the effect of ferrous ions. The comparative ascorbic acid values obtained in these two sets of experiments are shown in Table I.

These results led to the conclusion that the concentration of ferrous ions in these canned fruits, even after 11-month storage, was so low as to make its effect insignificant in oxalic acid extracts.

For assays of the canned juices duplicate 15- to 30-gram samples were taken; for tomatoes, grapefruit segments, and pineapple, 200 grams; and for peaches, 300 grams were reconstituted. In blending these samples the concentration of the oxalic acid used was varied as described (*9*). In the cases of the peaches and pineapple, because of the low concentration of ascorbic acid, the final dilutions were made in the original blending, and the concentrations of oxalic acid employed were 1.5 and 0.75%, respectively, to obtain pH values approximating 1.6 in the filtrates.

A few comparative experiments were made using 1, 2, 3, and 5 minutes for extraction of both pineapple and peaches. It was found that the extraction in 1 minute was as complete as that with longer time.

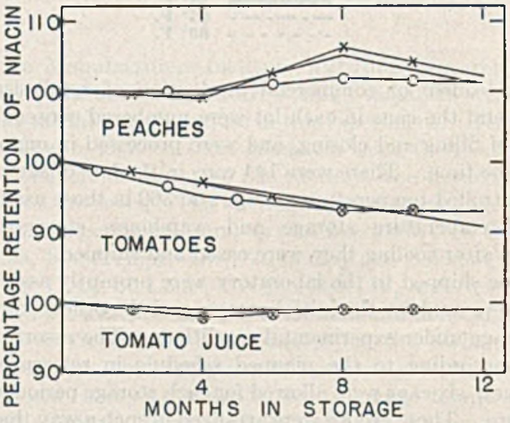

Figure 4. Effect of Storage Time on Niacin

———— 50° F.
—×—×—×— 65° F.
—○—○—○— 80° F.

Morrell (*19*) and others have suggested the calculation of total volume of extract as water of sample plus volume of extractant used. Thus, to calculate the so-called total volume of the extracts of pineapple, tomatoes, and grapefruit segments, moisture determinations of these foods were made (*1*) and used. For the peaches, because the proportion of sample was at a maximum and moisture at a minimum, it was thought that a better procedure would be to relate the 1-ml. aliquot of filtrate used in the reaction to the whole extract on a weight, rather than volume, basis. Therefore specific gravities of the filtrates of both lots of peaches were determined.

To calculate the total volume of extract for each of the canned juices, the volume of extractant and the volume of the sample were added. Since samples were taken by weight, their volumes were based on their respective specific gravities.

Riboflavin. Both chemical and microbiological methods were used.

Table I. Comparison of Reduced and Total Ascorbic Acid Values

	Ascorbic Acid Values, Mg./100 G.								
	Tomato juice			Pineapple			Peaches		
	Reduced (dye method)			Reduced (dye method)			Reduced (dye method)		
Extractant acid	15–30 sec.	5–10 sec.	Total (Roe)	15–30 sec.	5–10 sec.	Total (Roe)	15–30 sec.	5–10 sec.	Total (Roe)
Acetic	15.5	16.0	17.1	5.0	4.2	6.6	1.9	2.1	4.3
Oxalic	15.4	16.8	...	6.0	6.3	...	3.5	3.6	...
Metaphosphoric	15.0	16.4	16.0	5.7	...	...	3.5	3.7	4.3

Table II. Ascorbic Acid, Carotene, Niacin, Riboflavin, and Thiamine Content of Canned Fruits and Fruit Juices before Storage

	Milligrams/100 Grams				
Canned Food	Ascorbic acid	Carotene	Niacin	Riboflavin	Thiamine
Grapefruit juice					
Sample 1	45.5	...	...	...	0.043
Sample 2	40.6	...	...	...	0.040
Sample 3	35.6	...	...	...	0.040
Sample 4	36.6	...	...	...	...
Sample 5	32.2	...	...	...	...
Grapefruit segments	29.4	...	...	...	...
Orange juice					
Sample 1	38.2	...	...	...	0.095
Sample 2	38.2	...	...	...	0.092
Sample 3	49.2	...	...	...	0.070
Peaches, halved					
Freestone	2.9	0.10	4.5	...	...
Clingstone	4.9	0.24	6.5	...	0.008
Pineapple juice					
Sample 1	11.0	...	...	...	0.056
Sample 2	6.0	...	...	...	0.050
Pineapple, sliced	6.5	...	...	...	0.082
Tomato juice					
Sample 1	17.5	0.42	8.4	0.032	0.056
Sample 2	18.4	0.58	8.9	0.027	0.063
Sample 3	24.4	0.62	8.5	0.023	0.054
Tomatoes, whole					
Sample 1	17.3	0.54	8.3	0.025	0.078
Sample 2	20.1	0.62	9.2	0.026	0.069
Sample 3	24.5	0.55	8.5	0.025	0.064
Sample 4	18.3	...	...	...	0.060
Sample 5	22.4	...	...	...	0.060

In the chemical determinations, since thiamine also was to be ascertained on the samples, the double adsorption method of Conner and Straub (*4*) was used employing modifications in digestion, length of columns, internal standards, and blanks (*10*). Because of the very low riboflavin content in tomatoes, interference with adsorption seemed to be significant as the percentage variations between duplicate determinations were often over 10%, and good standard recoveries were difficult to obtain. The microbiological assays had given slightly higher (+10%) results in some comparative experiments; consequently it was decided to use this procedure for all assays after the 4-month storage determinations. For those samples on which both types of assays had not been previously carried out, values obtained with microbiological determinations on preserved blends were used as initial values. In each case these blends had been preserved from the initial sampling or that of the 4-month 50° F. storage.

The microbiological assays were carried out by the method of Snell and Strong (*24*).

Thiamine. The thiochrome technique of Hennessey (*8*) was employed with modifications which have been described (*9*).

Statistical Treatment. Analyses of variance (*23*) were calculated for the vitamin retentions where there was doubt as to the significance of the variations found with time and temperature of storage. The method suggested by Baten (*2*) for analyzing "degrees of freedom" in comparisons was used, since the "classes" did not contain the same number of items. Where the calculated *F* value showed the treatment variances to be significant, the *t* test was applied to determine the significance of the differences between the means of the various time and of the various temperature intervals. Those differences found significant at the 5% level ($P = 0.05$) are reported as significant and those at the 1% level ($P = 0.01$) as highly significant.

RESULTS AND DISCUSSION

The values for the vitamins determined in the canned foods before storage are listed in Table II. These are within the range previously reported for each food analyzed (*9, 12*). The percentage retentions of the five vitamins under the controlled-temperature experimental conditions are shown in a condensed form in Figures 1 to 6. The average results from the earlier experiment, in which retention of ascorbic acid in the two Texas grapefruit juices stored at 45°, 70°, and 98° F. was followed for a period of 18 months, are included in Figure 2. The data for the warehouse storage study are given in Table III. Comparison of the average temperatures from records made in the different warehouses showed that the highest temperature (80° F.) chosen for the controlled temperature experiment extended slightly above the highest average temperatures existing in any of the warehouses included in this study, even those in the southern states, whereas the lowest controlled temperature (50° F.) was well below any average natural condition.

Ascorbic Acid. There was an excellent retention of ascorbic acid in all canned fruit and fruit juice stored at 50° F. for 12 months and in grapefruit juice held as long as 18 months at 45° F. (Figure 2). These findings agree with those of Guerrant *et al.* (*7*) for canned tomato juice, lima beans, and whole kernel corn. The retention at 65° F. was also good. The data on the retentions of ascorbic acid in both peaches and grapefruit juice were treated statistically. The lower retentions in peaches (Figure 1) stored at 65° F. were not found to be significant, whereas the ones for the grapefruit juices (Figure 2) proved to be highly so. With the grapefruit juice any variation in means, for the different treatments, greater than 2.2 milligrams was found to be significant, and that of 3.1 milligrams highly so. The difference between the means for the 4-month 65° F. storage sample and the original assay mean was 3.5 mg. There was no further loss after 12 months of storage at this temperature. In the warehouses maintaining yearly average temperature of 65° F. or below the retentions of ascorbic acid in orange juice and tomatoes were excellent.

Table III. Comparison of Effect of Warehouse Storage and Constant Temperature Storage for 12 Months on Ascorbic Acid and Thiamine in Orange Juice and Tomatoes

	Storage Temp., ° F.		Ascorbic Acid Retentions, %		Thiamine Retentions, %	
Storage Location	Yearly av.	Yearly range	Orange juice[a]	Tomatoes[b]	Orange juice[a]	Tomatoes[b]
Const. temp. chambers, Univ. of Chicago						
No. I	80	...	76	82	89	82
No. II	65	...	92	93	98	93
No. III	50	...	97	95	100	94
New Orleans	77	50–98	73	83	96	83
Tampa	77	54–91	81	92	95	79
Tempe	72	50–92	81	100	99	89
Yuba City	70	54–104	86	105	99	88
Oakland	66	51–87	92	102	96	86
Washington, D. C.	63	42–79	91	101	103	90
St. Louis	61	36–87	91	101	95	89
Rochelle	59	28–92	90	98	99	89
New York	58	30–78	96	106	98	96

[a] Average of two lots in constant temperature storage; only one lot in warehouse storage.

[b] Average of three lots in constant temperature and of two lots in warehouse storage.

With 80° F. storage the greater losses in grapefruit juices were found to be highly significant after 4 months and those in peaches after 8 months. The average ascorbic acid loss in the several groups of foods held at 80° F. increased in general with time. At 8 months the losses ranged from 5 to 25% and at 12 months from 10 to 30%. Within this 12-month range the food groups can be ranked in the following order with regard to losses: pineapple juice, tomato juice, and tomatoes least, 10 to 20%; citrus fruit juices next, about 20 to 25%; and grapefruit segments, peaches, and sliced pineapple most, about 25 to 30%.

With every type of food analyzed, results of the 8- and 12-month storage assays showed, as is often predicted, that an increase in storage temperature results in an increased loss of vitamin C. The rate of loss was disproportionally higher at the higher temperatures. This was brought out even more clearly by the additional experiment on grapefruit juice, in which samples held at 98° F. showed retentions of ascorbic acid of 75, 54, and 31% after 4, 8, and 12 months, respectively. In the other grapefruit juice samples stored at 80° F., the retentions were 88, 79, and 75%, and at 65° F. they were 91, 91, and 90%, respectively, for the same storage intervals (Figure 2).

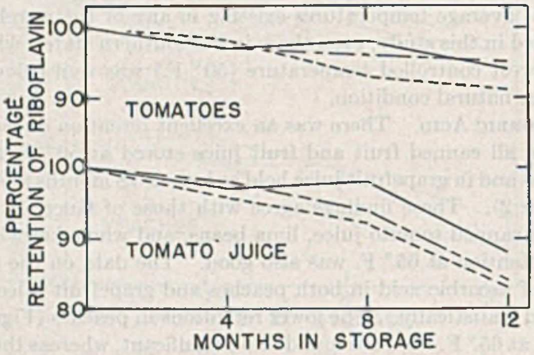

Figure 5. Effect of Storage Time on Riboflavin

——— 50° F.
— · — 65° F.
- - - - 80° F.

In the two samples of orange juice and three of grapefruit juice stored at 80° F. for 12 months the variations in retentions were slight; they ranged only from 73 to 77%, with an average retention of 75%. Ross also reported (*22*) a 75% retention of ascorbic acid in orange juice after a year's storage at approximately 75° F. In the two lots of Texas grapefruit juice stored at 70° F. (room temperature) for the same time the retention was found to be 85% (Figure 2). Orange juice held for 1 year in the three warehouses having average temperatures of the order 72–77° F. (Table III) retained its ascorbic acid to approximately the same extent, 81 to 73%.

Carotene. This provitamin seemed entirely stable in tomatoes, tomato juices, and peaches stored at 50° and 65° F. for 1 year (Figure 3). Temperature effect was decidedly less striking than with ascorbic acid, for tomatoes showed no statistically significant loss even at 80° F. However, peaches stored at 80° F. for a year retained only about 86% of their original pigment value as assayed.

Niacin. Niacin appeared to be quite stable in peaches (Figure 4) and tomato juice, as it was not adversely affected by the experimental conditions regardless of time or temperature of storage. There was practically no variation between the retentions found at the different temperature levels of each storage interval. This was also true for whole tomatoes; for these, however, an analysis of variance of the niacin retentions showed a highly significant difference with increased time of storage. Application of the *t* test showed any difference greater than 0.51 mg. from the initial mean of 8.64 mg. was highly significant. After 8 months of storage the difference between the means was 0.54 mg., and after 12 months, 0.68 mg. The average retentions, however, of all tomato and tomato juice samples for each storage period and temperature were never lower than 95%.

Riboflavin. Some tomatoes and tomato juices seemed to show a small loss in riboflavin after 8 months at 80° F., and by 12 months about half of the samples showed lowered retentions, around 80%, at all three temperatures. However, because of the difficulties discussed under methods, there is a question as to the significance of this apparent loss of riboflavin. Although all retentions were based on microbiological assays, beginning at the 8-month period, it was found that, in the long run, these gave no more consistent results (Figure 5) than did the earlier fluorometric results. The difficulties with precision in either type of riboflavin assay in tomato products no doubt resulted from the extremely low riboflavin contents.

Thiamine. There was no apparent loss in thiamine in any canned fruit or fruit juice stored at 50° and 65° F. for a period of 8 months. In 12 months, however, at both of these temperatures several products may have suffered slight losses, not exceeding 7% on the average. The statistical analysis on thiamine retention in tomatoes proved that the 6 and 7% variations at 50° and 65° F., respectively, after 12 months of storage were not significant. The highest temperature of storage definitely affected thiamine retention. In every case the samples stored at 80° F. for both the 8- and 12-month periods gave the lowest results. The 91% retention in tomatoes stored at 80° F. for 4 months (Figure 6) was not found to be a statistically significant loss, but those of 87 and 82% after 8 and 12 months, respectively, proved to indicate highly significant losses.

After a year's storage at 80° F. the thiamine retentions in related groups of products averaged 91% for citrus fruits and fruit juices, 88% for pineapple and pineapple juice, 83% for tomatoes and tomato juices, and 81% for peaches (Figure 6). There was excellent agreement between percentage retentions for individual samples of the same product.

The results from the warehouse-stored samples correlated well with these (Table III). The percentage retentions of thiamine in orange juice was practically complete, 95–100%, but that in tomatoes stored in the various warehouses for a year ranged from 79% at 77° F. (Tampa) to 96% at 58° F. (New York). These two particular foods stored in the constant temperature chambers for one year retained 89 and 82%, respectively, of their original thiamine when held at 80° F., 98 and 93% at 65°, and 100 and 94% at 50° F. Guerrant *et al.* (*7*) also found measurable losses of thiamine in canned tomato juices as a result of storage at 85° F. and no significant losses during storage at 30° and 42° F.

SUMMARY

The effect of 4, 8, and 12 months' storage at 50°, 65°, and 80° F. on the ascorbic acid, carotene, niacin, and thiamine contents of various canned fruits and fruit juices has been studied.

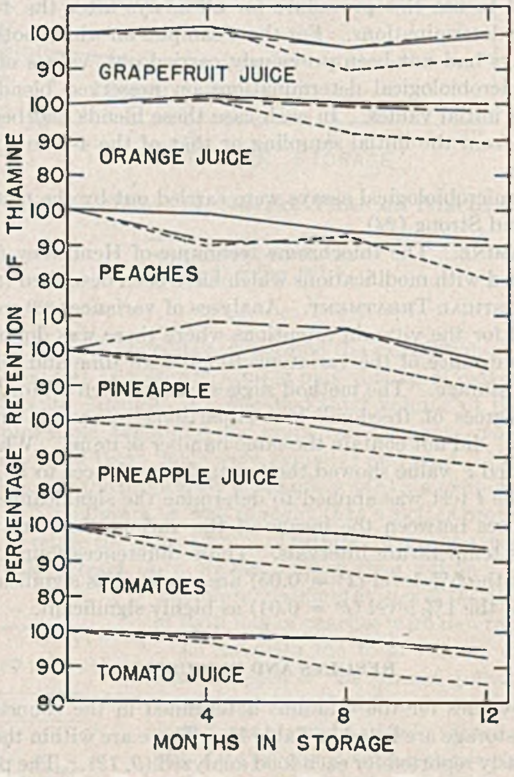

Figure 6. Effect of Storage Time on Thiamine

——— 50° F.
— · — 65° F.
- - - - 80° F.

In addition the effect of 2- to 4-week storage at the same temperatures on the ascorbic acid retention was investigated for seventeen lots of canned foods representing eight products. Comparisons were also made as to the effect of a year's storage in nine warehouses located in cities throughout the United States on the ascorbic acid and thiamine content of tomatoes and orange juice. The data indicated that the losses of ascorbic acid and thiamine in canned fruit and fruit juices depend more on temperature of storage than on length of the storage period.

The canned foods, held for 12 months under constant temperature conditions (50° F.) showed no significant losses in ascorbic acid, thiamine, or carotene. In general, storage at 65° F. also resulted in good retention of these vitamins. Niacin retention was also complete at 50° and 65° F. for peaches and tomato juice, but in tomatoes showed a significant reduction (93%) in 8 and 12 months regardless of temperature. Riboflavin retention was practically complete in tomatoes at both temperatures, but in tomato juice showed some questionable slight losses after 12 months.

When stored at 80° F. the fruit and fruit juices showed definite losses in ascorbic acid and thiamine after 8 months, which increased with 12-month storage at this temperature. The average retentions for the various vitamins for all fruits and fruit juices after a year's storage at 80° F. were: ascorbic acid 80%, thiamine 87%, carotene 94%, and niacin 98%. (Riboflavin was followed in tomatoes and tomato juices only, and the contents were so low that the 12-month retention of 87% was of questionable significance.)

The retention of ascorbic acid and thiamine in canned foods stored for 12 months in nine warehouses in different localities decreased as related to the yearly average temperature increase, except that thiamine in orange juice showed practially no loss. Furthermore the retention of each of these two vitamins in the warehouse samples of canned orange juice and canned tomatoes were of the same order as those for the same products held at closely related constant temperatures. The retentions of ascorbic acid varied from a low of 73% for orange juice and 83% for tomatoes at New Orleans (average temperature 77° F.) to a high of 96 and 106%, respectively, in New York (average temperature 58° F.). The retentions of thiamine in tomatoes varied from 79% at Tampa (average temperature 77° F.) to 96% in New York.

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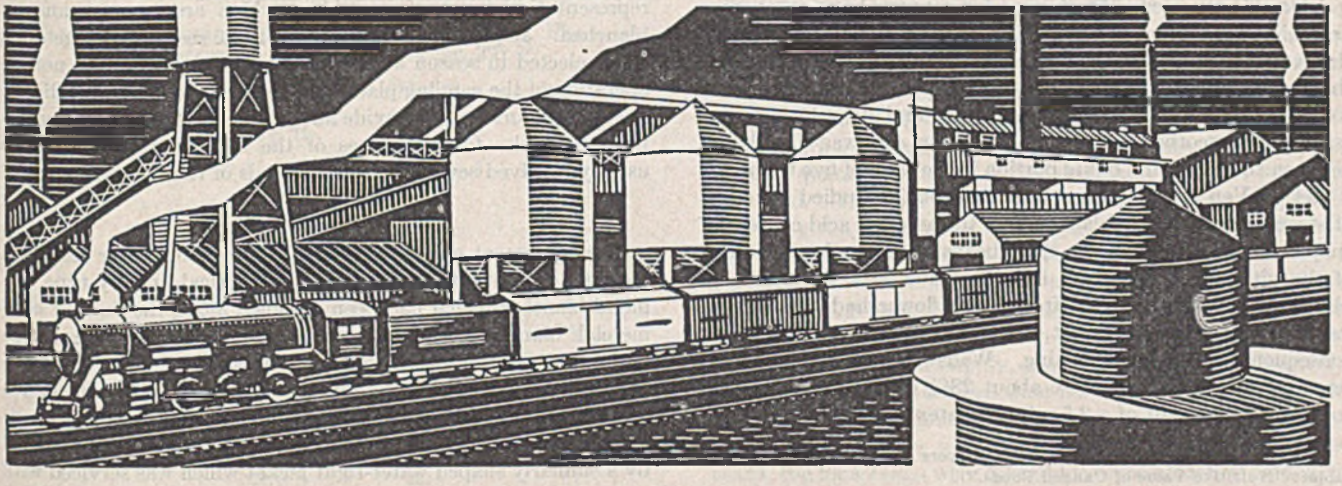
IN partial fulfillment of the requirements for the degree of doctor of philosophy by Dorothy S. Moschette



(*Nutritive Value of Canned Foods*)

EFFECT OF DURATION AND TEMPERATURE OF BLANCH ON VITAMIN RETENTION BY CERTAIN VEGETABLES[1]

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Four representative vegetables (peas, green beans, lima beans, and spinach) were investigated with respect to the amount of vitamin retained after being blanched at different temperatures for varying periods of time. Both steam and water blanching were employed. The vitamin content of each vegetable was determined before and after blanching by recognized methods of vitamin analysis. The data obtained in these studies show that vitamin retention varied with the time and temperature of the blanch, and the percentage retained depended on the vitamin under consideration. In general, high temperature blanching for short periods was found to be more conducive to high vitamin retention than was low temperature blanching for longer periods. Steam-blanched vegetables retained a greater proportion of their original vitamin content than did water-blanched ones.

THE results of a previous investigation by Guerrant, Vavich, Fardig, Dutcher, and Stern (*5*) demonstrated that commercially canned vegetables sustain appreciable loss of certain vitamins during canning and that a considerable portion of this loss was sustained during the blanching operation. Although loss of vitamins during blanching has been previously reported by other investigators, these reports do not fully reveal the adverse effect of blanching on vitamin retention, inasmuch as the investigations were limited in scope, particularly with respect to the number of products investigated and the number of vitamins concerned. Numerous reports deal with the loss of vitamins from various foods during the over-all canning operation, but only those studies which concern primarily the blanching operation will be considered in this connection.

In a report of an investigation designed to study mainly the effect of commercial canning on thiamine retention, Clifcorn and Heberlein (*3*) stated, "The retention of thiamine during commercial blanching of asparagus, green beans, lima beans, and peas (Alaska and sweet varieties) ranged from 64 to 100% and during commercial processing from 58 to 79%."

Adam (*1*) reported, "Fresh peas for canning have an average ascorbic acid content of about 30 to 35 mg. per 100 grams and the average figure for the canned peas is 9 to 10 mg. per 100 grams; the average retention is therefore about 30%. The average losses were roughly 40 to 50% during blanching and 10% during processing; the ascorbic acid remaining in the can was distributed between the solids and liquid portion in the ratio of five to three."

Retzer, Van Duyne, Chase, and Simpson (*9*) studied the effect of steam and hot-water blanching on the ascorbic acid content of snap beans and cauliflower. Snap beans were found to lose 15% of the vitamin during water blanching and 11% during steam blanching. When ready to freeze, cauliflower had lost 19% of its ascorbic acid as the result of water blanching and 18% as a consequence of steam blanching. Wadsworth and Wilcox (*13*) reported that lima beans lose about 28% of their ascorbic acid content as the result of a 2.5-minute water blanch.

Moyer and Stotz (*8*) reported negligible losses of ascorbic acid from cabbage when electronic blanching was used in contrast to losses of 30 to 40% of the vitamin when steam or water blanching was employed.

Since appreciable vitamin losses are frequently sustained during the blanching of vegetables preliminary to canning or to freezing, it seemed important that a systematic study should be made relative to the effect of time and temperature of blanching on the retention of vitamins by representative types of vegetables. The present report described such an investigation and presents some of the data obtained.

Since it was highly desirable that the studies involve both water and steam blanching and that the blanching be carried out under conditions simulating, as far as possible, actual commercial processing conditions, arrangements were made with The Birdseye Snider Corporation to conduct the blanching tests at its Mt. Morris, N. Y., plant, where the necessary experimental facilities were provided. These, together with a mobile laboratory unit and the laboratories at The Pennsylvania State College, constituted the over-all facilities used in carrying out the investigation.

Peas, green beans, lima beans, and spinach were selected as representative types of vegetables which are most commonly blanched. Representative samples of the respective vegetables were selected in season at the proper station during the normal operation of the canning plant. These samples were of sufficient size and uniformity to provide adequate quantities of the respective vegetables for all phases of the blanching studies. This usually involved several hundred pounds of the selected product.

BLANCHING EQUIPMENT

The equipment employed during the tests on water blanching consisted essentially of a small, cylindrical, rotary-type all-metal blancher which had been designed along the lines of commercial blanchers especially for experimental purposes. The perforated rotating drum was approximately 17 inches in diameter and 44 inches long. Attached to the inside of this drum was a spiral worm which served to propel the product toward the exit end of the drum as the drum rotated. This drum was surrounded by a similarly shaped water-tight jacket which was serviced with water inlet and water drain, steam inlet, thermometer insert, etc.

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[1] This is the twenty-third of a series of papers dealing with the general subject "Nutritive Value of Canned Foods."

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The amount of water in the surrounding drum could be regulated manually while the temperature of the water was controlled thermostatically. The speed of the rotating drum was regulated by means of a series of gear reducers inserted in series between the power source and the drive shaft. With this equipment the blanching temperature was controlled by the setting of the thermostat, and the blanching time by the speed of rotation of the drum. In studies with this equipment, 2.2 gallons of water were used for each kilogram of peas and green beans (1 gallon per pound) blanched and 5.1 gallons for each kilogram of lima beans (2.3 gallons per pound). A fresh supply of water was used with each experimental batch.

In the studies regarding the effects of steam blanching, a small, all-metal, belt type of steam blancher was used. The effective dimensions of the blanching belt as it passed through the steam compartment were approximately 10 × 95 inches. The vegetables were fed onto the belt at one end of the steam compartment in a unit layer and emerged in a similar condition at the opposite end, the entrance and exit of the steam compartment being closed by floating or suspended shields which served to minimize the loss of steam. In operation, the temperature of the compartment was always brought to the maximum operating temperature (210° F.) before the vegetable was fed onto the belt, and the time of blanch was regulated by the speed at which the belt moved forward. This again was controlled by gear reducers inserted between the power source and the drive shaft.

In commerical practice the rotary type of water blancher had proved unsatisfactory for use in blanching spinach because of the characteristics of the product; consequently, no attempt was made to use the described blancher in the blanching of spinach. Instead, two large steam-jacketed kettles were utilized. One kettle was used to heat and to maintain the blanching water at the desired temperature, the other kettle to hold the rinsing or the cooling water. The temperature of the blanching water was regulated manually by controlling the steam valve. For each kilogram of spinach 5.1 gallons of blanching water were used.

Effect on Holding. It was obvious that much was to be gained by using vegetables from the same source and of the same grade in the various blanching tests; however, the stability of the product during the course of the blanching studies was one of concern, since in some instances hours would elapse before all of the various conditions of blanching could be investigated. A holding room, operated at 34° to 39° F., was available; hence it was decided to study the stability of a representative unblanched vegetable when held for reasonable periods in the holding room. Furthermore, since the ascorbic acid content of unblanched peas was known to deteriorate rapidly when held at room temperature, the stability of the ascorbic acid content of several grades (quality) of peas was used as the criterion of the effectiveness of the available holding temperature over a reasonable period of storage.

Table I. Ascorbic Acid Content of Fresh Peas as Affected by Holding at 34° to 39° F.

Sample No.	Time of Holding, Hr.	Ascorbic Acid Content, Mg./100 G.	Ascorbic Acid Loss, %
Fancy Perfection, Sieve Size No. 4			
1	0.0	27.2	..
2	5.0	26.2	3.7
3	19.0	25.6	5.9
4	24.0	25.6	5.9
5	48.0	24.4	10.3
Extra Standard Perfection, Sieve Size No. 4			
1	0.0	25.4	..
2	3.0	24.8	2.4
3	4.5	24.4	4.5
4	24.0	24.0	5.5
Standard Perfection, Sieve Size No. 4			
1	0.0	25.3	..
2	4.5	23.8	5.9
3	18.0	23.3	7.9
4	22.0	22.4	11.4

The freshly vined, washed, graded, and inspected peas were cooled in a water and ice bath, drained, and stored in the holding room. Ascorbic acid determinations were made at the time the fresh peas were placed in the holding room and at intervals for the next 20 or more hours by the method previously indicated by Vavich, Stern, and Guerrant (*12*). The results obtained in these tests are given in Table I.

The ascorbic acid content of all three grades of unblanched peas remained reasonably constant during a workable period of 4 or 5 hours while stored in the holding room at 34° to 39° F. It was therefore concluded that this storage space would be satisfactory for storing batches of vegetables other than peas during the course of blanching.

BLANCHING OPERATION

Peas. Since no attempt was being made to study varietal differences and since Perfection peas were in abundance at the time of the investigation, this variety was used throughout the blanching studies. The peas were selected by the canner as having the size and the quality grade designated. The blanching operation was essentially as follows: Approximately 7 kg. of peas were taken from the holding room, dipped into cold water, drained on a screen for 2 minutes, and then weighed preparatory to blanching. The weighed peas were then fed gradually into the blancher. When all peas had emerged from the blancher they were again dipped in the same water, drained for 2 minutes on the screen, and reweighed. Samples for vitamin assays and for moisture determination were prepared immediately in a manner previously described by Feaster and Alexander (*4*). Eight No. 2 cans of the blanched peas were packed with a brine containing 12 pounds of salt and 20 pounds of sugar per 100 gallons of water, and processed for subsequent use in quality inspection. A second batch of peas was dipped and similarly drained in order to provide control samples of the unblanched product. Mineral analyses were made on samples prepared as for moisture determination.

Green Beans. Both whole and cut green beans were employed in these studies. These products were secured in quantity at the proper stations in the canning line and were stored in the holding room pending the actual blanching studies. The whole green beans graded No. 2 (size) and were of the Refugee variety; the cut beans were size No. 5 and were of the Tendergreen variety. The grade sizes designated were those of the canner.

As with peas, approximately 7-kg. portions of beans were removed from the holding room, dipped in cold water, drained on a screen for 2 minutes, and carefully weighed preparatory to blanching. The blanching operations were almost identical with those involved in the blanching of peas, the required unblanched and blanched samples being taken for the various assays and analyses.

Lima Beans. Because of the nature of the growing season, the lima bean pack was unusually light in the vicinity of Mt. Morris during the fall of 1945; hence the choice of variety, quality, and quantity of beans for experimental purposes was rather restricted. The lima beans employed in the blanching studies were all-green baby limas of a hybrid variety (Fish's Special). The beans were obtained at the plant after vining and washing. These beans were stored in the holding room pending the blanching tests. The beans were ungraded except that partially decomposed and off-colored beans were removed by hand. In consequence of the limited supply, the lima beans were blanched in considerably smaller batches than had been employed in connection with the blanching of peas and green beans. Approximately 3-kg. batches were used. As with the peas and green beans, the lima beans were first dipped into a bath of cold water, drained for 2 minutes on the screen, weighed accurately, and then put through the blanching operation. On emerging from the blancher, the beans were again dipped into the water bath, drained for 2 minutes, and reweighed. The necessary samples were taken at the proper time for vitamin assays, moisture determination, and mineral analyses.

SPINACH. Since the amount of spinach packed in the vicinity of Mt. Morris during the fall of 1945 was also limited as a result of the extremely wet season, it was not possible to obtain this product directly from the canning line in the required quality and quantity for the blanching studies which had been outlined. Therefore, through special arrangements, a suitable amount of spinach was selected in the field for these tests. After being harvested, washed, and hand-picked, the spinach was stored in the holding room pending the blanching studies. This spinach was of the Heavy-pack variety, and the product finally selected for blanching was of fair quality; however, the actual yield was low. As with the lima beans, approximately 3-kg. batches were used in the blanching tests. Here again the product to be blanched was removed from the holding room, dipped into cold water, drained on the screen for 3 minutes, weighed carefully, and then put through the blanching operation. The blanched product was immediately dipped again into cold water, drained for 3 minutes, and reweighed.

The steam blanching tests were carried out in the usual manner, and the water blanching was done in the large steam-jacketed kettle. In order to carry out the latter operation, the drained and weighed spinach was suspended on a large piece of clean cheesecloth and the cloth gathered at the corners to form a loose pouch surrounding the spinach. When the blanching water had been brought to the desired temperature, the spinach was immersed and continuously agitated, the temperature of the water being maintained practically constant by manual operation of the steam valve. The blanched spinach was removed from the blanching water and immediately immersed in cold water. The cooled spinach was allowed to drain on the screen for 3 minutes and weighed. The necessary samples were taken at the proper time from both the unblanched and blanched spinach for the various assays and analyses.

Throughout this investigation fresh portions of water were used with each batch of vegetable. In commercial practice the blanching water is not always renewed with each batch of the respective product but instead is frequently used continually, either for a prescribed time or for a definite over-all quantity of vegetable. The reason for this is apparently economic. However, there seems to be an opinion among some canners that this practice tends to conserve the nutritive value of the blanched product inasmuch as the solubility of certain nutrients is thought to be suppressed in a blanching medium already containing considerable concentration of these nutrients. It seemed important, in this connection, that a study be made of the effect on vitamin retention of blanching successive batches of the same vegetable in the same blanching water, since all of the water-blanching tests described had been conducted with the use of fresh portions of blanching water for each batch of product. Consequently the following experiments were carried out.

EFFECT ON ASCORBIC ACID RETENTION OF BLANCHING SUCCESSIVE BATCHES OF PEAS IN THE SAME WATER. Considerable data had already been obtained in studies relative to the effect of blanching conditions on vitamin retention in peas. Since this product was available in adequate quantities, peas were selected as the representative vegetable for use in these tests. Furthermore, in previous studies the ascorbic acid content of peas had been found to be markedly affected by blanching; therefore the distribution of this nutrient between the blanched product and the blanching medium was believed to constitute the basis on which a comparison could be made of the relative merits of the two blanching practices.

Five 20-kg. batches of peas (previously dipped and drained) were successively blanched in the same blanching water while using the small rotary blancher, dipped into cool water, drained for 2 minutes, and weighed. The temperature of the blanching water was maintained at 190° F., and the blanching time was 6 minutes. The ratio of blanching water to peas was initially 2.2 gallons of water for each kilogram of peas, with no allowance being made for small changes in volume during blanching or for the small volume of blanching water removed for ascorbic acid assay after each blanching.

Samples of peas were taken before and after blanching for ascorbic acid assays and for moisture determinations. A sample of the blanching water was also taken for ascorbic acid assay immediately following the blanching of each successive batch of peas.

ASSAY AND ANALYSIS

Samples for ascorbic acid determinations were stabilized with 6% solution of metaphosphoric acid and the assays completed at once by the method previously described by Vavich *et al.* (*12*).

Samples for carotene assays were stabilized by "blending" into a puree in the presence of alkaline ethyl alcohol, whereas those for thiamine, riboflavin, and niacin assays were stabilized in 0.1 *N* sulfuric acid, with chloroform and toluene as added preservatives in accordance with the recommendations of Feaster and Alexander (*4*). The latter assays were carried out in the home laboratory.

Carotene was determined by the method of Moore and Ely (*7*) petroleum ether (boiling range 35° to 60° C.) being used as the solvent and dicalcium phosphate in the chromatographic column. The carotene measurements were made at a wave length of 450 millimicrons by means of a Beckman quartz spectrophotometer which had been previously standardized against solutions of the purest available β-carotene.

The assays for thiamine and riboflavin were made in accordance with the procedure previously reported by Guerrant *et al.* (*5*), except that in carrying out the microbiological assays for riboflavin the concentrations of glucose and sodium acetate in the finally diluted medium were increased to 2.0 and 2.6%, respectively, as was indicated by Stokes and Martin (*11*).

Niacin assays were made according to the Krehl, Strong, and Elvehjem (*6*) modification of the Snell and Wright method (*10*).

Total solids, alcohol-insoluble solids, and crude fiber determinations were made on aliquots of the samples that had been preserved for moisture determination. These samples had formerly been prepared and preserved by placing equal weights of the product and distilled water in a No. 2 can, closing the can, and sterilizing the contents by heating in the retort under the usual processing conditions. Before proceeding with the analysis, the contents of several cans were pureed in a Waring Blendor to form a homogeneous puree. Analyses were made on appropriate aliquots of the pureed material.

Total solids were determined by subtracting from 100 the percentage of moisture obtained by means of a Brabender moisture tester operating at 85° C.

Since the sample of vegetable available for analysis was more highly hydrated than usual, the usual method of determining alcohol-insoluble solids was modified as follows: a 40-gram aliquot of the pureed material was transferred to a 600-ml. beaker, and 280 ml. of 86% ethanol were added. The beaker was covered with a watch glass, and its contents were brought to boil on a hot plate. After standing for 1 hour, the contents were carefully filtered by means of suction through an 11-cm. No. 5 Whatman filter paper which had been previously dried to constant weight at 100° C. Any residue remaining in the beaker was transferred to the filter paper by means of 80% ethanol. The filter paper containing the residue was returned to the drying dish and the dish placed in a hot-air oven operating at 100° C. After drying for 2 hours at this temperature, the dish and contents were cooled in a desiccator and weighed to the nearest milligram. The resultant increase in weight multiplied by the proper dilution factor yielded the percentage of alcohol-insoluble solids.

Crude fiber determinations were carried out in accordance with the A.O.A.C. method (*2*).

The data obtained in these blanching studies are presented in Tables II to V, inclusive. Since vitamin retention or losses during blanching are frequently difficult to interpret when expressed either on the fresh or the dry matter basis, because of moisture changes in the first instance and loss of solids in the latter, the majority of the vitamin retention data presented at this time were computed also on the basis of alcohol insoluble solids. In addition, the data regarding the vitamin retention in peas were computed on the basis of crude fiber.

EFFECTS OF BLANCHING

Since the effect of blanching on vitamin retention showed greater variations with respect to the different vitamins than to the different vegetables investigated, the results of the studies are discussed in relation to the effect of blanching on the respective vitamins.

Ascorbic Acid Retention. The data presented in Table II reveal that the ascorbic acid content of all four vegetables was affected adversely by both methods of blanching, regardless of temperature or time of blanching. However, the effect of steam blanching was considerably less marked in this respect than was water blanching. In general, increased blanching temperatures were found to have less effect on ascorbic acid retention than did increased blanching time. This was true throughout the investigation with peas, lima beans, and green beans at the higher blanching temperatures. When green beans (both whole and cut beans) were water-blanched at 160° F. for either 1 or 3 minutes, the loss of ascorbic acid was unexpectedly high, being greater from both types of beans during the 1-minute blanch than when the 3-minute blanch was used. At this temperature the loss of

Table II. Changes in Ascorbic Acid and Riboflavin Contents of Vegetables as Result of Blanching

Sample No.	Type of Blanch	Blanching: Temp., ° F.	Blanching: Time, min.	Ascorbic Acid Retained, Mg./100 G. of: Sample	Ascorbic Acid: Dry matter	Ascorbic Acid: Alcohol-insoluble solids	Ascorbic Acid: Crude fiber	Riboflavin Retained, Mg./100 G. of: Sample	Riboflavin: Dry matter	Riboflavin: Alcohol-insoluble solids	Riboflavin: Crude fiber
Fancy Grade Sweet Peas, No. 4 Sieve Size											
1	None	...	..	19.6	110	160	956	0.10	0.6	1.0	5.3
2	Water	180	3	14.2	81	120	625	0.09	0.5	0.8	4.0
3	Water	180	6	12.1	70	101	530	0.09	0.5	0.7	3.7
4	Water	180	9	10.0	60	85	457	0.08	0.5	0.7	3.6
5	Water	190	3	14.2	82	124	635	0.08	0.5	0.7	3.6
6	Water	190	6	11.2	67	101	496	0.08	0.5	0.7	3.1
7	Water	190	9	9.3	58	83	418	0.07	0.4	0.6	3.2
8	Water	200	3	13.1	75	119	563	0.07	0.4	0.4	3.1
9	Water	200	6	10.6	64	95	441	0.07	0.4	0.6	2.7
10	Water	200	9	8.3	53	73	371	0.05	0.3	0.5	2.4
1a	None	...	..	17.2	83	151	878	0.10	0.5	1.0	5.6
2a	Steam	210	1	15.4	83	127	635	0.10	0.5	0.8	3.9
3a	Steam	210	2	14.1	74	115	590	0.10	0.5	0.9	4.4
4a	Steam	210	3	13.2	69	107	539	0.10	0.5	0.8	4.2
Standard Grade Sweet Peas, No. 4 Sieve Size											
1	None	...	..	25.3	112	166	1100	0.09	0.4	0.6	4.1
2	Water	180	3	19.5	84	116	703	0.09	0.4	0.5	3.7
3	Water	180	6	16.6	75	101	673	0.08	0.4	0.5	3.2
4	Water	180	9	14.9	71	90	631	0.07	0.4	0.4	3.0
5	Water	180	12	12.7	61	76	517	0.07	0.3	0.4	2.7
6	Water	190	3	18.2	80	110	757	0.08	0.4	0.5	3.5
7	Water	190	6	16.6	75	99	692	0.07	0.3	0.4	3.1
8	Water	190	9	13.7	65	84	598	0.06	0.3	0.4	2.8
9	Water	190	12	11.1	53	70	473	0.07	0.3	0.4	2.8
10	Water	200	3	17.1	75	98	717	0.07	0.3	0.5	3.3
11	Water	200	6	16.5	75	99	706	0.08	0.4	0.5	3.3
12	Water	200	9	11.1	52	69	468	0.07	0.3	0.5	3.1
13	Water	200	12	9.5	46	56	355	0.07	0.3	0.4	3.0
14	Steam	210	1	20.6	87	125	852	0.10	0.4	0.6	4.1
15	Steam	210	3	19.8	83	117	822	0.09	0.4	0.6	3.9
16	Steam	210	6	18.2	75	110	698	0.10	0.4	0.6	3.8
Whole Green Beans, No. 2 Grade Size											
1	None	...	..	6.4	81	163	..	0.06	0.8	1.6	...
2	Water	160	1	2.4	32	65	..	0.06	0.8	1.7	...
3	Water	160	3	3.5	47	92	..	0.07	0.9	1.7	...
4	Water	160	5	3.2	44	84	..	0.07	0.9	1.8	...
5	Water	180	1	5.7	77	144	..	0.07	0.9	1.7	...
6	Water	180	3	4.7	62	119	..	0.07	0.9	1.8	...
7	Water	180	5	3.9	53	98	..	0.08	1.1	2.0	...
8	Water	200	1	5.9	76	144	..	0.08	1.0	1.9	...
9	Water	200	3	5.2	68	129	..	0.07	0.9	1.7	...
10	Water	200	5	4.7	63	122	..	0.07	0.9	1.7	...
11	Steam	210	1	5.9	73	148	..	0.07	0.9	1.7	...
12	Steam	210	3	5.0	64	120	..	0.07	0.9	1.6	...
13	Steam	210	5	4.8	61	112	..	0.07	0.9	1.6	...
Cut Green Beans, No. 5 Grade Size											
1	None	...	..	13.7	121	196	..	0.07	0.7	1.0	...
2	Water	160	1	7.8	75	117	..	0.07	0.7	1.0	...
3	Water	160	3	8.6	86	146	..	0.07	0.7	1.1	...
4	Water	160	5	9.4	94	146	..	0.06	0.6	0.9	...
5	Water	180	1	11.1	106	167	..	0.07	0.7	1.0	...
6	Water	180	3	9.4	100	152	..	0.06	0.7	1.0	...
7	Water	180	5	9.1	91	140	..	0.06	0.6	1.0	...
8	Water	200	1	10.9	108	164	..	0.07	0.7	1.0	...
9	Water	200	3	10.1	106	162	..	0.06	0.6	0.9	...
10	Water	200	5	8.1	88	132	..	0.06	0.6	0.9	...
11	Steam	210	1	10.7	104	165	..	0.07	0.7	1.0	...
12	Steam	210	3	11.1	108	168	..	0.08	0.8	1.2	...
13	Steam	210	5	10.7	103	160	..	0.07	0.6	0.9	...
Lima Beans											
1	None	...	..	17.7	50	63	..	0.07	0.2	0.2	...
2	Water	160	2	15.9	47	54	..	0.06	0.2	0.2	...
3	Water	160	4	12.2	36	40	..	0.06	0.2	0.2	...
4	Water	160	6	12.0	35	40	..	0.06	0.2	0.2	...
5	Water	160	8	12.0	37	40	..	0.05	0.2	0.2	...
6	Water	180	2	15.9	46	54	..	0.07	0.2	0.2	...
7	Water	180	4	14.2	41	48	..	0.05	0.2	0.2	...
8	Water	180	6	11.4	34	38	..	0.05	0.2	0.2	...
9	Water	180	8	11.6	34	38	..	0.04	0.1	0.2	...
10	Water	200	2	15.3	44	51	..	0.05	0.2	0.2	...
11	Water	200	4	12.0	35	40	..	0.05	0.2	0.2	...
12	Water	200	6	12.0	35	40	..	0.04	0.1	0.1	...
13	Water	200	8	11.9	36	40	..	0.04	0.1	0.1	...
14	Steam	210	1	18.3	53	65	..	0.06	0.2	0.2	...
15	Steam	210	3	16.1	44	56	..	0.06	0.2	0.2	...
16	Steam	210	5	17.1	47	56	..	0.06	0.2	0.2	...
Spinach											
1	None	...	..	40.5	675	1180	..	0.11	1.8	3.4	...
2	Water	170	1	35.8	430	720	..	0.13	1.7	2.8	...
3	Water	170	4	21.7	289	438	..	0.10	1.3	2.0	...
4	Water	170	7	13.9	198	291	..	0.08	1.2	1.8	...
5	Water	185	1	23.9	306	448	..	0.11	1.4	2.3	...
6	Water	185	4	14.1	189	271	..	0.07	1.0	1.4	...
7	Water	185	7	9.7	149	210	..	0.05	0.8	1.0	...
8	Water	200	1	28.9	360	568	..	0.09	1.2	1.9	...
9	Water	200	4	12.9	184	261	..	0.07	0.9	1.4	...
10	Water	200	7	6.4	96	129	..	0.03	0.6	0.7	...
11	Steam	210	0.75	38.6	491	713	..	0.13	1.7	2.4	...
12	Steam	210	1.5	41.4	515	852	..	0.13	1.7	2.8	...
13	Steam	210	3	41.0	513	891	..	0.12	1.6	2.7	...

TABLE III. CHANGES IN THIAMINE AND CAROTENE CONTENTS OF SOME VEGETABLES AS RESULT OF BLANCHING

Sample No.	Type of Blanch	Blanching		Thiamine Retained, Mg./100 G. of				Carotene Retained, Mg./100 G of			
		Temp., ° F.	Time, min.	Sample	Dry matter	Alcohol-insoluble solids	Crude fiber	Sample	Dry matter	Alcohol-insoluble solids	Crude fiber
				Fancy Grade Sweet Peas, No. 4 Sieve Size							
1	None	...	..	0.38	2.1	3.4	18	0.53	3.0	4.9	26
2	Water	180	3	0.37	2.1	3.1	16	0.56	3.2	4.8	25
3	Water	180	6	0.36	2.1	3.0	16	0.56	3.2	4.7	25
4	Water	180	9	0.34	2.1	2.9	16	0.57	3.4	4.8	26
5	Water	190	3	0.34	2.0	3.0	16	0.54	3.2	4.8	25
6	Water	190	6	0.33	2.0	3.0	15	0.56	3.3	5.0	25
7	Water	190	9	0.30	1.8	2.6	13	0.54	3.4	4.9	25
8	Water	200	3	0.32	1.9	2.1	14	0.52	3.0	4.8	23
9	Water	200	6	0.32	2.0	2.9	13	0.54	3.3	4.9	23
10	Water	200	9	0.25	1.5	2.2	11	0.53	3.4	4.7	24
1a	None	..	..	0.38	2.1	3.4	18	0.53	2.6	4.7	27
2a	Steam	210	1	0.39	2.1	3.3	17	0.54	2.9	4.5	22
3a	Steam	210	2	0.40	2.1	3.2	17	0.51	2.7	4.2	22
4a	Steam	210	3	0.37	2.0	3.0	15	0.50	2.6	4.1	20
				Standard Grade Sweet Peas, No. 4 Sieve Size							
1	None	...	..	0.37	1.7	2.5	16	0.50	2.3	3.3	22
2	Water	180	3	0.36	1.5	2.1	15	0.45	1.9	2.7	18
3	Water	180	6	0.32	1.5	2.0	13	0.46	2.1	2.6	18
4	Water	180	9	0.30	1.4	1.9	13	0.45	2.2	2.7	19
5	Water	180	12	0.27	1.3	1.6	11	0.43	2.1	2.6	18
6	Water	190	3	0.34	1.5	2.0	14	0.45	2.1	2.8	19
7	Water	190	6	0.30	1.4	1.8	13	0.47	2.1	2.9	20
8	Water	190	9	0.29	1.3	1.7	12	0.45	2.1	2.8	20
9	Water	190	12	0.26	1.3	1.7	11	0.44	2.1	2.8	19
10	Water	200	3	0.37	1.6	2.1	15	0.47	2.1	2.7	20
11	Water	200	6	0.33	1.5	2.0	14	0.47	2.1	2.8	20
12	Water	200	9	0.34	1.6	2.1	14	0.47	2.2	2.9	20
13	Water	200	12	0.30	1.5	1.8	11	0.44	2.1	2.6	16
14	Steam	210	1	0.36	1.5	2.1	15	0.44	1.9	2.7	18
15	Steam	210	3	0.38	1.5	2.1	15	0.46	1.9	2.7	19
16	Steam	210	6	0.37	1.5	2.2	14	0.46	1.9	2.8	18
				Spinach							
1	None	...	..	0.08	1.3	1.9	..	3.14	52	91	..
2	Water	170	1	0.08	1.0	1.6	..	4.10	49	82	..
3	Water	170	4	0.06	0.8	1.1	..	4.22	56	85	..
4	Water	170	7	0.04	0.6	0.9	..	4.85	69	101	..
5	Water	185	1	0.06	0.7	1.0	..	4.23	54	79	..
6	Water	185	4	0.04	0.5	0.8	..	4.72	63	91	..
7	Water	185	7	0.02	0.3	0.6	..	4.51	70	98	..
8	Water	200	1	0.05	0.7	1.0	..	4.43	55	87	..
9	Water	200	4	0.07	0.3	0.5	..	4.20	60	85	..
10	Water	200	7	0.02	0.3	0.4	..	4.62	69	92	..
11	Steam	210	0.75	0.07	0.9	1.6	..	4.36	45	81	..
12	Steam	210	1.5	0.08	1.0	1.6	..	4.21	52	87	..
13	Steam	210	3	0.08	1.0	1.7	..	4.34	54	94	..
				Lima Beans							
1	None	...	..	0.22	0.6	0.8	..	..	..	...	..
2	Water	160	2	0.18	0.5	0.6	..	..	..	...	..
3	Water	160	4	0.17	0.5	0.6	..	..	..	...	..
4	Water	160	6	0.15	0.4	0.5	..	..	..	...	..
5	Water	160	8	0.13	0.4	0.5	..	..	..	...	..
6	Water	180	2	0.16	0.5	0.6	..	..	..	...	..
7	Water	180	4	0.16	0.5	0.5	..	..	..	...	..
8	Water	180	6	0.14	0.4	0.5	..	..	..	...	..
9	Water	180	8	0.11	0.3	0.4	..	..	..	...	..
10	Water	200	2	0.16	0.5	0.5	..	..	..	...	..
11	Water	200	4	0.15	0.4	0.5	..	..	..	...	..
12	Water	200	6	0.14	0.4	0.5	..	..	..	...	..
13	Water	200	8	0.10	0.3	0.3	..	..	..	...	..
14	Steam	210	1	0.17	0.5	0.6	..	..	..	...	..
15	Steam	210	3	0.17	0.5	0.6	..	..	..	...	..
16	Steam	210	5	0.17	0.5	0.5	..	..	..	...	..

ascorbic acid from beans during the 5-minute blanch was not markedly different from that observed when the 3-minute blanch was employed. Blanching of beans at higher temperatures (180° and 200° F.), for comparable blanching periods, resulted in smaller losses of ascorbic acid than those sustained at 160° F. This apparent loss of ascorbic acid from beans during the course of being blanched at 160° F. remains unexplained at the present time.

The standard grade peas used in these studies were found to contain greater amounts of ascorbic acid than did the fancy grade peas. However, the percentages of this vitamin retained by the two grades of peas after being blanched under comparable conditions were not markedly different; this showed that, under the conditions of these studies, loss of ascorbic acid from peas did not vary appreciably with the quality of the products blanched.

Retention of ascorbic acid by water-blanched peas ranged from approximately 75% when the blanching was for 1 minute at 180° F. to approximately 40% when the blanching was for 12 minutes at 200° F. Under the most adverse conditions of steam blanching, peas were found to have retained approximately 75% of their initial ascorbic acid.

The cut green beans employed in these studies had a higher initial ascorbic acid content than did the whole green beans. However, the percentage of the vitamin remaining after water-blanching the two products under comparable conditions was found to be practically the same, with some indication of a slightly greater retention of the vitamin in the cut green beans under all conditions except where the blanching was done at 160° F. Retention of ascorbic acid by the steam-blanched beans ranged from 76 to 93%, whereas the retention by the water-blanched product ranged from 38 to 92%. The lowest ascorbic acid value was for whole green beans which had been water-blanched for 1 minute at 160° F. and the higher value was for the same type of beans blanched for 1 minute at 200° F.

Ascorbic acid retention by spinach was found to be reduced drastically by increasing the period of water blanching and to a lesser extent by increasing the temperature of the blanching water. For example, only 16% of the original ascorbic acid was retained when spinach was blanched for 7 minutes at 200° F., whereas 71% of the vitamin was retained where the blanching was carried out for 1 minute at this temperature. Comparable batches of spinach, when water blanched for 7 minutes at 170°, 185°, and 200° F. were found to have retained 34, 24, and 16%, respectively, of the vitamin. Ascorbic acid retention by spinach, following steam blanching, was found to be unusually satisfactory in all three instances.

The loss of ascorbic acid from lima beans as the result of blanching did not appear to be affected significantly by the blanching temperature, but an increase in the time of water blanching resulted in measurable losses of the vitamin. In general, ascorbic acid retention by this product was quite satisfactory, the minimum vitamin retention following water blanching being 64% and the minimum after steam blanching being 91%.

These values relating to percentage of ascorbic acid retention are based on vitamin content computed on the basis of 100 grams of unblanched or blanched material. If the vitamin retention values are computed on the basis of 100 grams of dry matter, 100 grams of alcohol-insoluble solids, or 100 grams of crude fiber, data are obtained for peas and green beans which show reasonably good agreement with the given values. With these products, vitamin retention data based on alcohol-insoluble solids or on crude fiber represent somewhat lower values than data based on either the sampled material or its dry matter. Similarly computed data for spinach and for lima beans, however, show considerably more variability. With the latter, considerably lower vitamin retentions are revealed when the calculations are based on alcohol-insoluble solids. This indicates that the proportion of ascorbic acid extracted from this product during water blanching was considerably greater than the loss in alcohol-soluble solids. In the blanching of spinach it also appears that considerably greater losses (on percentage basis) of ascorbic acid were sustained than of soluble solids. This greater loss in the vitamin resulted in a change in the ascorbic acid–dry matter–alcohol-insoluble solids ratios; this accounted for the low ascorbic acid retention revealed when the computation is based on dry matter or on alcohol-insoluble solids.

Riboflavin Retention. Table II also shows that riboflavin losses were sustained in the water blanching of peas, spinach, and lima beans, and that these losses increased more markedly as a result of increasing blanching time than of increasing the blanching temperature. Riboflavin losses from the whole green beans or from cut green beans during the course of water blanching were found to be insignificant whether computed on the basis of blanched material, dry matter, or alcohol-insoluble solids. The riboflavin losses from peas appeared to be somewhat related to losses in soluble solids, yet it appears that the losses in solids were not so extensive (on percentage basis) as were riboflavin losses. This is reflected by lower riboflavin retention values for this product when the data are expressed on the basis of alcohol-insoluble solids, crude fiber, or even dry matter. Water-blanched peas were found to retain from 40 to 90% of the original riboflavin content, the amount retained depending primarily on the duration of the blanching period and to a lesser extent on the temperature of blanching water. Under comparable blanching conditions fancy peas lost a greater percentage of this vitamin than did the standard peas. Lima beans were found to have lost a maximum of 43% of their initial riboflavin as the result of being water-blanched for 8 minutes at 200° F. Spinach, on the other hand, was observed to have lost 73% of its riboflavin content as the result of water blanching for 7 minutes at 200° F. In fact, riboflavin losses from spinach as the result of water blanching were more severe than in any other product, regardless of the basis of computation. Riboflavin retention data based on dry matter or on alcohol-insoluble solids showed that the percentage loss in this vitamin had exceeded somewhat the corresponding loss in soluble solids. Riboflavin losses resulting from steam blanching, on the other hand, were relatively insignificant.

Thiamine Retention. The effect of various conditions of blanching on thiamine retention by peas, spinach, and lima beans is illustrated by the data presented in Table III. When computed on the basis of 100 grams of blanched material, the retention of this vitamin by all three vegetables after water blanching decreased consistently with increases in both blanching time and temperature. Thiamine loss from peas ranged up to 34%, and this loss was sustained by fancy peas water-blanched at 200° F. for 9 minutes. Thiamine losses sustained by spinach during water blanching were considerably greater than those sustained by peas. Spinach was found to have lost 75% of its original thiamine content when water-blanched for 7 minutes at both 185° and 200° F. Lima beans, on the other hand, lost a maximum of 45% of the original thiamine when water-blanched for 8 minutes at 200° F. Computed on the basis of dry matter and alcohol-insoluble solids, the data regarding thiamine losses from peas and lima beans show that the relative loss of this vitamin exceeded but paralleled the loss in soluble solids. With spinach, the loss of vitamin was considerably greater than that of soluble solids; this accounted for the generally lower values where vitamin retention is computed on the basis of alcohol insoluble solids. The blanching of peas, spinach, and lima beans for varying periods by steam did not result in any significant loss of thiamine from any one of the products, regardless of the blanching period. This would seem to indicate that the loss of thiamine from these vegetables during water blanching is connected initially with the loss of soluble constituents rather than from the destruction of the vitamin by the heat treatment.

Carotene Retention. Of the five dietary factors concerned in the present investigation, carotene proved to be the least affected by the various conditions of blanching (Table III). In fact, when the vitamin retention data are expressed on the basis of blanched material or dry matter, there appears to have been actually an increase in carotene content in certain instances where water blanching was employed. This anomaly was, of course, due to the fact that extraction of soluble solids during blanching exceeded the corresponding loss of carotene through extraction from and destruction within the product. This condition is indicated even when carotene retention data are expressed in terms of alcohol-insoluble solids or crude fiber. When peas were subjected to steam blanching, there were small but measurable losses of carotene. These losses were undetectable except when the vitamin retention values are computed on the basis of alcohol-insoluble solids or crude fiber. The steam blanching of spinach was found to have no adverse effect on carotene retention.

Niacin Retention. Since lima beans are regarded as a relatively good source of niacin, studies were conducted regarding the effect of time and temperature of blanching on the retention of niacin by this vegetable. The results of these studies are presented in Table IV. These data show that niacin losses were sustained under all conditions of blanching. With water blanching, the loss in niacin increased with increase in both temperature and time, the latter effect being somewhat more marked than the former. The maximum niacin loss of 44% occurred when the lima beans were blanched for 8 minutes at 200° F. Significant but somewhat smaller losses of niacin occurred when the beans were steam-blanched than when they were water-blanched.

REPEATED USE OF WATER

When five successive batches (20 kg. each) of peas were blanched for 6 minutes in the same blanching water at 190° F. and an attempt made to account for the ascorbic acid losses, some interesting data were obtained (Table V). Ascorbic acid retention was relatively constant in the five batches of peas, with an indication that the fourth and fifth batches retained slightly higher percentages of the vitamin than did previously blanched

Table IV. Change in Niacin Content of Lima Beans as Result of Blanching

Sample No.	Type of Blanch	Blanching		Niacin Retained, Mg./100 G. of		
		Temp., ° F.	Time, min.	Sample	Dry matter	Alcohol-insoluble solids
1	None	...	.	1.9	5.3	6.7
2	Water	160	2	1.6	4.6	5.3
3	Water	160	4	1.5	4.5	5.1
4	Water	160	6	1.4	4.0	4.5
5	Water	160	8	1.4	4.4	4.8
6	Water	180	2	1.6	4.6	5.3
7	Water	180	4	1.4	4.0	4.5
8	Water	180	6	1.2	3.4	3.9
9	Water	180	8	1.2	3.5	3.9
10	Water	200	2	1.3	3.8	4.8
11	Water	200	4	1.3	3.6	4.2
12	Water	200	6	1.2	3.5	4.0
13	Water	200	8	1.0	3.1	3.4
14	Steam	210	1	1.5	4.2	5.1
15	Steam	210	3	1.3	3.6	4.5
16	Steam	210	5	1.2	3.3	4.0

TABLE V. EFFECT OF BLANCHING SUCCESSIVE BATCHES OF PEAS IN SAME WATER ON ASCORBIC ACID RETENTION

		Blanching		Ascorbic Acid				
Batch No.	Wt. of Batch, G.	Temp., ° F.	Time, min.	Retained by peas, mg./100 g.	Retained by peas, %	Accounted for in blanching water, %	Unaccounted for, %	Total amt. in blanching water, mg.
1	20,000	...	..	24.0	100.0	..	..	..
2	20,000	190	6	18.1	67.0	23.9	9.1	1145
3	20,000	190	6	16.2	67.5	16.7	15.8	1945
4	20,000	190	6	16.1	67.0	18.4	15.6	2829
5	20,000	190	6	16.7	69.6	18.9	11.5	3738
6	20,000	190	6	17.2	71.7	11.1	17.2	4269

TABLE VI. EFFECT OF TIME AND TEMPERATURE OF BLANCHING ON LOSS OF WEIGHT AND ASCORBIC ACID FROM PEAS, GRADE SIZE NO. 4, STANDARD QUALITY

		Blanching		Wt. of Batch, G.			Ascorbic Acid	
Sample No.	Type of Blanch	Temp., ° F.	Time, min.	Before blanching	After blanching	Loss in Weight, %	Retained, mg./100 g.	Loss, %
1	None	...	..	..	..	..	25.3	0.0
2	Water	180	3	7075	6415	9.3	19.5	22.9
3	Water	180	6	7272	6527	10.2	16.6	30.3
4	Water	180	9	7230	6574	9.1	14.9	37.4
5	Water	180	12	7275	6598	9.3	12.7	45.5
6	Water	190	3	7190	6550	8.9	18.2	28.1
7	Water	190	6	7222	6462	10.5	16.6	34.1
8	Water	190	9	7219	6533	10.5	13.7	42.4
9	Water	190	12	7275	6565	9.8	11.1	52.4
10	Water	200	3	7186	6414	10.7	17.1	32.4
11	Water	200	6	7212	6491	10.0	16.5	34.8
12	Water	200	9	7229	6509	10.0	11.1	53.4
13	Water	200	12	7315	6663	8.9	9.5	59.2
14	Steam	210	1	7362	6549	11.3	20.6	9.8
15	Steam	210	3	7244	6250	13.7	19.8	15.1
16	Steam	210	6	7267	6257	13.9	18.2	26.1

batches. Ascorbic acid retention ranged from 67 to 71.7%. Although the amount of ascorbic acid present in the water increased with the blanching of successive batches of peas, the percentage of the extracted vitamin present in the water showed a tendency to decrease. The data show that the destruction of the extracted ascorbic acid increased with continued use of the blanching water. The data presented in Table V further indicate that the practice of blanching successive batches of peas in the same water offers no appreciable advantage in increasing ascorbic acid retention. Hence the practice will have to be justified on the basis of other considerations.

TIME AND TEMPERATURE OF BLANCHING PEAS

Since substantial losses of water and soluble solids frequently accompany the blanching of vegetables, and since this loss in weight complicates the usual attempt to arrive at a close evaluation of the extent of vitamin losses during blanching, an attempt was made to establish some relation between weight loss and ascorbic acid loss under identical conditions of blanching. This was done by means of a compilation of typical data selected from those obtained in the previously mentioned blanching studies with peas. The results of this compilation are presented in Table VI.

There is no consistent relation between loss of weight during water blanching and ascorbic acid losses. In fact, the data show that loss of weight was relatively constant from all batches of peas, regardless of blanching time or temperature. These losses ranged from 8.9 to 10.7% for the thirteen batches of water-blanched peas. Ascorbic acid losses from the same batches ranged from 22.9 to 59.2%, the greater losses being attributable to higher blanching temperatures and longer blanching periods.

Under the conditions of these studies peas sustained a greater loss of weight in all three instances when steam-blanched than when water-blanched. However, ascorbic acid losses from steam-blanched peas were definitely less than those sustained during water blanching. Thus the data presented in Table VI show that there is no close relation between loss of weight from peas during blanching and ascorbic acid losses. However, this does not exclude the existence of such a relation in connection with the blanching of other vegetables, nor does it exclude the possibility of a definite relation existing between loss of weight and the loss of one or more of the vitamins other than ascorbic acid.

SUMMARY

Studies were made on the effect of duration and temperature of blanching on the vitamin content of certain vegetables. Four representative vegetables (peas, green beans, lima beans, and spinach) were investigated with respect to the amount of vitamin retained after being blanched at different temperatures for varying periods of time. Both water and steam blanching were employed. The vitamin content of each vegetable was determined by recognized methods of vitamin analysis before and after blanching. The data obtained in these studies led to the following general conclusions:

1. The ascorbic acid content of all four vegetables was adversely affected by both methods of blanching, irrespective of temperature or duration of blanch. However, the effect of steam blanching was considerably less marked than that of water blanching. Except where green beans were blanched at 160° F. for 1 or 3 minutes, the general consequence of increasing the blanching temperature on ascorbic acid retention was less severe than that of increasing the duration of blanch. When computed on the basis of 100 grams of sample, peas, green beans, and lima beans retained approximately 40% of their original ascorbic acid content as the result of the most severe blanching operations, whereas under comparable conditions of blanching and computation of data, spinach was found to have retained approximately 20% of its original content of this vitamin. However, under the most favorable conditions of blanching, ascorbic acid retention ranged from 72 to 93%, depending on the product.

2. Under the conditions of these studies riboflavin retention during the water blanching of peas, spinach, and lima beans was also affected more markedly by increasing the period of blanch than by increasing the temperature of blanch. Under the more severe conditions of blanching, peas, lima beans, and spinach were found to have retained only 50, 57, and 27%, respectively, of their former riboflavin content. These severe losses of vitamin were somewhat paralleled by severe losses of soluble solids. However, under the more favorable conditions of blanching, riboflavin retention ranged from 90 to 100%, the percentage retained varying with the different products. Green beans showed good retention of riboflavin after water blanching. All four vegetables lost relatively insignificant amounts of this vitamin as the result of steam blanching.

3. When computed on the basis of 100 grams of sample, peas, spinach, and lima beans were found to have retained consistently less thiamine after water blanching as the temperature and the duration of the blanch was increased. Under the most adverse conditions of water blanching employed in these studies, peas, lima beans, and spinach retained only 66, 55, and 33%, respectively, of their preblanched thaimine content, whereas under the more favorable conditions of blanching, from 82 to 97% of the vitamin was retained. Loss of vitamin was also accompanied by considerable loss of soluble solids. The loss of solids from spinach, however, did not account for the severe loss of the vitamin from this product. Relatively small losses of thiamine resulted from the steam blanching of the three vegetables.

4. Carotene retention by peas and spinach, after the various conditions of blanching as employed in these studies, was unusually good in each instance.

5. Lima beans sustained appreciable losses of niacin during all conditions of blanching. Increasing the period of blanching had a more adverse effect on niacin retention than did increasing the temperature of blanch. Only about 60% of the original niacin

content was retained when lima beans were water-blanched for 8 minutes at 200° F.

6. The practice of blanching successive batches of peas in the same blanching water was not found to be warranted on the basis of greater ascorbic acid retention.

7. Loss of ascorbic acid from peas during the course of blanching does not always parallel loss of weight (moisture and soluble solids), but the proportion of vitamin losses usually exceeds that of loss of weight.

Since these conclusions concern, for the most part, the more adverse effects of duration and temperature of blanch on vitamin retention, it is not to be construed that satisfactory vitamin retention was not observed under the more favorable conditions of blanching employed in these studies, nor that commercial canneries operating under optimal conditions do not produce canned foods having a high vitamin content.

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(*Nutritive Value of Canned Foods*)

EFFECT OF DURATION AND TEMPERATURE OF BLANCH ON PROXIMATE AND MINERAL COMPOSITION OF CERTAIN VEGETABLES[1]

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Studies were made on the effect of the duration, temperature, and type of blanching on the proximate and mineral composition of peas, green beans, lima beans, and spinach. Steam blanching caused no significant change in the composition of all but spinach, where moderate losses were noted in carbohydrates, ash, and phosphorus contents, and slight gains noted in calcium contents. For the water blanch in general the effect of time was more important than temperature. Carbohydrate losses were most serious in spinach; they reached about 30% of the total found in the unblanched sample, as compared to little over 10% for peas and lima beans, and only about 5% for green beans. Protein losses rarely exceeded 10% for the peas, lima beans, fancy green beans, and spinach, and reached only 5% for the more mature green beans. The mineral constituents were affected in about the same way, but to a greater extent than the carbohydrates; thus, for example, the severest water blanch caused a reduction of 54% in the ash content of spinach. The calcium content of green beans was not affected by the water blanch, that of lima beans slightly increased, and that of peas and spinach increased by as much as 79 and 54%, respectively. The phosphorus content of spinach was reduced by as much as 40% but rarely more than 10% for the other vegetables.

PREVIOUS investigations on the proximate and mineral composition of canned foods revealed surprisingly large variations among samples of the same commodity (*5*). In connection with similar work on vitamin content (*3*) this work was undertaken to show the effect of variations in blanching treatment on the composition of vegetables for canning.

There is little information available concerning the loss of soluble carbohydrates and proteins as a result of blanching. Magoon and Culpepper (*7*) reported a loss of about 30% of the total sugar and up to 10% of the protein in peas, and losses of over half the total sugars and 10% of the proteins from spinach. Horner (*4*) reported losses of 23% sugar and 22% proteins from peas, 8% sugar and no protein loss from beans, and 13% sugar and 18% protein loss from carrots, when each vegetable was blanched for 3 minutes at 100° C.

Adam, Horner, and Stanworth (*1*) reported sugar losses of about 20% when commodities consisting of small units, such as peas and diced or sliced vegetables, were blanched for 1 minute in water or 3 minutes in steam. The losses increased to about 35% when the duration of the water blanch was increased to 6 minutes. Large unit commodities, such as potatoes and whole beans, lost only 5 to 20% of their sugars. Protein losses rarely exceeded 20% for the small unit vegetables and 10% for the large unit vegetables.

More information is available for the mineral constituents, particularly calcium. Horner (*4*) and Lee and Whitcombe (*6*) agree that the calcium content of peas increases as a result of blanching in hard water. Horner (*4*) shows similar increases in calcium content for green beans, carrots, potatoes, and spinach, and considerable losses of magnesium, potassium, and phosphorus as a result of blanching of peas, potatoes, and especially spinach, whereas green beans and carrots retained almost all of

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[1] This is the twenty-fourth of a series of papers dealing with the general subject "Nutritive Value of Canned Foods."

Table I. Changes in Proximate and Mineral Composition of Canned Peas as a Result of Blanching, Fill-in Weight Basis

Type of Blanch	Blanching		Proximate Compn., %						Mineral Compn., Mg./100 G.	
	Temp., ° F.	Time, min.	Moisture	Protein	Fat	Fiber	Ash	Carbohydrates	Calcium	Phosphorus
Fancy Grade Sweet Peas, No. 4 Sieve Size										
None	...	..	82.19	5.04	0.36	1.86	0.56	9.99	19	63
Water	180	3	81.99	5.03	0.40	2.04	0.60	9.89	25	74
Water	180	6	82.65	4.82	0.37	2.09	0.54	9.53	30	61
Water	180	9	83.24	4.75	0.34	2.11	0.51	9.05	33	61
Water	190	3	82.22	4.94	0.40	2.11	0.56	9.77	29	65
Water	190	6	82.65	4.63	0.38	2.14	0.55	9.65	31	63
Water	190	9	84.28	4.57	0.36	1.97	0.58	8.24	32	65
Water	200	3	81.93	4.99	0.41	1.99	0.55	10.13	30	67
Water	200	6	83.04	4.76	0.38	1.92	0.56	9.34	32	65
Water	200	9	83.76	4.46	0.35	1.93	0.55	8.95	34	62
Steam	210	1	81.14	5.42	0.38	2.06	0.61	10.39	22	70
Steam	210	2	80.54	5.75	0.42	2.24	0.56	10.49	22	78
Steam	210	3	80.74	5.57	0.40	2.42	0.57	10.30	23	79
Standard Grade Sweet Peas, No. 4 Sieve Size										
None	...	..	77.10	5.96	0.46	2.34	0.71	13.45	33	107
Water	180	3	76.16	6.35	0.48	2.48	0.65	13.88	40	108
Water	180	6	77.07	6.34	0.42	2.31	0.60	13.26	42	106
Water	180	9	77.20	6.18	0.46	2.42	0.56	13.18	44	104
Water	180	12	78.82	5.88	0.50	2.42	0.51	11.87	45	117
Water	190	3	76.75	6.12	0.48	2.52	0.63	13.50	40	110
Water	190	6	77.57	6.01	0.51	2.38	0.56	12.97	43	105
Water	190	9	78.77	5.84	0.48	2.45	0.53	11.93	42	96
Water	190	12	78.80	5.64	0.50	2.53	0.56	11.97	48	98
Water	200	3	76.80	6.19	0.49	2.57	0.63	13.32	42	106
Water	200	6	77.56	5.78	0.53	2.40	0.62	13.09	46	107
Water	200	9	78.30	5.73	0.51	2.43	0.60	12.41	48	105
Water	200	12	79.25	5.33	0.50	2.50	0.54	11.88	45	99
Steam	210	1	75.62	6.24	0.56	2.57	0.83	14.15	38	119
Steam	210	3	76.20	6.19	0.51	2.54	0.82	13.74	38	119
Steam	210	6	78.38	6.29	0.50	2.36	0.82	11.75	34	112

the last three minerals. Lee and Whitcombe (*6*) report no significant change in iron content as a result of blanching in hard, carbonated, or iron-containing waters. According to Adam, Horner, and Stanworth (*1*), mineral substances in general were lost approximately at the same degree as the sugars.

SAMPLE TESTING

The preparation of the samples is described in detail by Guerrant *et al.* (*3*). The proximate and mineral constituents were determined from aliquots of the samples prepared by Guerrant *et al.* for moisture determination as follows: Equal weights of the properly blanched product and distilled water were placed in No. 2 cans, closed, and sterilized by heating in a retort under the usual processing conditions. Before proceeding with the analyses, the contents of two cans were pureed in a Waring Blendor to form a homogeneous puree. Analyses were made on appropriate aliquots of the pureed material.

Moisture, protein, fat, fiber, ash, calcium, and phosphorus were determined by methods approved by the Association of Official Agricultural Chemists (*2*). Carbohydrates other than crude fiber were determined by difference, and iron by a modification of Stugart's method (*5*).

The data are presented in Tables I to IV. Since the sample cans contained equal parts of the blanched product and distilled water, the results were multiplied by 2 and reported on the fill-in wet-weight basis, so that the composition of each product before blanching may be compared to its composition as affected by the blanching treatments. For certain purposes, such as comparisons of changes in the proportions of the proximate components, the data may be more informative when recalculated on a solids basis or on the basis of the moisture content of the raw material before blanching. Such recalculations may be readily made from the data included in the tables.

PEAS

Data on the effect of blanching on the proximate and mineral composition of peas are presented in Table I. Steam blanching reduced the moisture content by 1 to 2%. The corresponding small increases in all the components therefore indicate that there was little or no change in the proximate or mineral composition of the peas as a result of steam blanching.

Regardless of temperature, the short-water blanching period of 3 minutes caused a slight loss in moisture content. As the blanching time was increased, however, the moisture content increased with time and temperature until the 9-minute blanch at 200° F. resulted in a 1.57% increase in moisture for the fancy peas, and the 12-minute blanch at 200° F. resulted in a 2.15% increase in moisture for the standard peas. The increases in moisture content were compensated for by corresponding decreases in protein, ash, and carbohydrate contents. Almost one third of the loss in solids was accounted for by the proteins, and about two thirds by the carbohydrates. Although considerable losses were recorded for the ash content, especially of the standard peas, the total ash content of about 0.5% did not influence materially the general proximate composition.

Table II. Changes in Proximate and Mineral Composition of Green Beans as a Result of Blanching, Fill-in Weight Basis

Type of Blanch	Blanching		Proximate Compn., %						Mineral Compn., Mg./100 G.	
	Temp., ° F.	Time, min.	Moisture	Protein	Fat	Fiber	Ash	Carbohydrates	Calcium	Phosphorus
Whole Green Beans, No. 2 Sieve Size										
None	...	...	92.10	1.64	0.13	1.00	0.62	4.51	54	30
Water	160	1	92.29	1.55	0.16	0.94	0.57	4.49	52	31
Water	160	3	92.33	1.54	0.10	0.97	0.56	4.50	51	28
Water	160	5	92.46	1.48	0.10	0.93	0.55	4.48	51	29
Water	180	1	92.27	1.61	0.11	0.94	0.57	4.50	53	31
Water	180	3	92.33	1.53	0.12	0.95	0.56	4.51	50	31
Water	180	5	92.33	1.49	0.16	0.91	0.56	4.55	50	28
Water	200	1	92.26	1.61	0.16	0.88	0.57	4.52	50	30
Water	200	3	92.55	1.54	0.18	0.89	0.53	4.31	50	29
Water	200	5	92.68	1.45	0.18	0.85	0.55	4.28	51	28
Steam	210	1	92.11	1.75	0.17	0.92	0.65	4.40	52	26
Steam	210	3	92.02	1.69	0.17	0.90	0.62	4.60	53	28
Steam	210	5	91.84	1.74	0.18	0.89	0.65	4.70	54	28
Cut Green Beans, No. 5 Sieve Size										
Water	160	1	89.74	2.03	0.32	1.17	0.68	6.06	40	35
Water	160	3	90.00	1.99	0.32	1.21	0.64	5.84	40	35
Water	160	5	89.84	1.99	0.28	1.21	0.63	6.05	39	36
Water	180	1	89.58	2.04	0.26	1.24	0.69	6.19	39	35
Water	180	3	89.95	2.03	0.32	1.18	0.67	5.85	40	35
Water	180	5	90.10	1.91	0.24	1.25	0.59	5.91	44	35
Water	200	1	89.90	2.00	0.23	1.21	0.61	6.05	43	33
Water	200	3	90.56	1.78	0.22	1.21	0.55	5.68	42	32
Water	200	5	90.14	1.94	0.22	1.25	0.57	5.88	44	33
Steam	210	1	89.22	2.12	0.21	1.34	0.65	6.46	40	36
Steam	210	3	89.54	1.98	0.22	1.32	0.64	6.30	44	34
Steam	210	5	89.44	2.06	0.24	1.30	0.62	6.34	43	36

Table III. Changes in Proximate and Mineral Composition of Lima Beans as a Result of Blanching, Fill-in Weight Basis

Type of Blanch	Blanching		Proximate Compn., %						Mineral Compn., Mg./100 G.	
	Temp., ° F.	Time, min.	Moisture	Protein	Fat	Fiber	Ash	Carbohydrates	Calcium	Phosphorus
None	...	...	64.46	8.30	0.44	2.59	1.42	22.79	56	150
Water	160	2	65.86	8.19	0.42	2.52	1.30	21.71	59	141
Water	160	4	65.35	8.40	0.46	2.71	1.28	21.80	59	138
Water	160	6	67.46	7.98	0.46	2.49	1.23	20.38	58	135
Water	160	8	67.42	7.91	0.42	2.70	1.13	20.42	57	131
Water	180	2	65.38	7.53	0.44	2.49	1.28	22.88	59	138
Water	180	4	65.82	7.42	0.41	2.61	1.28	22.46	58	130
Water	180	6	66.40	7.82	0.40	2.68	1.23	21.47	57	135
Water	180	8	66.89	7.89	0.43	2.58	1.15	21.06	57	133
Water	200	2	65.74	8.30	0.44	2.62	1.29	21.61	59	144
Water	200	4	65.18	8.18	0.45	2.64	1.28	22.27	61	146
Water	200	6	67.06	8.19	0.42	2.52	1.18	20.63	60	136
Water	200	8	66.80	7.95	0.46	2.68	1.17	20.94	61	134
Steam	210	1	62.28	8.79	0.51	2.69	1.51	24.22	58	156
Steam	210	3	64.22	8.17	0.42	2.87	1.42	22.90	58	149
Steam	210	5	62.97	8.53	0.44	2.74	1.43	23.89	57	152

Table IV. Changes in Proximate and Mineral Composition of Spinach as a Result of Blanching, Fill-in Weight Basis

Type of Blanch	Blanching		Proximate Composition						Mineral Compn., Mg./100 G.	
	Temp., ° F.	Time, min.	Moisture	Protein	Fat	Fiber	Ash	Carbohydrates	Calcium	Phosphorus
None	...	...	90.85	2.81	0.56	0.96	1.74	2.98	119	70
Water	170	1	91.60	2.69	0.56	1.03	1.48	2.64	110	59
Water	170	4	92.63	2.47	0.56	1.04	1.21	2.09	137	49
Water	170	7	92.54	2.57	0.53	1.03	1.13	2.20	150	49
Water	185	1	92.37	2.63	0.51	0.86	1.31	2.32	141	50
Water	185	4	92.61	2.64	0.48	0.92	1.07	2.28	155	45
Water	185	7	93.00	2.61	0.42	0.92	0.98	2.07	144	49
Water	200	1	91.63	2.77	0.60	1.05	1.38	2.57	137	58
Water	200	4	92.61	2.66	0.52	1.10	0.92	2.19	153	42
Water	200	7	92.79	2.70	0.48	0.96	0.80	2.27	183	43
Steam	210	0.75	91.77	2.59	0.57	0.91	1.52	2.64	134	53
Steam	210	1.5	91.66	2.77	0.56	0.97	1.54	2.47	128	60
Steam	210	3	91.77	2.85	0.62	0.88	1.49	2.39	120	62

The calcium content increased rapidly with time and temperature of the water blanch, from 19 for the unblanched to 34 mg. per 100 grams for the fancy peas blanched for 9 minutes at 200° F., and from 33 for the unblanched to 48 mg. per 100 grams for the standard peas blanched for 12 minutes at 200° F. This is entirely in agreement with Lee and Whitcombe (*6*) and Horner (*4*). Phosphorus content was not materially affected by any of the blanching treatments, whereas Horner (*4*) reported considerable losses in phosphorus content of peas as a result of blanching.

The losses in total ash constituents are not due to losses in phosphorus, and certainly not in calcium, which was actually taken up from the blanching water, but to losses of other more soluble minerals, particularly potassium, which is present in large quantities (*4*).

GREEN BEANS

Data on the effect of blanching on the proximate and mineral composition of beans are presented in Table II. No appreciable change was caused by steam blanching, and the effect of water blanching was similar to that on peas but much less extensive. Thus the maximum increase in moisture was only about 0.5%, which was compensated for by approximately equal decreases in both the proteins and the carbohydrates. Moderate losses of both calcium and phosphorus were indicated for the fancy beans but not for the standard beans.

LIMA BEANS

Data on the effect of blanching on the proximate and mineral composition of lima beans are shown in Table III. As with the other vegetables, the steam blanch caused a reduction in moisture content and a compensating increase in the other components; this indicated no appreciable change in composition as a result of steam blanching. Water blanching again resulted in higher moisture contents. These increases in moisture contents continued with increased time of blanching, but the greatest increase of approximately 3.0% was obtained for the 6- and 8- minute blanches at 160° F., whereas the higher temperature blanches resulted in only approximately 2.5% increases. These increases in moisture content were compensated for largely by losses in carbohydrates, which accounted for about three fourths of the total losses; the proteins and ash constituents accounted for little more than one tenth each.

The calcium content of the water-blanched lima beans showed a maximum increase from 56 in the unblanched to 61 mg. per 100 grams in the most severe blanch; the greatest reduction in phosphorus content was from 150 in the unblanched to 131 mg. per 100 grams for the 8-minute blanch at 160° F.

SPINACH

Of all the vegetables studied, spinach is the only commodity showing increases in moisture content and losses in carbohydrates as a result of steam blanching (Table IV). Thus for the 3-minute steam blanch the carbohydrate content was reduced to 2.39% as compared to 2.98% for the unblanched sample. Moderate losses were also recorded for protein, ash, and phosphorus, and a moderate gain for calcium. Only slight losses in protein were noted for the water blanch, but considerable losses occurred in carbohydrates, the greatest being from 2.98 for the unblanched to 2.07% for the 7-minute blanch at 185° F. Losses in total ash as a result of water blanch were also significant; they showed a maximum reduction for the 7-minute blanch at 200° F. from 1.74 to 0.80, or more than a 50% loss. As with peas, the calcium content increased with increasing time and temperature of the water blanch until the 7-minute blanch at 200° F. resulted in a calcium content of 183 mg. per 100 grams compared to 119 mg. per 100 grams for the unblanched sample. The phosphorus content declined from 70 for the unblanched sample to 42 mg. per 100 grams for the most severe water blanch.

ACKNOWLEDGMENT

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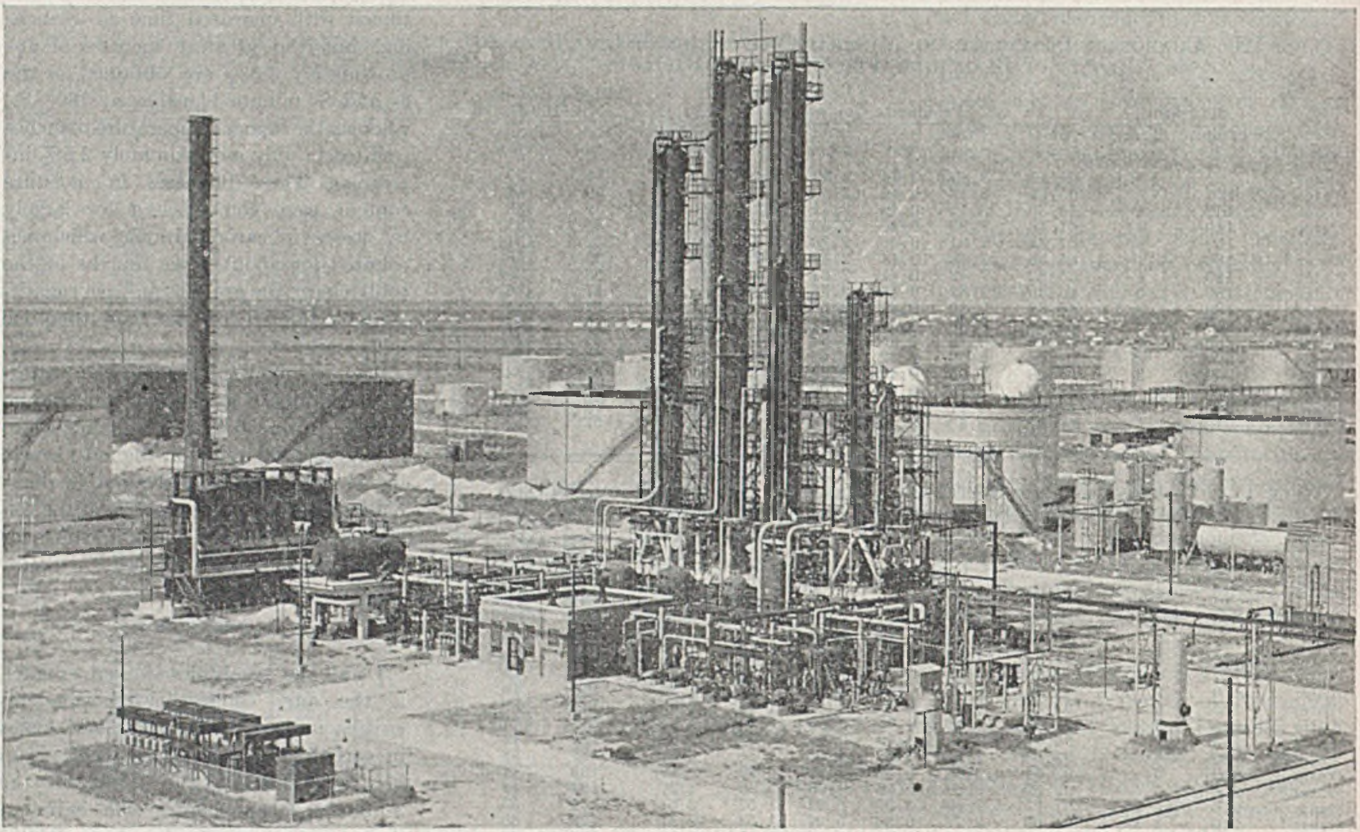

Extractive Distillation Unit for Production of Nitration-Grade Toluene

Chemical Refining of Aromatic Hydrocarbons from Petroleum

TOLUENE TREATING

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DURING the past several decades it has been common practice to subject crude or raw grades of benzene, toluene, xylene, and various solvent naphthas to sulfuric acid refining in the process of producing "pure" or refined grades of these aromatic hydrocarbons. Such treatment has been used to render the hydrocarbons suitable for nitration purposes and for certain solvent and chemical applications. In the case of aromatic hydrocarbons produced for subsequent nitration, particularly toluene for trinitrotoluene manufacture, the purpose of sulfuric acid treating has been to remove unsaturated hydrocarbons which, if not removed, might lead to the production of an unstable nitrated product or to possible hazards in the nitration operations. There are, however, practically no published data dealing with the basic considerations of toluene treating, aside from a few generalized statements (*1, 13, 15*) concerning the removal of olefins or unsaturates from toluene by acid treating. It appears that the practice has evolved in the coal tar industry, and, up to the time of World War II, toluene treating has generally been carried out in large batch agitators (*15*) in what appears to have been a rather inefficient manner, from the standpoint of acid requirements and toluene losses.

With the advent of World War II and the unprecedented demand for nitration-grade toluene, which was predominantly supplied for the first time by the petroleum industry, many problems were encountered in producing toluene meeting nitration-grade acid-wash color specifications. This was particularly true of toluene synthesized from naphthenes by high temperature dehydrogenation processes—for example, hydroforming—and toluene from high temperature cracking operations. Since practically no information was available on what types of components were responsible for poor acid-wash color, it was difficult to make changes in refining operations to correct deficiencies in this respect. Also, it was not possible to devise other toluene treating methods which would be more satisfactory than sulfuric acid treating. Consequently, investigations were undertaken to determine the types of compounds responsible for poor acid-wash color characteristics, and to devise more effective methods for treating toluene and similar aromatic hydrocarbons.

ACID-WASH COLOR

Of the many specifications for nitration-grade toluene, the acid-wash color specification has been one of the most difficult to meet so far as many petroleum refiners have been concerned. This has been a consequence of the lack of information on the causes of poor acid-wash color and the delayed nature of the problem arising from instability in storage.

The acid-wash color test (*4*, *7*, *21*), which was devised by the coal tar industry, was intended to indicate whether the content of undesirable unsaturated hydrocarbons in the toluene was sufficiently low for nitration purposes. This extremely sensitive test comprises shaking the aromatic hydrocarbon (21 ml.) and sulfuric acid (7 ml.) together for 20 seconds at 70° ± 2° F. under specified conditions. After a 15-minute standing followed by slight swirling of the bottle, the color of the sulfuric acid layer (the acid wash) is compared with a set of Barrett color standards (*21*). In the case of nitration-grade toluene, a minimum acid-wash color of 2 (light amber) was established as representing toluene of satisfactory purity from the standpoint of limiting the content of unsaturated hydrocarbons and possibly other acid-reactive components. However, this empirical test sets no exact limitation on the allowable percentage of unsaturated hydrocarbons, and very little has been known concerning the type or types of components particularly deleterious with respect to acid-wash color. Moreover, no definite specification (such as bromine number) has been set to limit the content of unsaturated hydrocarbons, other than those limitations inherently imposed by the specific gravity specification (0.871 + 0.002 at 60/60° F.) and the acid-wash color test. These limitations have been more than adequate in the case of toluene refined by treating with sulfuric acid, since practically complete olefin removal was necessary in the acid-treating step in order to meet the acid-wash color specification. However, it has been found that diolefins are chiefly responsible for acid-wash color difficulties, whereas mono-olefins have little effect. Hence, when using the improved treating procedures designed to remove diolefins in particular, as described later, it may be desirable to establish a limiting mono-olefin content to supplement the acid-wash color specification. The exact magnitude of this specification is a matter which should be evaluated in terms of the effect of mono-olefins on nitration of toluene and is beyond the scope of this paper. However, an unnecessarily rigid limitation in this regard should not be imposed, since it would place an undue burden on the refiner and limit toluene supplies in time of emergency.

Other acid-wash color specifications have been established by The Barrett Company and others for various refined grades of benzene, toluene, xylene, and high-solvency naphthas (*7*, *13*). Kenney (*13*) states in this connection that the acid-wash test is a criterion of the degree of purification that a solvent has received in its manufacture. The impurities removable by acid treating include substances which give rise to gummy bodies on aging, heating, or exposure to air. If present in large amount, the gummy bodies may cause darkening in color. The acid-wash test is, according to Kenney (*13*), of importance to the paint and varnish industry as a measure of the removal of these impurities to an extent that ensures satisfactory behavior of the solvent.

Table I. Effect of Air and Oxygen on B.O.W. Toluene Stability Test

Time on Test, Hr.	A.W.C. on B.O.W. Test		
	With air	With O_2	Heat only
0.0	0–1	0–1	0–1
0.7	...	2+	2–3
2.1	3–4	3–4	3–4
3.1	...	3–4	3–4
4.5	4	3–4	4
8.0	4–5	...	...
12.0	5	...	5
16.0	6+	...	...

The problems connected with the chemical refining of toluene from petroleum sources were studied, and the application of the information to the refining of various other aromatic hydrocarbons is indicated. Investigations with specific hydrocarbons showed that the presence of diolefins in toluene is harmful in the acid-wash color test, even at low concentrations (0.005–0.01%). Reactions with maleic anhydride confirmed these conclusions. A toluene-treating process using 0.005–0.01% maleic anhydride was shown to produce toluene of exceptional acid-wash color characteristics. Vapor-phase treating with U.O.P. phosphoric acid polymerization catalyst was demonstrated as an effective method of toluene refining. Data are presented on the variables in conventional sulfuric acid treating and on accelerated test methods to compare the efficiency of different treating conditions and to predict the acid-wash color stability of the product.

It is the belief of the authors that the causes of poor acid-wash color and stability, and the improved methods of toluene treating described in this paper, will be widely applicable to various other aromatic hydrocarbons used in the solvent field. Hence, although the present work was confined to nitration-grade toluene, its wider implication should not be overlooked.

ACID-WASH COLOR STABILITY

In addition to the initial acid-wash color of freshly produced toluene, the acid-wash color stability or storage stability of the toluene must be seriously considered in evaluating the merits of different treating processes. Many cases were encountered in the present work, for example, where freshly produced toluene of petroleum origin was found to have satisfactory initial acid-wash color, but its acid-wash color degraded rapidly to an unsatisfactory level in a matter of a few days. To predict the stability of toluene with respect to acid-wash color deterioration, studies were made of storage characteristics *vs.* two accelerated aging tests. One such accelerated test developed by the Humble Oil & Refining Company and the Baytown Ordnance Works (B.O.W.) when properly correlated for toluene from a given source, was found to enable fairly reliable prediction of the actual stability of the toluene during normal storage and shipping periods (at least 1–3 months). Another test, the Pan American rapid ultraviolet test developed in the course of this work, was found to be a valuable test for routine plant control.

The B.O.W. accelerated test developed by the Humble Oil & Refining Company (*8*) is carried out as follows: Approximately 600 ml. of the sample to be tested are placed in a flask equipped with a reflux condenser and immersed in a water bath maintained at a temperature of 195° ± 5° F. Purified air (sulfuric acid scrubber and caustic tower) is passed through a heating coil also immersed in the heating bath and thence into the sample through a tube of 4–5 mm. inside diameter at a rate such that there is rapid bubbling. Ground-glass joints are used throughout; joint lubricants should be avoided. Samples are taken initially and at 4-hour intervals thereafter for the determination of acid-wash color. The test is run for 24 hours, or until the acid-wash color reaches a value in excess of No. 6 standard. Typical data are shown in Table I. The test results are reported as the acid-wash color after 24 hours—for example, 3–4 A.W.C. after 24 hours—or the time required to reach 6+ color—for example, 6+ A.W.C. in 16 hours. It is important that the test equipment be set up where it will not be exposed to direct sunlight or bright reflected light. Every precaution must also be observed regarding cleanliness in sampling and avoidance of exposure of the samples to sunlight even for a matter of minutes, since sunlight causes extremely rapid degradation of acid-wash color. The importance of this precaution on regular acid-wash color determinations in routine plant sampling operations as well cannot be too strongly stressed.

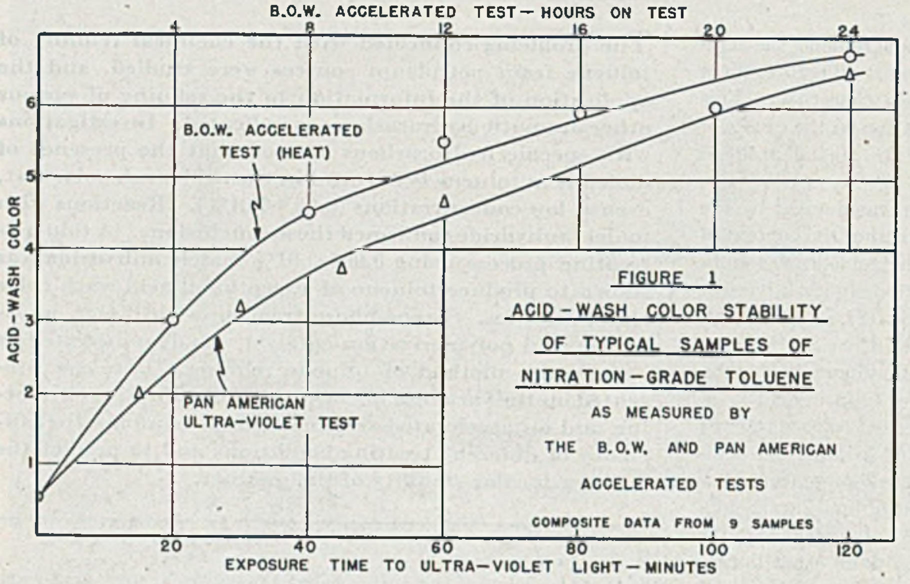


FIGURE 1
ACID-WASH COLOR STABILITY OF TYPICAL SAMPLES OF NITRATION-GRADE TOLUENE AS MEASURED BY THE B.O.W. AND PAN AMERICAN ACCELERATED TESTS
COMPOSITE DATA FROM 9 SAMPLES

The effect of bubbling air or oxygen through the sample in the B.O.W. test was found to have little effect on the results obtained, as compared with the accelerating action of heat alone. This is shown for a typical commercial nitration-grade toluene sample in Table I, with the temperature at 200° F. However, the original test procedure using air as described was followed in all work reported here.

Based on extensive experience with toluene produced by hydroforming followed by extractive distillation (phenol system) and mild sulfuric acid treating (3–5 pounds per barrel), the B.O.W. test results are interpreted qualitatively as follows: excellent and unusual stability if the toluene sample showed an acid-wash color (A.W.C.) of 1–2 after 24 hours on test; good stability for an A.W.C. of 3–6 after 24 hours; satisfactory if A.W.C. is 6 after 12–20 hours; and questionable or unsatisfactory stability if A.W.C. is 6 in less than 12 hours by this accelerated method.

A second accelerated test for acid-wash color stability evaluation—the Pan American ultraviolet test—was developed based upon the accelerating effect of ultraviolet light on acid-wash color deterioration. The advantage of the ultraviolet test over the B.O.W. procedure lies in the fact that a sample can be evaluated in 30–120 minutes as compared to 8–24 hours by the B.O.W. test. For this reason the ultraviolet method is most useful in plant control. However, the B.O.W. test is considerably more sensitive to slight differences in stability and is usually relied upon in connection with tank-car shipments. Because of this greater sensitivity, the B.O.W. method was used as the control test in all investigations reported here regarding improved treating methods and in studies of the factors influencing acid treating and poor acid-wash color.

The Pan American test is carried out in the following manner:

APPARATUS. Mineralite ultraviolet lamp (Model V41, manufactured by Ultra-Violet Products, Inc.) was obtained from the Braun Corporation as No. 361 Mineralight lamp. The equipment consisted of a 250-ml. beaker, a 50-ml. beaker, and a 25-ml. pipet.

PROCEDURE. A sample of 200 ml. at 80–90° F. is placed in a 250-ml. beaker under the center of the window area of the lamp, and the whole apparatus is covered with a cloth or housed in a closed box. The distance from the quartz tube of the lamp to the surface of the toluene is 6–7 cm. Samples (25 ml.) are withdrawn at 20- or 40-minute intervals, and the acid-wash color is determined until it has reached 6+ (usually 2 hours or less). Since the thickness of the toluene layer is gradually decreased by this procedure as the samples are removed, it would appear that the rate of deterioration might vary. It was found in practice, however, that exposing the total 200 ml. sample for 2 hours gave practically the same results as were obtained on the material remaining at the end of 2 hours when 25 ml. samples had been removed at 20-minute intervals.

ALTERNATE PROCEDURE. For plant control purposes the following method was found to be useful as a rapid check on the quality of production: Thirty milliliters of the sample in a 50-ml. beaker are placed directly under the center of the window area of the lamp. The whole apparatus is then covered with a heavy cloth. The sample is exposed for 40 or 60 minutes, and the acid-wash color determined. The results are reported as acid-wash color after 40 or 60 minutes of ultraviolet exposure.

It has been our general experience in plant control work that, if the toluene shows an acid-wash color of 3 or less after 40-minute exposure, the stability will be satisfactory. Unstable and unsatisfactory toluene will show an acid-wash color of 4–6 in 40 minutes or less by this test, although the initial acid-wash color may be completely satisfactory (0–2). A comparison of the results obtained by the B.O.W. and ultraviolet tests is shown in Figure 1. This figure should not be construed to be a general correlation chart between the two methods, since different samples were observed to show some divergence when tested by the two methods. The correlation between the ultraviolet and B.O.W. tests shown in Figure 1 holds fairly well for the first 30–40 minutes of ultraviolet exposure. Thereafter the increase in acid-wash color may be slower on some samples on the ultraviolet test than would be predicted from Figure 1.

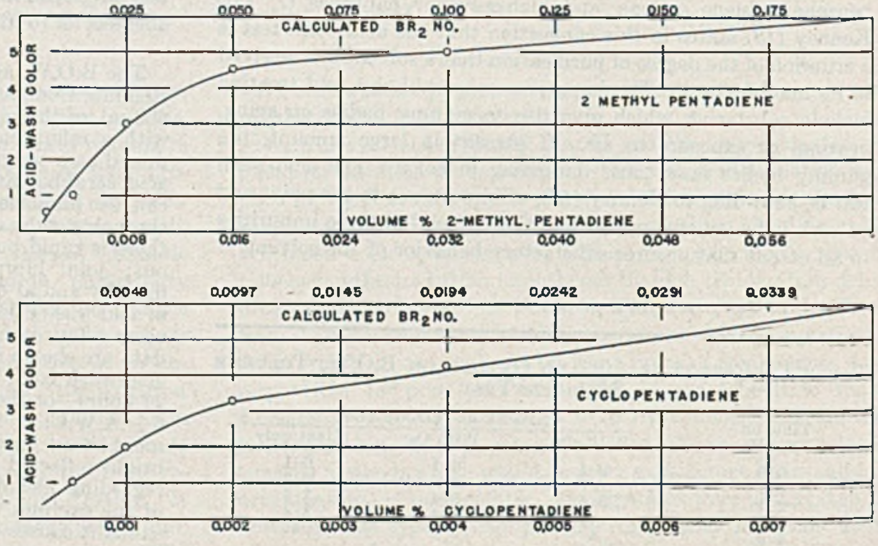


Figure 2. Effect of Diolefins on Acid-Wash Color of Toluene-Diolefin Blends Made Up in Olefin-Free Toluene

Table II. Effect of Mono- and Diolefins on Acid-Wash Color of Toluene

Concn. of Added Compound, %	A.W.C. of Toluene with: Mixed C_8 mono-olefins	2-Methylpentadiene	Cyclopentadiene
0.000	0	0	0
0.005	...	...	0–1
0.001	...	...	2
0.002	...	0–1	3+
0.003	...	1	...
0.004	...	1	4+
0.006	...	3	...
0.008	...	3	6
0.016	...	4+	...
0.032	...	5	...
0.064	...	6	...
0.167	0	...	...
0.67	1	...	...
0.79	2+	...	...
1.00	3	...	...
1.96	4+	...	...
3.85	5–6	...	...
5.66	6+	...	...

COMPONENTS RESPONSIBLE FOR UNSATISFACTORY RESULTS

The cause of unsatisfactory acid-wash color in the case of refined toluene has been attributed in a general way to unsaturated hydrocarbons, principally olefins (*15*). However, exhaustive studies by Brooks and Humphrey (*2*) on the refining of cracked distillates showed the importance of removing reactive tar- and resin-forming diolefins for the production of satisfactory motor gasoline. Similar data by numerous other investigators (*1, 6, 16, 17*) also indicated the deleterious nature of diolefins in gasoline with respect to color (not acid-wash color) and gum formation. By implication, therefore, it was suspected that diolefins might be responsible for unsatisfactory acid-wash color characteristics in the case of toluene. No reports were found in the literature, however, of attempts to determine the effect of the various classes of unsaturates on the acid-wash color of toluene, so that the more deleterious class could be singled out.

The problems of finding the causes of unsatisfactory acid-wash color of toluene was attacked from two standpoints: (*a*) an investigation to determine the type or types of compounds which would lead to poor acid-wash color and the concentration at which they would be detrimental, and (*b*) a study involving the treatment of unrefined toluene of poor (6+) acid-wash color with reagents and under conditions known to remove specifically or react with various types of diolefins.

Effect of Selected Mono- and Diolefins. In order to determine the effect of olefins and diolefins on acid-wash color and acid-wash color stability, blends of several individual olefins and diolefins were made with a highly purified sample of toluene. The components of the blends were prepared as follows:

1. Olefin- and diolefin-free toluene: Best quality nitration-grade toluene was further exhaustively treated with 98% sulfuric acid, caustic-washed, and distilled slowly from a flask containing maleic anhydride. The distillate was finally washed with aqueous caustic and water.
2. Isomeric eight-carbon branched-chain mono-olefins (codimer): A sample of codimer produced by the polymerization of mixed butenes was fractionated through a 35-plate laboratory column. The fraction boiling 225–235° F. was separated for this work and treated with 5% maleic anhydride for 2 hours at 200° F. This material possessed a bromine number of 133; this showed it to contain virtually 100% olefins.
3. Aliphatic diolefin (2-methylpentadiene): This compound, purchased from Commercial Solvents Corporation, was a mixture of the difficultly separable 2-methyl-1,3-pentadiene and 2-methyl-2,4-pentadiene. The sample was redistilled prior to use.
4. Cyclic diolefin (cyclopentadiene): This material was freshly prepared from the dimer, dicyclopentadiene (Eastman Kodak Company), by depolymerization over stainless steel turnings at 350° F. followed by fractionation.

In preparing the blends of the diolefins, stock solutions of 1% 2-methylpentadiene and cyclopentadiene, respectively, were made with the toluene (olefin- and diolefin-free) and aliquot portions made up with additional toluene to give the desired concentration. The acid-wash color and accelerated acid-wash color stability were determined on the blends as previously described.

It was soon evident that extremely small quantities of diolefins had a pronounced effect on the acid-wash color. After orientation as to the concentration range required to keep the blends within the range of the acid-wash color standards, a series of blends were prepared to show the effect of concentration of the mono- and diolefins on the acid-wash color. These data are shown in Table II and graphically in Figure 2.

Very low concentrations (0.001–0.01%) of diolefins have a serious effect on the acid-wash color of toluene, whereas C_8 mono-olefins, as represented by codimer, are relatively ineffectual even in concentrations as high as 0.7% corresponding to a bromine number of 1.1. Since diolefins are detrimental in extremely low concentrations, and since mono-olefins appear to have practically no effect on acid-wash color at the concentrations normally encountered, bromine number (or other comparable measure of olefin content) has no significance in predicting acid-wash color or color stability. Furthermore, the more reactive cyclic diolefin (cyclopentadiene) shows a pronounced effect at a considerably lower concentration (0.001–0.002%) than the aliphatic diolefin (2-methyl pentadiene). This fact will be referred to again in connection with maleic anhydride treatment of raw toluene.

In hypothetical refining of cyclopentadiene blends from a 6 acid-wash color (0.008% cyclopentadiene) to a 0+ color, a bromine number reduction of only about 0.05 unit is involved; whereas with the aliphatic diolefin the same reduction in acid-wash color would be equivalent to a reduction of 0.2 bromine number. A comparable effect was noticed in the catalytic treating of a sample of commercial toluene. For example, in this catalytic treatment of raw toluene the acid-wash color was reduced from 6+ to 1 while the bromine number reduction amounted to only about 0.05–0.1 unit. This observation is advanced as further confirmatory evidence that reactive diolefins, probably cyclic in nature, are the main cause of unsatisfactory acid-wash color.

Acid-Wash Color Stability *vs.* Mono-olefin and Diolefin Content. The authors' data on the effect of mono- and diolefins on the acid-wash color stability are not so complete as would be desired. However, a number of blends of both types of unsaturates with toluene were prepared and the stability measured by the B.O.W. accelerated test, so that the trend is quite apparent. The data are shown in Table III.

The diolefins also contribute to poor stability of the toluene, whereas mono-olefins seem to have little effect. In the latter case the acid-wash color remains very close to the initial level after accelerated aging. For comparison the data for three typi-

Table III. Effect of Mono- and Diolefins on Acid-Wash Color Stability of Toluene

Added Compound	Vol. % Added	A.W.C. of Blend	B.O.W. Accelerated A.W.C. Stability Test: 4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
None	0.00	0	0+	0+	0+	0–1	0–1	0–1
C_8 mono-olefins	0.17	0	0–1	0–1	0–1	0–1	3	...
C_8 mono-olefins	1.00	3	3–4	3–4	3–4	3–4	3–4	...
2-Methylpentadiene	0.006	2	2	2	2–3	2–3	4–5	6+
2-Methylpentadiene	0.10	6+	...	...	...	...	...	...
2-Methylpentadiene C_8 mono-olefins	0.025 0.17	3	3+	4	5–6	6+	...	...

Typical Tank Car Shipment	Bromine No.	Initial A.W.C.	A.W.C. Stability: 4 hr.	8 hr.	12 hr.	16 hr.
A	0.07	0–1	4–5	6+	...	...
B	0.10	0–1	2–3	3–4	6+	...
C	0.14	0–1	3–4	5	5–6	6

cal toluene samples from commercial production are included. These were selected to substantiate a previous statement that bromine number is no index of the acid-wash color stability of the sample. Sample A is definitely of questionable stability, although it had the lowest bromine number of the group.

In the light of these data and the fact that toluene produced by hydroforming normally contains only relatively small amounts of diolefins as compared to mono-olefins, which are normally present in concentrations of 1% or less, the most important function of acid treating appears to be the removal of small quantities of diolefins (0.1% or less). It is evident, therefore, that intimate and thorough contacting of sulfuric acid and toluene are necessary for the successful and efficient application of acid treating, especially if small amounts of treating acid (that is, 3 pounds per barrel of toluene) are used.

EFFECT OF MALEIC ANHYDRIDE TREATMENT

From the data just presented on the effects of mono- and diolefins on the acid-wash color of toluene, it appears that conjugated diolefins can be mainly responsible for poor acid-wash color and unsatisfactory acid-wash color stability. Since maleic anhydride is fairly specific for the removal of conjugated diolefins (*3*, *5*), treatment with maleic anhydride should result in a product of improved acid-wash color and improved stability, if conjugated diolefins are present in the toluene and if they are the compounds mainly responsible for bad acid-wash color. Furthermore, the type of diolefin (cyclic or aliphatic) influences the rate and temperature at which reaction with maleic anhydride occurs (*1*, *3*). For this reason a study of the effect of time and temperature in the treatment of raw toluene should give additional information useful in explaining the causes and peculiarities of poor acid-wash color.

Maleic Anhydride Treatment of Raw Toluene and Toluene of Poor Acid-Wash Color Stability. A sample of plant acid-treated toluene of poor stability was treated with 0.28 weight % of maleic anhydride for 2 hours at 200° F. Unreacted maleic anhydride and reaction products were removed by washing with 15% potassium hydroxide, and the treated toluene was distilled. A control sample was given identical treatment except that no maleic anhydride was used. Table IV shows the surprisingly good stability of the toluene treated with maleic anhydride as compared with the poor stability of the control sample.

Table IV. Maleic Anhydride Treatment of Toluene at 200° F. for 2 Hours

Sample Treated	Maleic Anhydride Used, %	B.O.W. Accelerated A.W.C. Stability Test						
		Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
Acid-treated toluene	None	0+	3–4	6+	...	...	...	...
Same, M.A.-treated	0.28	0+	0+	0+	0+	0+	0+	1
Raw toluene	None	6+	...	...	...	...	...	...
Same, M.A.-treated	0.20	2	2	3–4	4–5	5–6	...	...
Same, M.A.-treated	1.0	1	1–2	1–2	1–2	2+	2+	3+
Typical tank car shipment of satisfactory toluene	None	0–1	2–3	4–5	5–6	6+	...	...

In view of the effectiveness of maleic anhydride treatment in stabilizing acid-treated toluene, some work on the treatment of raw toluene (not previously acid-treated) seemed in order. Samples of raw toluene of 6+ acid-wash color were treated in one case with 1% and in another example with 0.2% of maleic anhydride for 2 hours at 200° F. Caustic washing followed; no distillation step was used. Other data in Table IV show that treatment with maleic anhydride alone produced a color-stable toluene without sulfuric acid treatment; this is convincing evidence that conjugated diolefins are responsible for the unsatisfactory acid-wash color and color instability of incompletely refined toluene.

The evidence of the presence of a reactive conjugated diolefin in raw toluene was just presented. If this type of diolefin is present, maleic anhydride treatment at room temperature (80–90° F.) rather than at 200° F. should be effective in reducing the acid-wash color and stabilizing the toluene. This proved to be the case. For example, raw toluene of 6+ A.W.C. was treated with 1% maleic anhydride for 20 minutes at 80° F. The treated toluene was caustic-washed and filtered; acid-wash color and color stability were then determined. The acid-wash color after treatment was 2–3, and a 3+ A.W.C. was obtained after 24 hours on the B.O.W. accelerated stability test. Removal of the reactive diolefins is seen to improve the initial acid-wash color from 6+ to 2–3. Of even greater interest is the fact that the unsaturates, some of which are probably relatively unreactive diolefins, remaining after this maleic anhydride treatment do not contribute appreciably to poor acid-wash color stability. It seems then that if the most reactive diolefins are removed from the raw toluene, even though the acid-wash color is not reduced to 0–1, the toluene is extremely stable against further deterioration. This fact is confirmed in the work on treatment of raw toluene with phosphoric acid polymerization catalyst described later.

Restoration of Acid-Wash Color of Finished Toluene Deteriorated to 6+ A.W.C. The mechanism of the reaction which accounts for the deterioration of acid-wash color is obscure. The nature of the degradation products formed by this reaction are also unknown. To clarify this situation at least partially, a sample of refined toluene (initial A.W.C. = 0+) was deteriorated to 6+ A.W.C. by means of the B.O.W. accelerated test by heating at 200° F for 16 hours. The resultant toluene sample, now of 6+ A.W.C., was given the following successive maleic anhydride treatments:

Maleic Anhydride, %	Time of Reaction, Hr.	Temp., ° F.	A.W.C. after Treatment Shown
None	...	...	6+
1	0.4	200	4+
3	2.0	200	3+
3	5.0	200	3

It would appear that the degradation products causing the deterioration in acid-wash color are not entirely compounds reactive with maleic anhydride, since even the comparatively drastic succession of maleic anhydride treatments described did not reduce that color to the original value (0+). Moreover, the compounds present in unrefined toluene which are responsible for the high A.W.C. are not the same as the compounds present in refined toluene which has deteriorated in acid-wash color; the former can be practically completely removed with maleic anhydride treatment, whereas the latter cannot. This suggests that A.W.C. deterioration is caused, at least in part, by the polymerization of conjugated diolefins to higher polymers of nonconjugated structure.

Effect of Treatment Time with Maleic Anhydride. It was shown in the preceding discussion that the acid-wash color of unrefined toluene could be reduced from 6+ to 1 by means of treatment solely with 1% maleic anhydride. The stability of the toluene so treated was found to be much superior to that of toluene generally produced by commercial acid treating.

The effect of time of maleic anhydride treatment on the reduction in acid-wash color of raw toluene (6+ initial A.W.C.) was studied next. A sample of raw toluene was heated to 200° F. at which time 1% by weight of maleic anhydride was added and vigorously agitated; 25-ml. samples were withdrawn at regular time intervals and immediately shaken with 15% potassium hydroxide to quench the reaction. The toluene layer was separated and filtered to remove suspended water; after that the acid-wash color was determined. The treated toluene was not distilled, since distillation was shown to be unnecessary with maleic anhydride treatment. The data, shown in the following table, were obtained for raw toluene (bromine number 0.31) treated with 1% by weight of maleic anhydride at 200° F.:

Time of Treating, Min.	Acid-Wash Color	Time of Treating, Min.	Acid-Wash Color
0	6+	7	2
1	3+	10	2
2	3+	20	2
3	3	120	1
5	3		

The initial rate of removal of the undesirable diolefins is rapid since the acid-wash color decreased from 6+ to 3+ during 1 minute of treatment, whereas 20 minutes were required for a further decrease to 2 A.W.C. and 100 additional minutes for 1 A.W.C. From the rate of reaction observed, there is evidence of the presence of two or more types of conjugated diolefins—that is, a very reactive diolefin, probably cyclic, which reacts with maleic anhydride almost instantaneously, and a less reactive type which reacts only very slowly. Similar conclusions were reached by Birch and Scott (*1*) in studies concerned with the identification of the diolefins in the low-boiling fractions of vapor phase cracked gasoline. It is also of possible interest that Kramer and Spilker (*14*) isolated the reactive cyclopentadiene from coke-oven benzene.

STABILIZATION OF ACID-TREATED TOLUENE WITH MALEIC ANHYDRIDE

Experience has shown the toluene, which has been refined by sulfuric acid treatment and which meets all specifications for nitration grade toluene, frequently deteriorates on storage to a point where the A.W.C. is greater than the specification limit of 2. When this occurs, it invariably entails reprocessing of the toluene together with any other contaminated production. Since preliminary experiments showed the remarkable stabilizing effect of maleic anhydride treatment against acid-wash color deterioration, and since only small quantities (0.01% or less) of maleic anhydride were required, it appeared that this method of treating could be advantageously employed on a commercial scale. Accordingly, further development of this procedure was carried out particularly with reference to optimum maleic anhydride concentration, temperature, and time of treatment.

Data from the maleic anhydride treatment of four toluene samples of widely divergent character previously refined by sulfuric acid treatment are collected in Table V. The A.W.C. stability data for samples A and B indicate that maleic anhydride treatment effectively stabilizes freshly produced toluene against A.W.C. deterioration; moreover, the quantities of maleic anhydride required are extremely small, of the order of 0.005–0.01%.

Samples C and D, representing finished toluene which had deteriorated in storage to high A.W.C. (5 and 6+), exemplify the ability of maleic anhydride partially to reduce the initial A.W.C. and to stabilize the A.W.C. at the reduced value. Generally speaking, a reduction in A.W.C. of 1–1.5 units can be expected when toluene of 2–5 A.W.C. is treated with 0.01% maleic anhydride. The important point, however, is that the acid-wash color is stabilized at this reduced level.

Table V. Stabilization of H_2SO_4–Treated Toluene by Maleic Anhydride Treatment at 89° F.[a]

Sample Designation	Treatment: Maleic anhydride, %	Treatment: Time, min.	A.W.C. after Treatment	B.O.W. Accelerated A.W.C. Stability Test: 4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
A	0	0	0–1	2–3	3+	5+	5–6	6	6+
	0.01	5	0–1	0–1	0–1	0–1	0–1	0–1	0–1
B	0	0	0–1	4	4–5	4–5	4–5	4–5	5
	0.01	0.5	0–1	1	1–2	...	2	...	3–4
	0.01	1.0	0–1	1	1–2	...	2	...	2–3
	0.01	2.5	0–1	1	1–2	...	1–2	2	2–3
	0.005	2.5	0–1	1+	1–2	2	2	2	3+
C	0	0	5	6+	...	...	...	...	...
	0.01	30	3–4	3–4	3–4	3–4	3–4	4–5	4–5
D	0	0	6+[b]	...	...	...	...	...	...
	0.01	30	6+	...	...	...	...	...	...
	0.1	30	6+	...	...	...	...	...	...
	1.0	30	4–5	5+	5–6	5–6	5	5	5+

[a] Samples A and B were taken at different times from plant production; samples C and D were toluene samples which had deteriorated in plant storage. All four samples had been refined originally by conventional sulfuric acid treating and met all nitration-grade toluene specifications.

[b] Estimated to be 7–8 A.W.C.

Maleic anhydride is not an inhibitor in the sense of a gasoline inhibitor which is added permanently to the gasoline. The mechanics of maleic anhydride treating comprise dissolving maleic anhydride in the toluene for a short period and then removing the unreacted maleic anhydride and adduct (reaction product) by caustic washing. The maleic anhydride thereby reacts with the undesirable reactive diolefins which are responsible for A.W.C. difficulties forming a stable acidic reaction product which is removed from the toluene by caustic washing.

A patent issued to I. G. Farbenindustrie (*9*) claims the use of maleic anhydride for purification of crude benzene from coke ovens or gas plants. The treatment as described recommends adding 0.3–10% (preferably 1–3%) of maleic anhydride to crude benzene, refluxing for 2 hours, and distilling off the purified benzene. In the case of the stabilization of acid-treated toluene as described in this report, only trace amounts (0.005–.01%) of maleic anhydride and short reaction times at 90–100° F. are required, whereas the 1–3% figures are economically unattractive. This work is further described in a patent recently issued to one of the authors (*20*).

CATALYTIC TREATING OF TOLUENE

The previous section established quite definitely that diolefins are the main cause of acid-wash color problems associated with nitration-grade toluene production; consequently, certain catalysts known to effect the polymerization of diolefins should be effective for the treatment of toluene. A few preliminary experiments showed that unrefined toluene can be treated with either Attapulgus clay or solid phosphoric acid polymerization catalyst (*7, 12*) to give an improvement in the acid-wash color. Both liquid-phase and vapor-phase treating were tried with results shown in Table VI.

Table VI. Preliminary Experiments in One-Hour Catalytic Treating of Raw Toluene of Bromine No. 0.31

Catalyst	Wt. % Catalyst	Method of Treating	Temp., ° F.	A.W.C.	Catalyst Life Reached, Bbl./Ton
....	..	No treatment	...	6+	...
Attapulgus clay	16.4	Liquid phase	230	5–6	40
	16.4	Liquid phase	450	4–5	40
	..	Vapor phase	230	6+	15
Phosphoric acid polymerization catalyst[a]	3.3	Liquid phase	230	4	200
	3.3	Liquid phase	450	3	200
	..	Vapor phase	230	1+	50

[a] Catalyst used had reached maximum economical life in commercial propylene-butylene polymerization.

The liquid-phase treatments at 230° F. were conducted by refluxing the toluene with the catalyst at atmospheric pressure. The experiments at 450° F. were conducted in a steel bomb of the rocking type. The vapor-phase studies were made at atmospheric pressure in a glass reactor. In all cases the treated product was redistilled to remove polymers before determining acid-wash color. The preliminary results indicated that the vapor-phase treating of raw toluene with U.O.P. solid phosphoric acid polymerization catalyst (*10*) was most promising. This method of treating is similar to that described by Ipatieff and Corson (*12*) for the vapor-phase refining of cracked gasoline to improve color (Saybolt) and reduce gum-forming tendencies.

Partial Life Test on U.O.P. Polmerization Catalyst. The catalyst used in this continous partial life study was standard U.O.P. solid phosphoric acid catalyst composed of

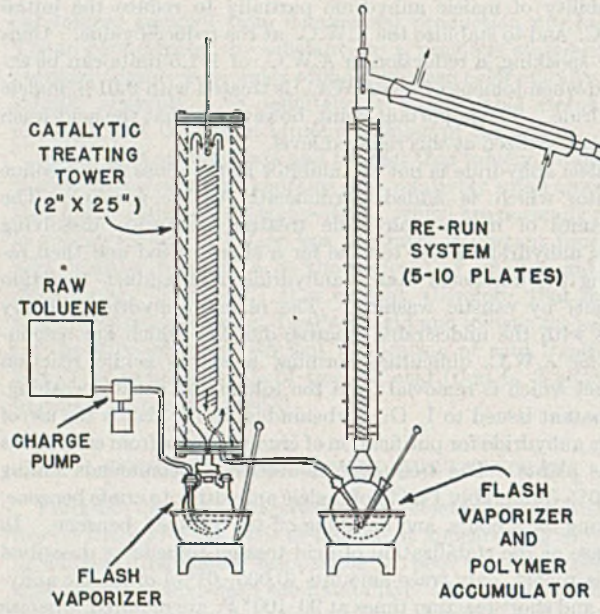


Figure 3. Catalytic Treating Equipment

phosphoric acid on kieselguhr (*5*, *12*). The catalyst had previously been used in the Pan American commercial polymerization unit on the polymerization of propylene and butylenes (*11*) until the catalyst was considered economically unsuitable for further use. This spent catalyst was employed, since there was a large supply available for potential toluene treating purposes; hence catalyst costs would be negligible if commercial application were undertaken.

The treating studies were conducted in a continuous manner up to a catalyst life of 1130 barrels of toluene per ton of catalyst (178 pounds per pound). The apparatus is shown in Figure 3, which is self-explanatory. The polymer produced in the treating operation accumulated in the rerun-tower pot. The results from this work are summarized in Table VII. These data show that the initial A.W.C. and the A.W.C. stability measured by the B.O.W. and ultraviolet accelerated procedures were good throughout the test. This is an alternative toluene treating procedure which appears quite attractive.

Treatment with U.O.P. polymerization catalyst lowers the bromine number only slightly (0.31 to 0.22), whereas normal plant and laboratory acid treatments (5 pounds of 98% sulfuric acid per barrel) usually reduce the bromine number to 0.05–0.1; yet both methods of treating give a product of satisfactory acid-wash color. The explanation for this surprising difference has been outlined in the previous sections where it was shown that mono-olefins have little or no effect on acid-wash color, whereas diolefins cause serious color difficulties. Apparently this vapor-phase treating method removes predominantly only the more reactive and undesirable diolefins.

SULFURIC ACID TREATING OF TOLUENE

Comprehensive studies were carried out on the refining of toluene with sulfuric acid. The crude toluene used was produced commercially by hydroforming (catalytic dehydrogenation) of petroleum naphthas rich in methylcyclohexane followed by extractive distillation using phenol as solvent. Space limitations make it impossible to present all the data obtained; however, some of the more pertinent data are presented in the following sections.

No data were found in the literature dealing with the variables in sulfuric acid treating of toluene. There are, however, several excellent references (*2*, *6*, *16*, *17*, *19*) on the acid treating of cracked gasolines and the like, since acid refining dates back to the nineteenth century (*18*).

The preceding work showed that the problem of toluene treating to give a product of good A.W.C. and A.W.C. stability actually resolves itself into the removal of very small quantities (0.1% or less) of diolefins. The mono-olefins which are present to a greater extent, although less detrimental, will also be removed simultaneously with the diolefins. It is evident, therefore, that intimate contacting of the sulfuric acid and toluene is necessary for successful application of acid treating. Moreover, because of the interrelation of the many treating variables, a thorough knowledge is required of the effect of contact time, temperature, and quantity and concentration of acid on treating efficiency.

Comparison of Treating Efficiency of 98, 93, and 87% Sulfuric Acid. There is no doubt that 98% sulfuric acid is the most effective of these three acids; however, the higher the acid concentration, the greater the acidity of the acid-treated toluene; hence the problem of caustic washing becomes more difficult. In addition, the losses of toluene through sulfonation are much larger in treatment with 98% acid. For these reasons a comparative study of the efficiency of 98, 93, and 87% sulfuric acid was made. Figure 4 shows the reductions in unsaturate content (as measured by the bromine number) attainable by the acid treating of raw toluene using various amounts of 98, 93, and 87% sulfuric acid. In the work reported, the quantity of acid employed is expressed as pounds of 98% acid (or equivalent) per barrel (42 gallons or 305 pounds) of toluene. For orientation purposes, therefore, a 3 pound per barrel treat is virtually equivalent to treating with 1 weight % of sulfuric acid. It is noteworthy that 14.5 and 4.5 pounds of H_2SO_4 per barrel of toluene were required when used in 87 and 93% concentration to give the same reduction in unsaturate content as a 3 pound per barrel treatment with acid of 98% concentration (Figure 4). For this reason the use of 87% acid is not to be recommended in commercial treating operations. Further comparisons based on acid-wash color stablity data of the treated and redistilled toluene are as follows.

Samples of raw toluene (bromine number 0.67) were treated in glass bottles (approximately two thirds full) for 15 minutes in a Schaerr mechanical shaking machine, in a series of treatments with various quantities of 98, 93, and 87% sulfuric acid. Intimate contacting was obtained in this mechanical shaker, which oscillated horizontally at approximately 425 strokes per minute. After 30 minutes of settling time, samples were taken for determination of acidity; after caustic washing, another set of samples was taken for bromine number determinations. This method was also used in the work which follows.

Time of Contact *vs.* Acid Requirements. A comparison of 98 and 93% sulfuric acid and spent alkylation acid was also made in which the A.W.C. stability of the treated toluene was used as a criterion of the relative treating efficiencies. Data were obtained simultaneously concerning the effect of time of contact on A.W.C. stability when these three acids were used. Mixing of acid and toluene was achieved in a mechanical shaker as discussed previously. This comparative study (Table VIII) showed that, when treating with fresh 98% sulfuric acid, 1–2 minutes of laboratory contacting resulted in a finished toluene of

Table VII. Treating of Raw Toluene with Spent U.O.P. Polymerization Catalyst

(Charge, raw toluene, bromine No. 0.31, 6+ A.W.C.: temperature, 230° F.; pressure, atmospheric; rate, 5.7 barrels per ton per hour or 0.7 volume per volume per hour)

Catalyst Age, Bbl./Ton	A.W.C. of Rerun Overhead		
	As produced	After 40-min. ultraviolet test	After 24-hr. B.O.W. test
23	0–1	1+	1–2
68	1	2	1
433	1+	2+	...
684	1–2	3+	3–4
913	1+	2–3	...
981	2	2–3	...
1028	1–2	3	...

excellent A.W.C. stability, whereas, with 93% acid and particularly with discarded alkylation unit acid, substantially longer contact times (5–20 minutes) were required to yield toluene of similar stability.

Table IX shows that the average effective contact time in the continuous-type commercial acid treating plant of this corporation (orifice mixers and time drum) is equivalent to about 0.5–1.0 minute of laboratory treating. Therefore, spent alkylation acid and 93% sulfuric acid are not to be recommended for use in many commercial toluene treating plants of similar design: In order to produce toluene of good stability by treatment with these less concentrated acids, laboratory contact times of 5–10 minutes were necessary. These longer contact times, based on equivalence to laboratory mixing, are probably not obtainable in most continuous commercial units. With batch treating methods, where long contact periods would be available, any of the acids mentioned would be satisfactory and in many cases more economical.

The laboratory contact times referred to here represent actual minutes of intimate and persistent dispersal of acid in toluene. Accordingly, residence time in a plant acid mixer of inefficient design should not be confused or construed to be equivalent to these laboratory contact times. Rather, the A.W.C. stability data on toluene samples representative of plant operations should be compared with the corresponding A.W.C. in Tables VIII and IX or similar tabulations; the equivalent laboratory contact time can then be obtained as the value corresponding to the point of matching of laboratory and plant A.W.C. stability data obtained by the B.O.W. accelerated test. This comparison is helpful in correlating plant and laboratory studies, and provides a means of checking the efficacy of changes in mixer design or other variables.

The quantity of acid (pounds per barrel) required for treating toluene to a definite A.W.C. stability varies with the available acid contact time, and, conversely, the minimum contact time can be lowered by increasing the quantity of acid used. This relation was studied for common ratios of acid to toluene (3, 5, and 10 pounds of 98% acid per barrel) over a fairly wide range of contact times (Table IX). These data show that the A.W.C. stability of the treated toluene at constant contact time can be markedly improved by increasing the quantity of acid from 3 to 5 to 10 pounds per barrel. The disadvantage to this expedient of using larger quantities of acid to counteract poor mixing lies in the fact that toluene losses through sulfonation are increased, and obviously acid and possibly caustic costs are greater.

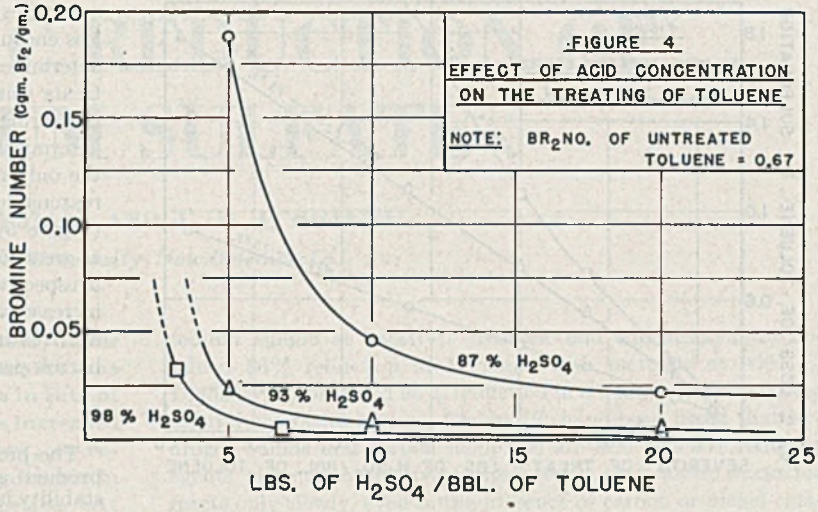


FIGURE 4
EFFECT OF ACID CONCENTRATION ON THE TREATING OF TOLUENE

Table VIII. Time of Contact *vs.* Acid-Wash Color Stability, and Comparison of 93 and 98% H_2SO_4 with Spent Alkylation Acid in Acid Treating of Toluene

(Raw toluene treated, bromine No. 0.30; temperature of treating, 90° F.; settling time, 30 minutes; further treatment, toluene phase caustic-washed and redistilled)

Time of Contact[a], Min.	B.O.W. Accelerated A.W.C. Stability Test on Treated Toluene						
	Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
	5 Lb. Spent Alkylation Acid/Barrel Toluene[a]						
3	1	1	3–4	5+	6+	...	...
7	0–1	0–1	1–2	1–2	3–4	4–5	4–5
10	1	1	1–2	2–3	3	3+	3+
20	0–1	0–1	0–1	0–1	0–1	0–1	0–1
	5 Lb. Fresh 93% H_2SO_4/Barrel Toluene						
0.5	2–3	4–5	6+	...	...	...	...
1	2	1–2	2	5	6+	...	...
2	1–2	1–2	3–4	3–4	4	5–6	...
5	0–1	0+	0–1	0–1	1–2	1–2	1–2
15	0+	0+	0+	0+	0+	1	0–1
	5 Lb. Fresh 98% H_2SO_4/Barrel Toluene						
0.5	0–1	3–4	5–6	6+	...	...	...
1.0	1	2	3–4	5	5–6	6	6+
2.0	0–1	0–1	0–1	0+	0–1	1	1–2
5.0	0+	0+	0–1	1	1	1+	1–2
15.0	0+	0+	0+	0+	0–1	0–1	0–1

[a] Treatment in mechanical shaker.

In connection with this work on the effect of contact time in acid treating, data were also accumulated showing the increase in the acidity of acid-treated toluene and decrease in bromine number as a function of contact time (Table X). These data, particularly in graphical form, show that the acidity developed in toluene treating increases rapidly during the first 5 minutes of contacting, and thereafter the rate of change is slight; this shows that the sulfonating ability of the acid has been expended. Therefore since toluene of good A.W.C. stability can be produced by acid treating for an equivalent (to laboratory) contact time of 1–2 minutes, as shown in the preceding section, it would not be desirable to use longer contact times, because not only would greater toluene losses ensue through sulfonation, but a heavier load would be thrown on the caustic treating system.

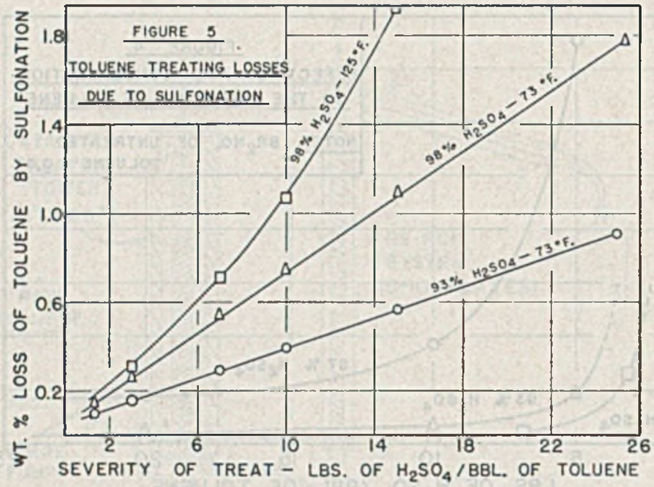
Treating Temperature. The effect of increasing the temperature of treating from 90° to 130° F. was studied at acid contact times ranging from 0.5 to 2.0 minutes; the data are presented in Table XI.

Table IX. Time of Contact and Quantity of 98% H_2SO_4 *vs.* Acid-Wash Color Stability in Acid Treating of Toluene

(Raw toluene treated, bromine No. 0.30; settling time, 30 minutes; further treating, toluene phase caustic-washed and redistilled)

Time of Contact[a], Min.	B.O.W. Accelerated A.W.C. Stability Test after Heating Time of						
	Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	14 hr.
	3 Lb. 98% H_2SO_4/Barrel Toluene at 90° F.						
2	1	3–4	5–6	5–6	6+	...	...
3.5	0–1	1	2	3–4	4	4	4–5
5	0–1	0–1	1	2–3	3–4	3–4	4+
8	0+	0–1	0–1	0–1	1	1	1
12	0+	1	0–1	1	1	2–3	2–3
	5 Lb. 98% H_2SO_4/Barrel Toluene at 90° F.						
0.5	0–1	3–4	5–6	6+	...	...	...
1	1	2	3–4	5	5–6	6	6+
2	0–1	0–1	0–1	0+	0–1	1	1–2
5	0+	0+	0–1	1	1	1+	1–2
15	0+	0+	0+	0+	0–1	0–1	0–1
	10 Lb. 98% H_2SO_4/Barrel Toluene at 90° F.						
0.25	1–2	3–4	6+	...	...	...	...
0.50	0+	0+	1–2	1–2	1–2	3–4	4–5
	Typical Plant Acid Treating, 3 Lb. 98% H_2SO_4/Barrel Toluene at 90–95° F.						
Unknown[a]	0–1	3–4	5	6+	...	...	...
	Typical Plant Acid Treating, 5 Lb. 98% H_2SO_4/Barrel Toluene at 120° F.						
Unknown[a]	0–1		3–4	4–5	5–6	6+	...
	0–1	1–2	3–4	4–5	5	5–6	6+

[a] Comparison of the B.O.W. stability of the product with the data from laboratory treats indicates the contact time in the plant to be equivalent to 0.5–1.0 minute of controlled laboratory treating.



The enhanced A.W.C. stability resulting from acid treating at the higher temperature (130° F.) is evident. The disadvantages to this method of increasing treating efficiency are increased equipment corrosion and substantially greater toluene losses due to increased sulfonation at the higher temperature. These objections are not too serious, however, especially if the use of high temperatures constitutes the difference between toluene production of satisfactory A.W.C. stability and unstable production.

Toluene Losses in Acid Treating System. Losses of toluene in the acid treating system occur in three ways: (*a*) Toluene is sulfonated by the sulfuric acid and converted to toluene sulfonic acids, part of which dissolve in the acid sludge, and the remainder, dissolved in the toluene phase, are removed in the caustic washing step; (*b*) toluene is alkylated by the unsaturates present in raw toluene, the resulting alkylated toluenes being removed as bottoms in the final rerun tower; and (*c*) toluene is lost by entrainment in the acid sludge and with the spent caustic. With adequate settling time, the latter loss should be small.

The loss of toluene through sulfonation, which comprises the major part of the total loss, was accurately evaluated by laboratory work on olefin-free toluene during treatment with various quantities of 98% acid at both 73° and 125° F.; the sulfonation loss encountered in treatment with 93% acid at 73° F. was also determined. These loss data were deduced from laboratory treats using accurately weighed quantities of acid and toluene, measuring weights and volumes of the two phases after treating, determining the acidity of the hydrocarbon phase, and assuming the only reaction involved was sulfonation of toluene; this is a reasonable premise under the conditions employed. These data (Figure 5) indicate that sulfonation losses are practically twice as great for treatment with 98% as for treatment with 93% acid, irrespective of the quantity of acid used. Losses are also seen to increase with an increase in treating temperature. Under average treating conditions (3–7 pounds acid per barrel), a loss of 5 barrels per 1000 barrels treated can be expected.

Table X. Effect of Contact Time on Acidity and Bromine Number in Sulfuric Acid Treating of Toluene at 80° F.

Time of Acid Contacting, Min.	Treatment with 3 Lb. 98% H_2SO_4/Bbl. Acidity[a]	Bromine No.[b]	Treatment with 10 Lb. 98% H_2SO_4/Bbl. Acidity[a]	Bromine No.[b]
Charge	0.0	0.33	0.0	0.50
1	0.32	0.26	0.18	0.08
2	0.33	0.26	0.20	0.07
3	0.35	0.13	..	..
4	0.37	0.11	..	..
5	0.37	0.06	0.48	0.02
10	0.37	0.01	0.53	0.02
20	0.37	0.01	0.63	..
30	..	..	0.73	0.01

[a] Acidity expressed as weight per cent toluene sulfonic acid.

[b] Bromine number expressed as centigrams of bromine absorbed per gram of sample (modified Francis method).

Table XI. Effect of Temperature of Acid Treating on A.W.C. Stability

(Raw toluene treated, bromine No. 0.30; quantity of acid; 5 pounds of 98% H_2SO_4 per barrel of toluene)

Contact Time, Min.	Temp. of Treating, ° F.	A.W.C.[a] After Heating Time of Initial	4 hr.	8 hr.	12 hr.	16 hr.	20 hr.	24 hr.
0.5	90	0–1	3–4	5–6	6+	...	...	...
0.5	130	0–1	1	4+	5+	6+	...	...
1.0	90	1	2	3–4	5	5–6	6	6+
1.0	130	0–1	0–1	0–1	0–1	0–1	1	1
2.0	90	0–1	0–1	0–1	0+	0–1	1	1–2

[a] B.O.W. accelerated stability test.

CONCLUSION

The problem of refining toluene from petroleum sources to a product of satisfactory acid-wash color and acid-wash color stability is shown to be intimately connected with the presence of certain reactive olefins. Investigations with pure hydrocarbons showed that diolefins are harmful in the acid-wash color test even at very low concentrations (0.005–0.01%). Most mono-olefins have little effect on acid-wash color. Reactions with maleic anhydride confirmed these conclusions, and it is shown possible to refine toluene recovered from hydroformed naphthas with maleic anhydride.

Vapor-phase treating with U.O.P. phosphoric acid catalyst is shown to be an effective method of toluene treating. Data are also presented on the variables in conventional sulfuric acid treating.

ACKNOWLEDGMENT

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This paper summarizes experimental work carried out at the Pan American Refining Corporation during World War II in connection with the refining of nitration-grade toluene produced by hydroforming petroleum naphthas. The data have been previously supplied to the United States Army Ordnance Department and the Toluene Technical Committee in the form of reports. The present paper consolidates and summarizes the more pertinent points of general interest and of possible wider application in the field of chemical refining of aromatic hydrocarbons.

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CATALYTIC REDUCTION OF SODIUM SULFATE

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The reduction of sodium sulfate by various gases under different conditions and with a variety of catalysts was investigated. Increase in temperature, increase in rate of flow of reducing gas, and the presence of catalysts increased the rate of reduction. At 550–600° C., and below, no reduction occurred; at 600° C., reduction with hydrogen in the presence of an iron catalyst was quite effective. At 650° C. and above, the catalytic effect of copper was equivalent to iron. A eutectic at 665° C. for the sodium sulfide–sodium sulfate system was found at 43 weight % sodium sulfide. The maximum operating temperature, therefore, should not be above 650° C. because of the formation of this undesirable liquid phase. It was found that the reduction product was mainly sodium sulfide, and only occasional small amounts of sodium sulfite and sodium thiosulfate were formed.

THE common method of preparing sodium sulfide from sodium sulfate involves reduction with carbon at temperatures of 750–1000° C. according to the equation $Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$. White and White (*10*) modified this method by the addition of calcium oxide to the mixture of sodium sulfate and carbon which, at temperatures below 750° C., removes the carbon dioxide as it is formed. Budnikov (*1*) reported that the rate of reduction was affected by the source of the carbon used.

Sodium sulfate has also been reduced to sodium sulfide in relatively poor yields by reducing gases such as hydrogen, methane, and hydrogen sulfide. The reaction $Na_2SO_4 + 4H_2 \rightarrow Na_2S + 4H_2O$ has been investigated at temperatures ranging from 500° to 900° C. without catalysts and in the presence of such catalysts as iron, nickel, sodium sulfide, and sodium hydroxide, with conflicting results. White and White (*10*) reported 18.5% reduction with hydrogen at 650° C. in 18 hours. Budnikov (*2*) reported a 44% reduction in 45 minutes at 800° C. using pure sodium sulfate; under the same conditions using a nickel catalyst, he obtained 81% reduction in 45 minutes. Ley and Teichmann (*7*) reported 40–60% reduction at 700° C. in 6 hours with hydrogen, using 10% sodium sulfide as catalyst. Nikrick and Kazanskaya (*8*) obtained 86% reduction in 18 hours with methane at 900° C. Dionisiev (*4*) obtained 95% reduction in 3 hours at 850° C., using natural combustible gas. Claims (*9*) have been made that hydrogen sulfide and carbon monoxide are also effective reducing agents, although other investigators report that carbon monoxide reacts only slowly, even in the presence of carbon or nickel catalysts.

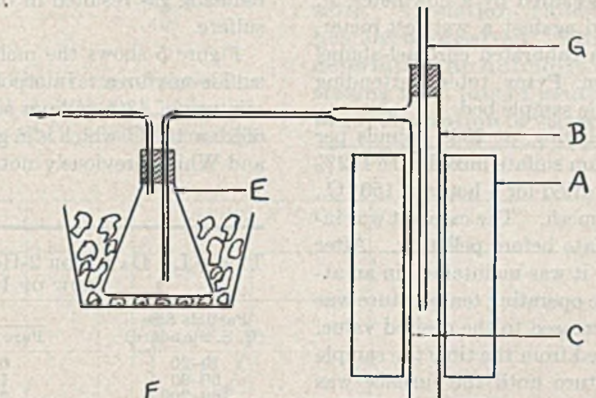

Figure 1. Diagram of Heating Units and Tube Arrangement

The disadvantages of the carbon reduction are: (*a*) It is a batch process; (*b*) the carbon must be completely oxidized or the product is badly colored and must be recrystallized; and (*c*) at the reaction temperature liquefaction occurs. Reducing gases have the advantage of offering the possibility of a fluid flow process as well as avoiding recrystallization of the product. There is also the possibility of employing lower temperatures and thus avoiding the formation of a liquid phase.

This study was undertaken to determine the most efficient reducing gas, the effect of time, temperature, particle size, and rate of flow of gas on the conversion, and the effect of various catalysts on the rate of reaction.

Several low melting eutectics of sodium sulfide–sodium sulfate have been reported, none of which are in close agreement. White and White (*10*) found two mixtures melting between 684° and 700° C., one of 34.6% sulfide and 65.4% sulfate and the other of 42.5% sulfide and 57.5% sulfate. These authors list the 30% sulfide–70% sulfate and the 50% sulfide–50% sulfate mixtures as melting above 700° C. Ley (*6*) reports a eutectic at 620° C. containing 20% sulfide and 80% sulfate; Courtois (*3*) found a eutectic of the equimolecular mixture at 730° C.

APPARATUS

The heating units consisted of two 1.25-inch-diameter tube furnaces, *A*, arranged vertically as shown in Figure 1. Tube *B* in which the reaction was carried out was either quartz or Pyrex of 1-inch diameter and contained a disk, *C*, to hold the sample. It was found possible to seal a porcelain filter disk of suitable size in the glass tube, but with quartz it was necessary to rest the disk on a constriction in the tube. With the tube in place the charge was in the center of the upper furnace. An 8–10 inch layer of 6–8 mesh aluminum oxide, *D*, was in the portion of the tube heated by the lower furnace acting as a preheater.

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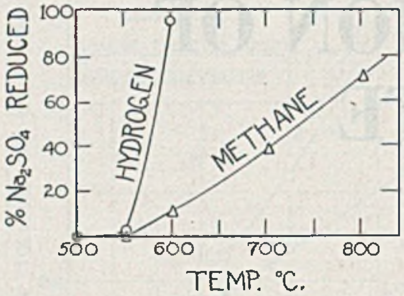

Figure 2. Effect of Variation in Temperature in 4-Hour Runs with 1.4 Liters of Gas per Minute and 1.5% Iron Catalyst

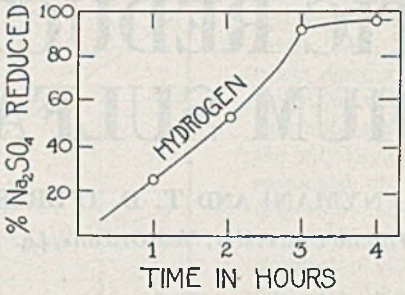

Figure 3. Effect of Time Variation in Runs with 1.4 Liters of Hydrogen per Minute at 600° C. and 1.5% Iron Catalyst

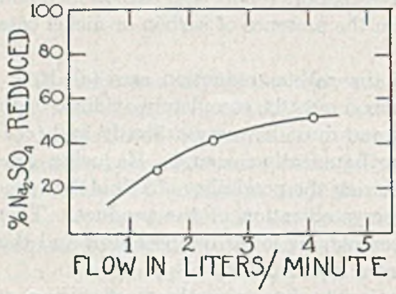

Figure 4. Effect of Flow Rate in One-Hour Runs with Hydrogen at 600° C. and 1.5% Iron Catalyst

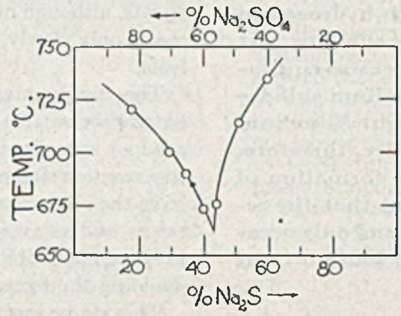

Figure 5. Melting Points for Mixtures of Sodium Sulfate and Sulfide

The gas was passed into the bottom of the tube, up through the preheater and reactor, and then out through the side arm at the top of the tube into a trap, *E*, which removed the water formed in the reaction. The exit gas was then vented to the atmosphere.

The rate of flow of the gas was measured by a flowmeter, *F*, which had been previously calibrated against a wet test meter. The temperature was measured by a calibrated chromel-alumel thermocouple in a well, *G*, of 8-mm. Pyrex tubing extending from the top of the tube down into the sample bed.

The samples were prepared by pelleting, at 2000 pounds per square inch pressure, anhydrous sodium sulfate mixed with 1-2% water as a binder. The pellets were dried for 4 hours at 150° C., crushed, and screened to the desired mesh. The catalyst was intimately mixed with the sodium sulfate before pelleting. After the sample was placed in the reactor, it was maintained in an atmosphere of the reducing gas until the operating temperature was reached. The flow rate was then increased to the desired value. The duration of each run was measured from the time the sample first reached the operating temperature until the furnace was turned off. The rate of flow was again decreased to such a value as to maintain a nonoxidizing atmosphere until the product cooled to room temperature.

All products were analyzed for sulfide, sulfite, and thiosulfate by the differential titration method of Kurtenacker and Goldbach (*5*), and the unreduced sulfate was obtained by difference. This procedure was checked against known samples and found to be accurate to ±0.6%.

REDUCTION RESULTS

All reactions were carried out with 40-gram samples of 10-20 mesh sodium sulfate unless otherwise noted (Figures 2 to 5). Figure 2 shows that the threshold value of the temperature of reduction with hydrogen is between 550° and 600° C. At 650° the rate of reduction was increased, but local hot spots caused some fusion of the sample, which made it difficult to remove from the reactor. Methane also gave no reduction at temperatures below 550° C., and at 600° only 12% reduction was obtained. However, the amount of reduction increased with increasing temperature. Temperatures above 800° could not be used because of complete fusion of the sample.

Figure 3 shows that the rate of reduction under a given set of conditions is nearly a linear function of time, up to about 90% conversion; after that it levels off and approaches quantitative conversion very slowly.

Pure sodium sulfate in sizes ranging from 10 to 200 mesh was not materially reduced by hydrogen at 600° C. in the absence of a catalyst (Table I). Of the several catalysts, iron (added either as the sulfate or the oxide) proved to be the most effective. Concentrations above 1.5% were not investigated as a result of the undesirable color imparted to the reduction product. A decrease in particle size also increased the amount of conversion. It was not practical to use salt of less than 200 mesh in the apparatus because fluid flow was obtained and all the salt was swept from the reactor. The fluid flow reduction warrants further investigation. Table II summarizes the data with various gases and catalysts.

With a few exceptions the reduction product was only sodium sulfide. Several scattered runs produced 1-2% sodium sulfite, and only those runs in which hydrogen sulfide was used as the reducing gas resulted in the formation of small amounts of thiosulfate.

Figure 5 shows the melting points for sodium sulfate-sodium sulfide mixtures. Interpolation of the curve indicates a eutectic mixture of 43% sodium sulfide-57% sodium sulfate melting at 665° ± 10° C. which is in good agreement with the result of White and White previously noted.

Table I. Data for 2-Hour Runs at 600° C. with Hydrogen Flow of 1.4 Liters per Minute

Particle Size (U. S. Standard)	Weight % Na_2SO_4 Reduced: Pure salt	0.4% Fe	1.5% Fe
10-20	0	26	54
60-80	1	32	73
.160-200	2	58	80

Table II. Summary of Data

Temp., ° C.	Catalyst	Weight %	% Na_2SO_4 Reduced: H_2, 1.4[a]	CH_4, 1[a]	NH_3, 1[a]	H_2S, 0.6[a]
600	Fe	0.4	26	1	2	10
	Fe	1.5	54	..	..	..
	$CuSO_4$	1.0	11	1	0	..
	Cu chromite	1.0	12	2	3	..
	CuO	1.0	12	..	..	..
	NiS	1.0	12	..	..	..
	PtO_2	1.0	1	..	..	..
650[b]	Fe	0.4	46	6	12	21
	$CuSO_4$	1.0	46	10	7	13
	Cu chromite	1.0	16	5	11	
	NiS	1.0	2	0	0	15
	PtO_2	1.0	3	..	..	..

[a] Liters per minute for 2 hours.
[b] Sulfur vapor at 650° C. gave no appreciable reduction.

CONCLUSIONS

For temperatures up to 700° C. hydrogen was the most efficient of the reducing gases investigated. Above 800° C., however, methane was quite reactive, perhaps as a result of some thermal cracking of the gas at these temperatures.

Iron proved the most effective catalyst in all reductions, although with hydrogen at 650° C. 1% copper sulfate gave the same conversions as 0.4% iron.

ACKNOWLEDGMENT

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Hygroscopicity of Penicillin Salts

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DURING development work on the production of crystalline sodium penicillin, the crystalline salts were found to be more stable to heat and much less hygroscopic than the amorphous salts (*2*). This study was undertaken to determine the humidity conditions necessary for minimum absorption of water when bulk lots of crystalline penicillin salts were processed.

The several approximate relative humidities were maintained in desiccators containing saturated aqueous solutions of various salts in contact with an excess of the solid phase. The humidity-temperature relations follow:

Solid Phase	I.C.T. Data (*3*) *t*, ° C.	I.C.T. Data (*3*) Humidity, %	Humidity at 27–28° C. (Estd.), %
$Ca(NO_3)_2.4H_2O$	24.5	51%	48
$NaBr.2H_2O$	20	58	58
$NH_4Cl + KNO_3$	25	71.2	70
$(NH_4)_2SO_4$	25 & 30	81.1	81
H_2O (liquid)	...	...	100

The estimated relative humidities at the average temperature range of the experiments were obtained as follows: Calcium nitrate was extrapolated from the 18.5–24.5° C. points, assuming a straight-line function for the interval 18.5° to 28° C. The humidity for sodium bromide dihydrate is given at only one temperature, 20° C., but similar salts do not show an appreciable change in relative humidity with change in temperature within the range 20° to 30° C. The ammonium chloride–potassium nitrate value was interpolated between the 25° and 30° C. values given in International Critical Tables (*3*). The ammonium sulfate system does not vary between 25° and 30° C.

The hygroscopicity has been determined for amorphous sodium and calcium penicillins and for crystalline sodium, potassium, and ammonium penicillins. The crystalline sodium salts are less hygroscopic than the amorphous salts. A relation, called the "critical humidity point," has been observed. This relation makes it possible to determine the humidity control necessary for handling or storing bulk lots of penicillin in order to secure the minimum absorption of water.

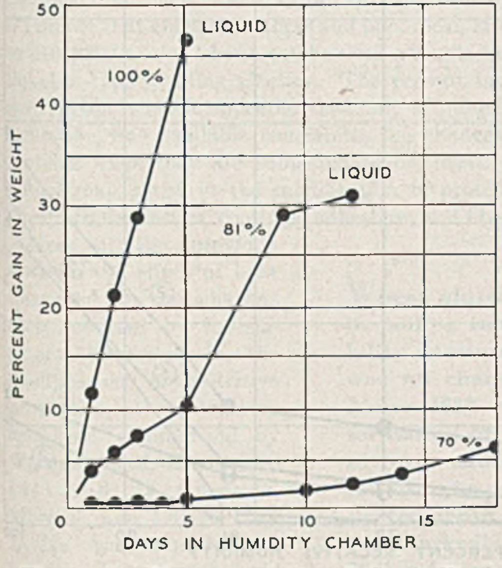

Figure 1. Hygroscopicity of Crystalline Sodium Penicillin

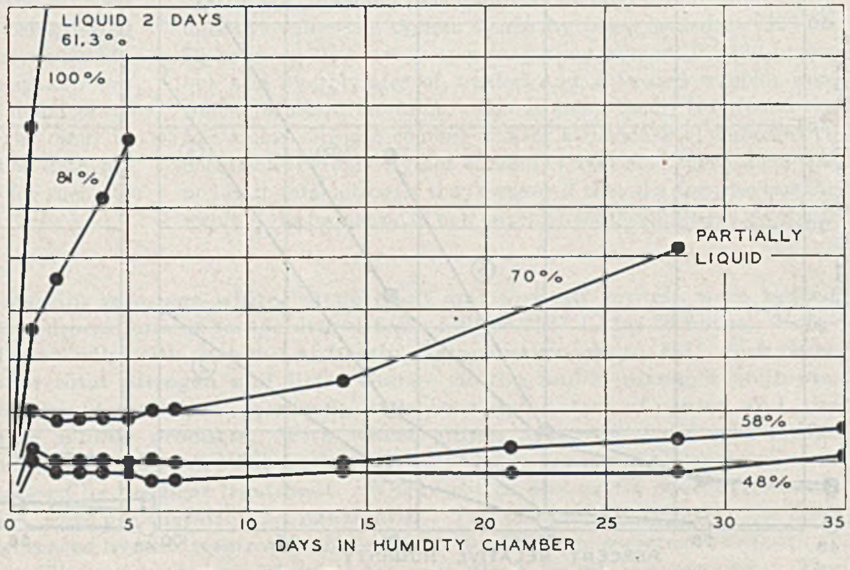

Figure 2. Hygroscopicity of Amorphous Sodium Penicillin

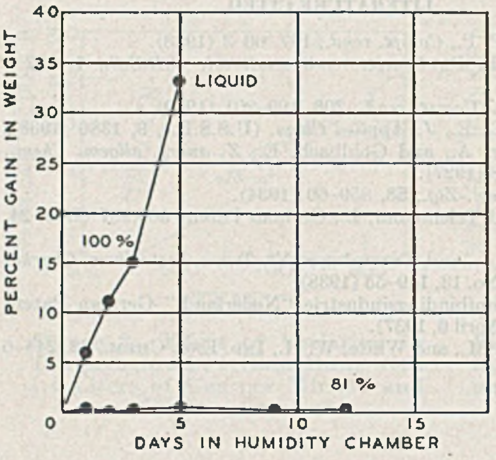

Figure 3. Hygroscopicity of Crystalline Potassium Penicillin

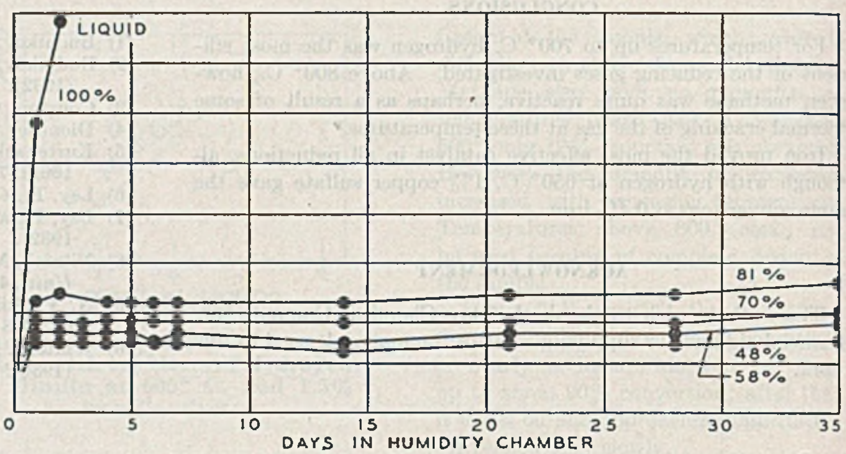

Figure 4. Hygroscopicity of Amorphous Calcium Penicillin

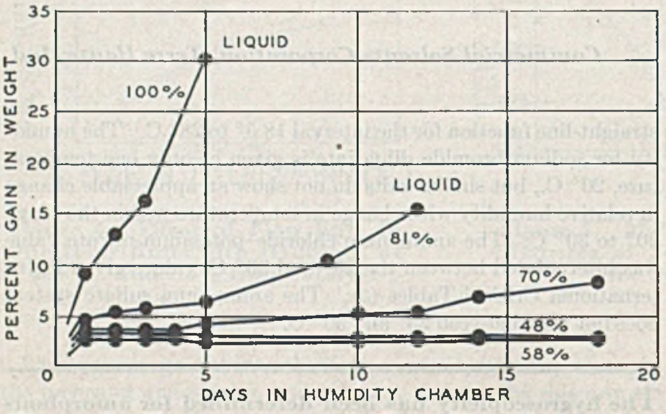

Figure 5. Hygroscopicity of Crystalline Ammonium Penicillin

The amorphous sodium penicillin was obtained in 200,000-unit vials and was from a regular plant run. The amorphous calcium penicillin and crystalline sodium, potassium, and ammonium penicillins were prepared in the laboratory. Subsequent chromatographic analyses indicated that approximately 90% of the penicillin potency of the amorphous salts and over 90% of the potency of the crystalline salts was penicillin G. The assays of the various penicillin salts follow:

	Biological Assay, μ/Mg.
Amorphous sodium penicillin	1422
Amorphous calcium penicillin	1200
Crystalline sodium penicillin	1656
Crystalline ammonium penicillin	1760
Crystalline potassium penicillin	1756

Approximately 0.5 gram of each of the crystalline salts was weighed into tared, ground-glass stoppered weighing bottles and dried overnight at room temperature and 50 mm. pressure in a vacuum oven. The sodium and potassium salts were further

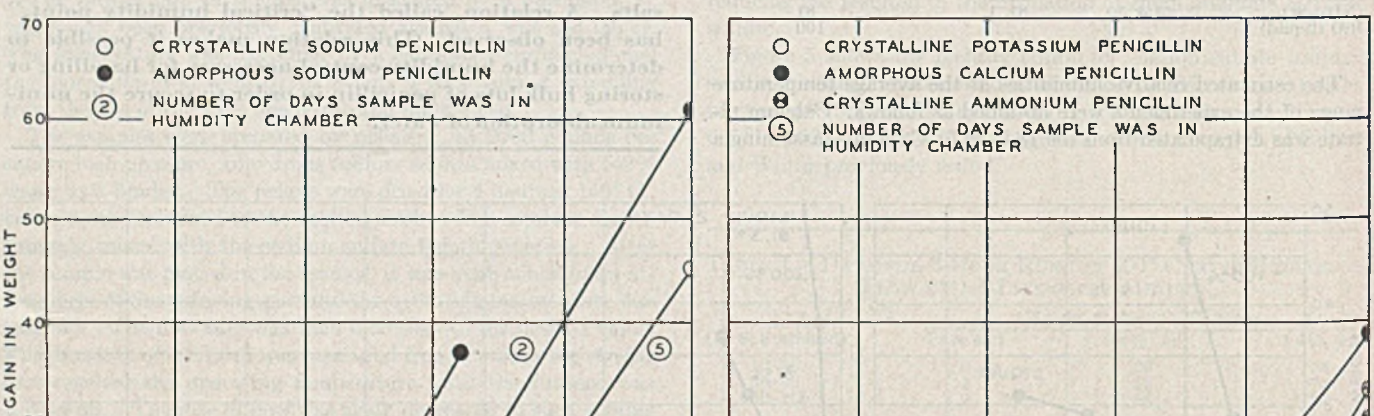

Figure 6. Critical Humidity Points of Penicillin Salts

dried 8 hours at 80° C. and 50 mm. pressure. The ammonium salt was not dried above room temperature because of its low heat stability. The amorphous sodium and calcium salts were dried overnight at 80° C. and 50 mm. pressure. The stoppers were left out of the weighing bottles during the drying period and replaced as soon as the bottles were removed from the oven. Tests in this laboratory indicate that the above method of drying gives substantially water-free material when tested according to the method set forth by the Food and Drug Administration (*1*), except that the ammonium salt may contain 0.1 to 0.2% water.

The weighing bottles were weighed when cool and placed in the respective humidity desiccators with the top out of the bottle. They were removed from the humidity chambers at intervals and weighed to determine the amount of moisture absorbed.

The hygroscopicity data for a single salt species were plotted as per cent gain in weight against time in the humidity chamber (Figures 1 to 5). It is apparent that potassium penicillin (Figure 3) is the least hygroscopic of the salts tested. The gain in weight for 48, 58, and 70% humidities was less than 0.4% at the end of 12 days. Crystalline sodium penicillin absorbed less than 0.3% moisture at 48 and 58% humidities in 12 days.

An interesting characteristic was exhibited by ammonium, calcium, and amorphous sodium salts. The dry salts absorbed water rapidly the first day to a limiting value and then remained at a constant weight or absorbed much more slowly. The absorption at 100% humidity for all three salts and at 80% for the amorphous sodium salts did not exhibit this characteristic. The absorption of a limiting amount of water was not an indication of hydrate formation because the limiting amount of water was increased with increased humidities. This is ideally exhibited by the calcium salt (Figure 4).

The 100% humidity curves for the amorphous and crystalline salts showed a marked difference in general slope. The slopes for the amorphous salts are much steeper than those of the crystalline salts, being almost perpendicular as plotted in Figures 2 and 4.

When the percentage increase in weight was plotted against the relative humidities for a given time period, the increase in hygroscopicity with increasing humidity became apparent. All penicillin salts tested exhibited a decided break in this relation (Figure 6) at one of the test humidities. The humidity at which the slope of the curve increased appreciably has been called the "critical humidity point." Both sodium salts showed a critical humidity point at 70%. The other three salts showed this characteristic at 81%. The differences between the humidity values studied are rather large. The critical humidity point as given represents the experimental humidity at which there is a decided change in the rate of absorption of moisture by the salt. This point may not represent the highest humidity at which this change occurs. Figure 6 points out clearly that crystalline sodium and potassium penicillins may be handled or stored for at least 5 days in any space where the humidity is below the critical humidity point without absorbing more than a fraction of a per cent of water. It is not advisable to handle or store, even for a short time, any of the penicillin salts at a humidity above their critical humidity point because of the rapidity with which they absorb moisture.

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Effect of Dry Heat on Proteins

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Wheat gluten, casein, zein, egg white, cattle hoof, and soybean protein were heated in boiling inert hydrocarbons at temperatures from 110° to 203° C. for 18 hours. Solubility decreased markedly with increase of heating temperature up to 153°, but there was no change in total nitrogen and little change in the amide nitrogen contents. Above 153° extensive degradation occurred, with continuing loss of water and the formation of more soluble products. With wheat gluten and zein, total and amide nitrogen contents were decreased. The amino and total basic groups of all proteins were found to be decreased by the heat treatment. Wheat gluten and cattle hoof, after being heated above 153°, were not digestible by pancreatin. The cystine content of cattle hoof was markedly decreased by heat treatment above 153°. Equilibrium moisture contents at 70% relative humidity were decreased by heat treatment at all temperatures. The equilibrium moisture contents continued to decrease at temperatures above 153° despite the increasing solubility of the heated products.

THE successful application of proteins to industrial uses ma require modification of the proteins by simple physical or chemical treatment. For example, Brother, Binkley, and Brandon (*7*) report that chicken feathers and hoof meal, after being heated to 210–220° C. for 1 hour, can be used advantageously to modify Bakelite-type molding plastics. The present investigation was undertaken when it appeared that only a limited amount of information was available concerning the changes that occur in proteins when they are subjected to dry heat. The data obtained may assist in the modification of proteins for such applications as plastics, coatings, adhesives, and fibers.

Most of the previous work on the effect of heat treatment on proteins has been reported by investigators interested in the modification of nutritive properties; the literature has been summarized by Waisman and Elvehjem (*21*) and by Greaves, Morgan, and Loveen (*10*). Lysine was reported to be the first amino acid damaged by heat treatment (*10*), but Block, Jones, and Gersdorff (*6*) found no difference between the lysine contents of hydrolyzates of heated and unheated casein. Seegers and Mattill (*18*) observed that beef liver suffered considerable loss in nutritive value as a protein source by being heated at 120° for 72 hours or by extraction with boiling ethanol for 130 hours; but acid hydrolyzates of treated and untreated samples were similar in nutritive value. Harris and Mattill (*11*) found the free amino nitrogen content of liver and kidney globulins to be decreased (by half) by hot ethanol extraction. Since there was no loss in total nitrogen, they suggested that the decrease was the result of the formation of new enzyme-resistant linkages involving

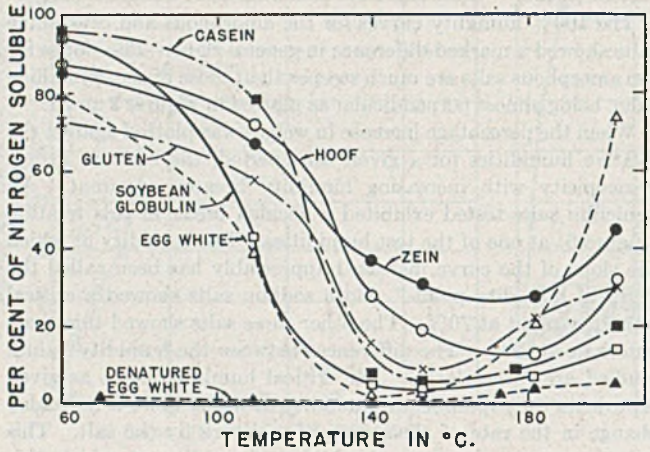

Figure 1. Effect of Heat on Solubility of Proteins

the ε-amino groups in lysine. In accord with this suggestion, Eldred and Rodney (*8*) found less free lysine in enzyme digests of a casein that had been heated at 150° for 70 minutes than in similar digests of the unheated protein.

Barker (*2*) reviewed previous work on the effect of heat on egg albumin and determined the temperatures and times at which egg albumin samples of varying moisture content became half insoluble. For constant time of heating, the temperature required was a linear function of the relative humidity with which the protein had been in equilibrium. Egg albumin that had been stored over phosphorus pentoxide became half insoluble after 60 minutes at 140° or 10 minutes at 162° C. Bernhart (*4*) studied the effect of heat on dry egg albumin by measuring the rate of formation of insoluble protein. The curves resembled those characteristic of autocatalytic reactions. Beckel, Bull, and Hopper (*3*) reported that solvent-extracted soybean heated at 120° and 0% relative humidity for 2.5 hours contained only 49% as much water-extractable protein as did unheated meal.

HEATING TECHNIQUES

In the present work several proteins were heated at temperatures from 110° to 203° C., and the effects of such treatment on loss of water, total nitrogen content, amide nitrogen content, solubility, equilibrium moisture content in an atmosphere of 70% relative humidity, and, in some cases, on amino nitrogen, acid, and basic groups, cystine content, and pancreatin digestibility were determined. Most of the data were obtained with samples heated in boiling aromatic hydrocarbons; the temperature of treatment then could be controlled by the choice of hydrocarbon, the rate of removal of water from the sample could be followed by the use of a Bidwell-Sterling moisture determination tube (*5*) and in addition any possible oxidative effect of air was effectively prevented. After the time periods indicated the samples were filtered and washed with petroleum ether. Traces of residual hydrocarbon were removed in a vacuum oven at 60° C. Other techniques for heating the proteins were sometimes used, as described below.

Proteins. Wheat gluten (gum gluten), soybean protein (α-protein), acid casein, and zein were commercial products. Dried egg white was prepared from fresh egg white by exposing a thin layer to an air stream at room temperature. Denatured egg white was prepared as follows: A filtered solution of dried egg white was adjusted to pH 5 with dilute hydrochloric acid, heated to 70° C. for 15 minutes, and filtered. The filter cake was washed with water, dried in an air stream (room temperature) and finally in a vacuum oven (65° C.). Powdered hoof was obtained from washed cattle hoofs. These were dried at 70° C. until brittle, broken into small pieces by being pounded in an iron container, ground for 24 to 48 hours in a porcelain ball mill, and sieved. Material passing a 60-mesh and retained by an 80-mesh screen was used. Heated samples were prepared from a single lot of each protein.

Table I. Elimination of Water from Wheat Gluten and Cattle Hoof Heated in Boiling Hydrocarbons[a]

Temp., ° C.	Wheat Gluten, %		Cattle Hoof, %	
	2 hr.	18 hr.	2 hr.	18 hr.
110	6.6	6.7	9.3	9.5
140	6.8	6.9	9.4	9.7
153	7.2	7.2	9.9	9.9
182	8.0	9.3	10.7	11.8
203	9.3	11.8	12.3	15.6

[a] Per cent loss in an air oven at 105° C. for 16 hours, wheat gluten 6.0, hoof 9.3. Compare Sair and Fetzer (*17*).

Hydrocarbons. The hydrocarbons used, together with their observed boiling points, were: toluene, 110°; xylene, 140°; cumene, 153°; cymene, 177°; diethylbenzene and *n*-butylbenzene, 182°; diisopropylbenzene, 203° C. They were commercial products. Traces of water were removed by a preliminary distillation.

REMOVAL OF VOLATILE SUBSTANCES

The following technique was used in the preparation of most of the heated protein samples. Thirty grams of protein were suspended in about 250 ml. of the hydrocarbon held in a 500-ml. round-bottomed flask connected through ground-glass joints to a Bidwell-Sterling type of moisture-determination tube of 5-ml. capacity and to a reflux condenser. With the hydrocarbons of

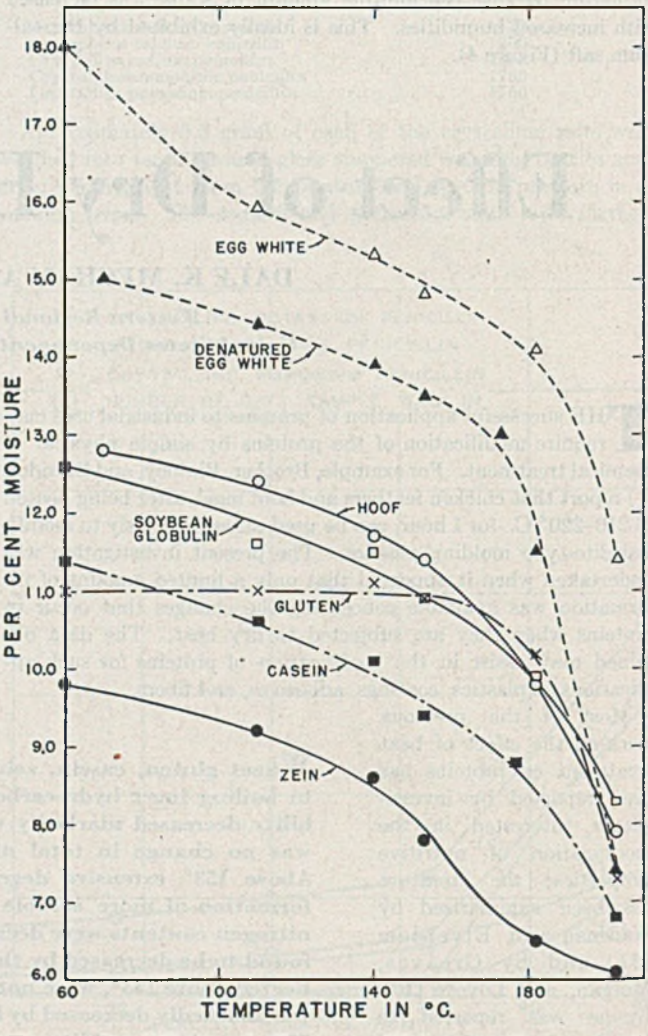

Figure 2. Effect of Heat on Moisture Content of Proteins in Equilibrium with 70% Relative Humidity at Room Temperature

high boiling point it was found advantageous to insulate the upper part of the boiling flask to ensure continual elimination of the water being formed. The duration of heating was measured from the time the liquid started to boil.

The amounts of water obtained from wheat gluten and cattle hoof at various temperatures after 2 and 18 hours are given in Table I. The data indicate that, at temperatures of 153° and below, any reactions that result in a chemical loss of water from the protein are practically completed in 2 hours. At the higher temperatures, additional dehydrating reactions continue during the entire period of heating.

At 153° C. and above, the samples darkened rapidly, an offensive odor was produced, and, with some of the proteins, a deposit formed in the condenser above the Bidwell-Sterling tube. These deposits, usually yellow, were partially soluble in ethyl ether; the white crystalline remainder was found to be chiefly ammonium carbonate. The ether-soluble material also contained nitrogen and may be assumed to consist at least in part of pyrroles.

In order to determine whether water-soluble nitrogen compounds were being eliminated at lower temperatures and from samples giving no condenser deposit, some samples of the water collected in the Bidwell-Sterling tubes were analyzed for nitrogen. The results indicated that traces of nitrogen were eliminated even at 110°; at 153° as much as 0.3% of the total nitrogen of soybean protein, hoof, and casein was found, although collection of evolved nitrogenous compounds would be expected to be incomplete.

SOLUBILITY OF HEATED PROTEINS

Solubilities at room temperature were determined in solvents appropriate for each protein. The procedures used were as follows.

Wheat Gluten. One gram of sample was suspended in 5 ml. of 95% ethanol, 25 ml. of 0.1 *N* acetic acid were added and the mixture was permitted to stand, with occasional shaking, for 16 to 18 hours (*14*).

Zein. Two grams of sample were suspended in 15 ml. of 95% ethanol, 10 ml. of water were added, and the mixture was permitted to stand 16 to 18 hours.

Cattle Hoof. To 1.75 grams were added 25 ml. of 0.5 *M* sodium sulfide. The mixture was shaken at 15-minute intervals for 4 hours. The solutions were then at pH 10.8–10.9.

Soybean Protein, Casein, and Native and Denatured Egg White. To 1.00 gram were added 25 ml. of a phosphate buffer (800 ml. of 0.2 *M* disodium hydrogen phosphate and 132 ml. of 1 *N* sodium hydroxide per liter). The mixtures were shaken mechanically for 16–18 hours. The solutions were then at pH 10.6–10.8. In all cases the undissolved residue was removed by centrifugation and filtration (No. 4 Whatman paper), and the extent of solution was determined by nitrogen analyses of aliquots of the filtrate. The results obtained are plotted in Figure 1. All figures are for a heat treatment of 18 hours in boiling hydrocarbons at the temperatures indicated on the graphs.

In general, minimum solubility was obtained with those samples that had been heated at 153° C. The exceptions, zein and hoof samples, were those whose solubilities were determined in solvents of quite different nature than were used for the other protein samples. Samples of these proteins showed a definite minimum solubility when heated at temperatures below the highest used.

Table II. Effect on Total Nitrogen Content of Heating Proteins in Boiling Hydrocarbons for 18 Hours

Temp., ° C.	Total Nitrogen Content[a], % Wheat gluten	Zein	Denatured egg white
Control	14.4	15.7	15.0
110	14.2	15.6	15.1
140	14.2	15.5	15.2
153	14.0	15.2	15.0
182	12.0	12.8	15.1
203	11.5	13.2	15.0

[a] Moisture-free basis.

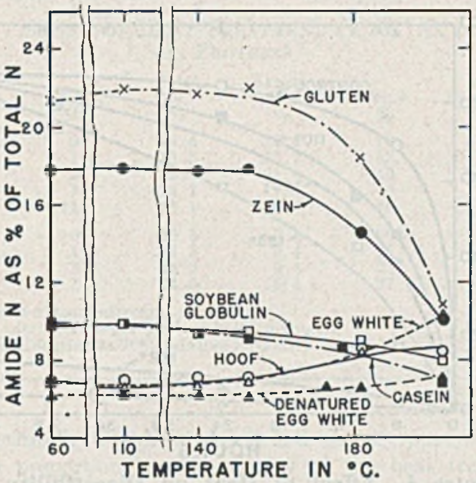

Figure 3. Effect of Heat on Amide Nitrogen Content of Proteins

The occurrence of minimum solubilities in samples heated at 153° C. and the continuing loss of water from samples heated at temperatures above 153° C. suggest that the increased solubilities found for the latter samples are the result of the formation of soluble degradation products.

ANALYSES

Moisture Content at 70% Relative Humidity. Samples of the heated proteins and unheated controls were permitted to come to constant weight at room temperature in an atmosphere of 70% relative humidity maintained within a closed container by means of a solution kept saturated with both ammonium chloride and potassium nitrate. The moisture content of the equilibrated sample was then determined by drying to constant weight in an Abderhalden dryer heated with boiling toluene (110°). The drying chamber contained fresh phosphorous pentoxide, and vacuum was maintained with a mechanical pump. Results are shown in Figure 2.

Significant decreases in the equilibrium moisture contents at 70% relative humidity were found in samples heated at 110°, and the amounts of water adsorbed continued to decrease as the temperature of treatment was raised. Samples heated at 203° showed the unusual properties of having decreased moisture content in spite of the fact that they were more water soluble than the samples heated at lower temperatures. The sharpest decrease in water adsorption occurred in samples heated above 182° C. Gluten appeared to differ from the other proteins by showing no lowering of water adsorption until it was heated above 153°.

Total Nitrogen and Amide-Nitrogen Contents. Total nitrogen was determined by the Kjeldahl-Gunning-Arnold method. Wheat gluten and zein were the only proteins that showed apparent change in total nitrogen content, and these only when heated at the higher temperatures (Table II). Denatured egg white, as an example of the other proteins, at corresponding temperatures underwent no appreciable change in nitrogen content.

Amide nitrogen was determined by measuring the ammonia produced by heating 0.500-gram samples with 12.5 ml. of 1.2 *N* sulfuric acid for 40 minutes in an autoclave at 20 pounds steam pressure. The autoclaved sample was made to 25 ml. volume with water and filtered. The ammonia present in an aliquot of filtrate was then distilled from a suspension of magnesium oxide. This procedure has been found to give satisfactory results for amide nitrogen in proteins. No additional ammonia is evolved

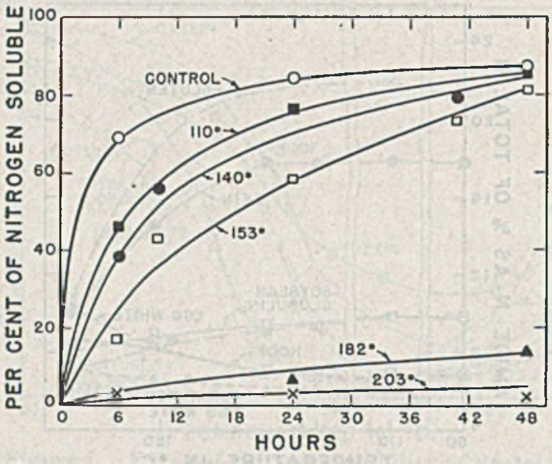

Figure 4. Effect of Heat on Digestibility of Wheat Gluten by Pancreatin

until the samples are heated for an appreciably longer time. Results are plotted in Figure 3.

The proteins of relatively high amide nitrogen content, gluten and zein, showed marked decreases in amide nitrogen content when heated to temperatures above 153° C. The loss of amide nitrogen would appear to be responsible for the definite lowering of the total nitrogen content of these proteins at the higher temperatures.

Amino Nitrogen, Acid, and Basic Groups. The amino nitrogen contents of some of the heated proteins were determined by the manometric method of Van Slyke with a 15-minute reaction period (*20*). Total acid and basic groups were determined for some of the samples by the dye methods of Fraenkel-Conrat and Cooper (*9*). The data are given in Table III.

Consistent decreases in amino nitrogen were found, in agreement with the observations of earlier investigators (*11*). The decrease in basic groups was similarly in proportion to the severity of the heat treatment. However, the data are not of sufficient accuracy to indicate whether basic groups other than the amino groups were involved.

The increase in the number of acid groups of heated wheat gluten and zein can be attributed to the transformation of the neutral amide groups to carboxyl groups through the loss of ammonia. The losses in acid groups in other proteins are probably the result of the interaction of basic with acid groups to form new amide-type linkages. If these two reactions occur to a somewhat similar extent, the total change in acid groups might be small, as was found with dried egg white (Table III).

Cystine. Preliminary results of Binkley and Jones of this laboratory had indicated that the cystine content of feathers that had been heated at 210° for 2 hours was negligible. In the present study attempts were made to determine the cystine contents of the samples of hoof meal that had been given various heat treatments. Three different methods (*12*, *13*, *19*) were found to give agreeing values for unheated hoof (approximately 6%) but could not be used satisfactorily with the heated samples. With each method no appreciable loss of cystine appeared to have occurred in those samples which had been heated at 153° or below. At the higher temperatures erratic results were obtained. Thus, for one sample heated at 203° for 18 hours, the apparent cystine content was 2.8% by the Sullivan method and 0.3% by the modified Vassel method (*12*). It may be concluded that an unknown but appreciable amount of cystine is destroyed in keratins that have been heated to temperatures above 150°. Unheated hoof meal and the sample that had been heated 18 hours at 153° contained 2.0% total sulfur, but the sample that had been heated to 203° for 18 hours contained only 0.8% sulfur; this indicated that sulfur was lost by volatilization.

The increase in flow observed with heated feathers (*7*) is possibly ascribable to the decrease in disulfide cross links in the keratin structure.

Digestibility by Pancreatin: One gram portions of the protein samples were incubated 6, 24, and 48 hours at 30° C. with 25 ml. of a 0.2 *M* phosphate buffer, pH 7.5, containing 0.3 mg. pancreatin nitrogen per ml. The digests were filtered (No. 4 Whatman paper), and aliquots were analyzed for nitrogen. All filtrates were at pH 7.1 to 7.5. The data shown in Figure 4 were corrected by subtracting the amounts of nitrogen soluble in the buffer alone.

In the case of wheat gluten samples, the initial rate of digestion was decreased markedly by 18 hours of heating at 110°, 140°, and 153° C.; each increment in temperature resulted in a further decrease in the initial rate. After 48-hour digestion, however, these samples and an unheated sample had become soluble to approximately the same extent. Samples heated at 182° and 203° C. were practically not digested under the conditions used.

Hoof samples were digested at much slower rates, so that even after 48-hour digestion the data permitted no estimation of the extent to which digestion might eventually have gone. The rate of digestion was again definitely reduced by heat treatment of the hoof at 110° or 140°, and treatment at 153° C. or higher prevented any detectable digestion.

EFFECT OF VARIABLES

Time of Heat Treatment at 203° C. Proteins that had been heated for 18 hours at temperatures near which degradation began

Table III. Number of Amino, Total Acid, and Total Basic Groups[a] in Unheated and Heated Proteins[b]

Protein	Temp., ° C.	Amino Groups	Basic Groups	Acid Groups
Dried egg white	Control	3.6	7.0	12.1
	110	3.3	7.0	11.5
	140	2.6	6.5	10.3
	153	2.4	6.3	10.1
	182	1.4	3.9	12.0
	203	2.1	2.9	13.8
Wheat gluten	Control	1.8	3.2	5.5
	182	1.1	1.3	9.7
Zein	Control	...	1.3	5.2
	182	...	0	9.2
Hoof	Control	3.3	9.4	8.6
	182	1.2	1.5	5.6
Soybean protein	Control	4.9	8.5	14.9
	182	1.4	4.6	12.0
Casein	Control	5.3	6.3	17.8
	182	1.0	0	13.6

[a] Equivalents per gram protein × 10^4. Moisture-free basis.
[b] The heated samples had been refluxed for 18 hours in hydrocarbons at the temperatures indicated.

Table IV. Effect of Time of Heating at 203° C. on Wheat Gluten and Casein

	Time of Heating, Hr.	Total N, %	Amide N[a], %	Soly.[b] %	Moisture Content[c], %	Amino N[d], %
Wheat gluten	0	14.4	21.4	73	11.0	...
	1	14.2	21.8	24	10.2	...
	3	13.0	19.5	28	9.7	...
	7	11.5	14.8	23	8.0	...
	11	10.7	12.7	18	6.3	...
	18	11.5	11.8	30	7.3	...
Casein	0	13.8	9.8	96	11.4	0.74
	1	13.9	9.6	15	8.6	0.14
	3	14.0	8.3	18	8.3	...
	7	13.7	7.8	19	8.0	0.12
	11	13.8	7.3	20	7.2	...
	18	14.1	6.8	20	6.8	0.06

[a] As per cent of total nitrogen.
[b] Soluble nitrogen as per cent of total nitrogen.
[c] After equilibration at 70% relative humidity.
[d] The amino nitrogen content of wheat gluten is too low (0.25%) for determinations of changes.

showed minimum solubility. The possibility that heating at higher temperatures for a shorter time might give even less soluble products was investigated. Samples of casein and wheat gluten were heated at 203° C. for various periods of time and examined as described. Results are given in Table IV. The data indicate that samples heated at 203° for 18 hours were more soluble than those heated for shorter times, but the minimum solubilities found were not so low as those of samples heated 18 hours at 140° or 153°. However, in the case of casein particularly, heating times less than 1 hour might have given lower values.

HEATING IN AIR AND IN VACUO. The possibility existed that heating the protein samples in contact with the hydrocarbons had led to results of a different type than might have been obtained if contact with hydrocarbon had been avoided. This possibility was investigated by examining samples of proteins which had been heated at 110°, 153°, and 182° C. in an oven in open flasks. Analyses of these samples showed the same trends observed with samples heated in contact with hydrocarbons, although the samples heated in an oven at 110° showed somewhat less, and those at 153° and 182° somewhat more, change than samples heated in hydrocarbons at corresponding temperatures. Proteins heated in air were darker than those heated in hydrocarbons.

A further set of protein samples was heated in side-arm test tubes, fitted with thermometers, connected to a water aspirator (29-inch vaccum), and immersed in boiling diisopropyl benzene (203° C.) for various periods of time. This assembly was used to decrease the possibility of oxidative changes and to aid in the removal of volatile substances formed. Examination of these samples showed the trends in all analyses to be the same as those found after heating in hydrocarbon; the changes appeared to occur more slowly, however, and the decreases in solubility were less marked. Data are presented in Table V.

When wheat gluten was heated at 153° C. in vacuo for periods of 1, 3, and 7 hours, relative solubilities of 43, 36, and 27%, respectively, were obtained; the relative solubility of gluten heated for 3 hours while immersed in cumene (153° C.) was 25%.

TABLE V. EFFECT OF HEAT TREATMENT AT 203° C. IN VACUO ON PROTEINS

	Time, Hr.	Total N, %	Amide N[a], %	Soly.[b], %	Moisture Content[c], %
Wheat gluten	0	14.4	21.4	73	11.0
	1.5	13.5	22.2	33	10.6
	3	13.5	21.4	40	10.3
	7	13.1	17.4	48	9.0
	11	13.1	15.5	40	8.6
Casein	0	13.8	9.8	96	11.4
	1.5	14.3	9.4	17	9.4
	3	14.3	9.1	21	9.2
	7	14.3	8.4	27	8.5

[a] As per cent of total nitrogen.
[b] Soluble nitrogen as per cent of total nitrogen.
[c] After equilibration at 70% relative humidity.

DISCUSSION

When proteins are heated in the dry state, the following reactions occur in turn as the temperature and time of heating are increased: At relatively low temperatures (100–140° C.) there are only slight losses of water and nitrogenous compounds, but readily measurable changes in solubility and rate of digestion by pancreatin. Even samples heated at 110° C. show significant decreases in moisture content after equilibration at 70% relative humidity. This may be interpreted as a loss of some polar groups (*16*), possibly by internal ester or amide formation, which reaction may also be the source of some water. At 150° C. and above, definite signs of decomposition occur. Foul odors are evolved, the proteins darken, considerable amounts of ammonia are lost from proteins containing relatively large amounts of amide nitrogen, and solubility falls to a minimum. At temperatures around 200° C. decomposition occurs to the extent that the residual material has become again more soluble. The amounts of water absorbed at 70% relative humidity by samples which had been heated at 153° to 203° C. decrease, irrespective of the increase in solubility occurring in most samples at the higher temperature.

There are consistent decreases in amino and basic groups with increase in heating temperature. The changes in number of acid groups are complicated by the conversion of amide groups to carboxyl groups by loss of ammonia, as indicated particularly by the behavior of zein and wheat gluten. If the content of polar groups determines the water absorption of the heated samples, the basic groups would appear to exert considerably more influence than the acid groups. A similar suggestion has already been made (*15*), based upon different lines of evidence.

The digestibility of wheat gluten and hoof by pancreatin decreases in proportion to the severity of the heat treatment. Preliminary experiments with egg white (by H. Lineweaver) indicate that this material is more readily digested by papain after being heated 18 hours at 60° C. than is the unheated protein. This is in accord with the concept that denatured proteins are more readily digested than are native proteins (*1*). However, treatment at higher temperatures caused egg white to become progressively more resistant to digestion. In studies in this laboratory yet to be reported, Lundgren, High, Lindquist, and Ward have shown that dry heat treatment of synthetic protein fibers results in an increase of tensile strength—additional evidence for the formation by heat of new cross linkage, presumably of an amide type. A method of differential thermal analysis was used to determine the optimal temperature (165°) for this reaction.

ACKNOWLEDGMENT

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ANTIFOULING PAINTS

Inactivation of Highly Pigmented Antifouling Films Applied to Steel

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Although the value of copper pigments as active ingredients for antifouling paints has been recognized for a long time, metallic copper pigments have been avoided generally in favor of cuprous oxide where the paint is intended for application to steel hulls. Recent shortages of high grade cuprous oxide stimulated investigations of the use of copper flake and copper powder with a view to adapting them for use over metal, while eliminating simultaneously the accompanying danger of accelerated corrosion of the steel to which they were applied. The current study reports the behavior of such metallic pigments when dispersed in a typical antifouling matrix and applied to steel under varying conditions. Limitations have been established between which metallic copper may be used safely as an antifouling pigment for application to steel. Evidence is presented to indicate that, above definite limits, inactivation of the paint will occur, and corrosion of the steel will be accelerated. The maximum limit of pigmentation is well above that required for prolonged protection from the attachment of fouling organisms.

IN THE study of antifouling compositions for application to the steel hulls of ships, significant data have been obtained on the optimum pigment-volume relation that retard the attachment of marine fouling and simultaneously inhibit excessive corrosion, in cases where the toxic pigment consists of metallic copper in the form of flake or powder. Young and Schneider (*3*) reported that antifouling efficiency is directly a function of the copper content of the paint, with a stipulated minimum toxic loading for complete protection. The studies reported here indicate that toxic loadings above an established minimum do not improve the day-by-day performance, although no consideration is given to the total effective life of such compositions beyond a period of 8 months. The galvanic corrosion of steel hulls induced by contact with metallic copper is well known. The rate of corrosion of steel in contact with paint containing metallic copper indicates that some paints rich in copper flake perform somewhat as a metal conductor. In view of the possibility of accelerated corrosion due to presence of metallic copper in paints for steel, most antifouling compositions have depended on cuprous oxide as the active ingredient. In experiments in which it was hoped to establish the efficiency of metallic copper, there was evidence to indicate that loss of fouling resistance resulted in antifouling paints containing high volumes of metallic copper when placed in contact with steel. It has been shown (*2*) that steel strips bolted to either primed steel or wooden panels painted with copper flake antifouling formulations reduce markedly the antifouling properties of the film. This phenomenon is analogous to the performance of a sheet of metallic copper employed in a like role. Additional evidence (*2*, *4*) indicates that this effect can extend for a distance of several feet from the point of metallic contact, the distance and intensity being proportional to the ratio of metallic copper to the resinous constituents of the formulation. LaQue (*1*) reported on experiments at Kure Beach showing that copper paints increase the corrosion of bare steel areas above that caused by control paints containing no copper. It was observed also that intense fouling occurs near the edges of the bare areas.

Some effort has been made (*4*) to investigate the electrical conductance of metallic copper paints on the assumption that they possess sufficiently low resistance to support galvanic action. The reported results indicated that, although accelerated corrosion does occur and fouling resistance is impaired, the conductivity of the film is so low that accurate measurements have been difficult. The foregoing results indicate that some type of electrical contact exists between the pigment particles of highly pigmented antifouling paints and steel areas adjacent to them. The effects of such contacts have been observed and reported, and several theories have been proposed as to the mechanism of this phenomenon. Young (*4*) suggested that copper, whether present in the paint film as oxide or metal, passes into solution, from which it subsequently plates out in the form of metallic copper on the surface of the metal directly beneath the paint film. This immediately sets up a galvanic couple, the nature of which is well known.

This paper presents the results of studies on the conductivity of highly pigmented films and antifouling efficiency when applied to panels of steel and nonconducting media, such as wood and Lucite.

MEASUREMENTS OF FILM CONDUCTIVITY

Earlier published data (*4*) indicated the difficulty involved in measuring the resistance of pigmented films in the plane of the film, and no evidence was presented of any extremely low resistance, such as would be demanded if the antifouling paint were to act as a cathode in a galvanic couple with the substrate metal to which it was applied. To explore such a possibility more thoroughly, a series of antifouling paints was prepared with varying pigment-volume ratios from 5 to 45%, the pigment being a high-purity copper flake dispersed in a vehicle consisting of a rosin-Pliolite-Hercolyn blend. Two spray coats of the paints were applied to Lucite sheets size 3 × 3 × $^1/_4$ inch masked $^1/_2$ inch along each edge. After drying, the masking tape was removed and left a 2-inch square of paint film exactly in the center of the panel. When thoroughly dry, two opposite edges were covered with colloidal silver conducting paint, which possesses a resistance of only 0.5 ohm when measured longitudinally across 2 × 8 inch strips at a thickness of 2 to 3 mils. The finished panel is shown in Figure 1 (right). Five sets of identical panels were prepared and permitted to reach equilibrium in a constant temperature-humidity room at 25° C. and relative humidity 50%. Duplicates were prepared for each paint, and conductivities were determined daily until a constant value was reached by means of a megohm bridge. The bridge is operated with alternating current which is capable of measuring resistances from 87,000 ohms to 1,000,000 megohms with an impressed voltage across the unknown resistance of 100 volts. The average resistances of duplicate determinations are listed in Table I. An average period of 1 to 2 weeks was required before the values became constant. After reaching equilibrium the panels were immersed in artificial sea water, where they were removed at the intervals indicated in Table I. Upon removal, the panels were thoroughly washed with distilled water to dislodge any loosely adhering salt particles and returned to the

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Table I. Surface Resistance in Ohms of Copper Flake Antifouling Paint

Pigment-Vol. Ratio, %	Set 1		Set 2		Set 3		Set 4		Set 5	
	I[a]	45 hr.	I	96 hr.	I	144 hr.	I	168 hr.	I	216 hr.
5	Infinite	Infinite	Infinite	1.50×10^{11}	Infinite	1.0×10^{11}	Infinite	1.5×10^{11}	Infinite	1.75×10^{11}
10	Infinite	1.25×10^{11}	Infinite	1.0×10^{11}	Infinite	6.0×10^{10}	Infinite	1.5×10^{11}	Infinite	1.25×10^{11}
15	Infinite	7.5×10^{10}	Infinite	3.0×10^{10}	Infinite	3.5×10^{10}	Infinite	2.8×10^{10}	Infinite	1.7×10^{10}
20	1.3×10^{10}	1.0×10^{10}	7.0×10^{9}	5.5×10^{9}	3.5×10^{10}	1.0×10^{10}	1.7×10^{10}	1.1×10^{10}	1.5×10^{10}	1.0×10^{10}
25	8.0×10^{8}	1.1×10^{9}	2.0×10^{9}	1.5×10^{9}	1.5×10^{9}	1.5×10^{9}	1.5×10^{9}	1.5×10^{9}	9.0×10^{8}	7.0×10^{8}
30	3.0×10^{8}	2.6×10^{8}	3.75×10^{8}	3.3×10^{8}	5.0×10^{8}	7.0×10^{8}	4.5×10^{8}	8.0×10^{8}	3.1×10^{8}	6.3×10^{8}
35	5.0×10^{7}	3.0×10^{8}	4.0×10^{7}	4.0×10^{8}	1.0×10^{8}	6.0×10^{8}	9.5×10^{7}	4.1×10^{8}	7.1×10^{7}	1.95×10^{8}
40	2.4×10^{8}	8.6×10^{8}	1.5×10^{8}	9.0×10^{8}	3.2×10^{8}	1.5×10^{9}	2.5×10^{8}	1.7×10^{9}	1.8×10^{8}	1.35×10^{9}
45	1.0×10^{8}	5.25×10^{8}	4.0×10^{6}	7.5×10^{8}	1.5×10^{8}	8.5×10^{8}	2.0×10^{8}	1.4×10^{9}	2.0×10^{8}	1.00×10^{9}

[a] Average resistance of duplicate determinations.

Table II. Galvanic Current of Paint-Steel Couples

Couple No.	Pigment-Vol. Ratio, %	Current in Milliamps after Soaking for			
		6 hr.	23 hr.	28 hr.	45 hr.
11	30	0	0	0	0[a]
12	30	0	3.0	3.2	1.2
14	35	0	2.8	3.8	1.5
15	35	0	3.2	5.2	1.5

[a] No current after 114 hours.

Table III. Resistance of Paint Films Coupled with Steel

Panel or Couple No.	Pigment-Vol. Ratio, %	Resistance, Ohms	
		Original	After soaking
1[a]	15	Infinite	1.5×10^{11}
2	15	Infinite	2.0×10^{11}
3	15	Infinite	2.8×10^{10}
4[a]	20	1×10^{10}	2.2×10^{9}
5	20	1.1×10^{10}	1.35×10^{9}
6	20	7.8×10^{9}	1.25×10^{9}
7[a]	25	1.75×10^{8}	1.2×10^{8}
8	25	1.90×10^{8}	1.45×10^{8}
9	25	2.00×10^{8}	1.20×10^{8}
10[a]	30	6.0×10^{7}	1.2×10^{10}
11	30	6.0×10^{7}	9.0×10^{9}
12	30	6.5×10^{7}	2.5
13[a]	35	4.7×10^{7}	8.5×10^{7}
14	35	6.8×10^{7}	60
15	35	5.4×10^{7}	3

[a] Uncoupled controls.

constant temperature–humidity room, where they were permitted to come to equilibrium; resistance measurements were then repeated until constant values were obtained.

The data of Table I showing the initial resistance values along with values obtained after soaking for varying periods in artificial sea water appear to confirm earlier conclusions (*4*) that even highly pigmented films do not possess sufficiently low resistances in the dry state to perform as a cathode when coupled to steel.

GALVANIC CURRENT AND CONDUCTIVITY

Pigmented Films Coupled with Steel. In order to determine any current values resulting from coupling heavily pigmented copper antifouling paints with steel, a series of antifouling paints, as described, was prepared with varying pigment-volume ratios ranging from 15 to 35%. Lucite panels size 5 × 5 × 1/4 inch were masked 1/2 inch on three sides and given two spray coats of antifouling paint. After thorough drying the masking tape was removed and a copper strip 1/2 inch in width was bolted carefully along the edge of the panel which had not been masked. A copper rod had been soldered to the copper strip to serve as a means of support as well as a conductor. After final assembly all metal parts were covered thoroughly with two coats of aluminized spar varnish and then a thick coat of heavy wax to ensure against any electrical contact between metal parts and the sea water. A film of the silver conducting paint was applied to the edge of the panel opposite the copper strip to serve as another contact for measuring the resistance across the 4-inch square of paint. The assembled panel is illustrated in Figure 1 (left). The silver-copper paint junction is entirely local, and any galvanic effect resulting from it would not appear in the measurement of the value of the large cell. Five sets of copper paint–steel couples were prepared and immersed in sea water along with the uncoupled control. All couples were prepared in duplicate for each paint and connected through a 10-ohm resistor. Currents resulting from the couples were determined periodically by measuring the voltage drop across the known resistance. Measurements were made over a total interval of 114 hours, at which time no couple prepared from a paint having a pigment-volume ratio below 30% showed any indication of producing a measurable current. The two sets of couples prepared from paints of 30 and 35% pigment-volume ratio, respectively, reacted as indicated in Table II.

At the end of 114 hours all panels were removed from the sea water bath, and adhering salt particles washed from the paint films with distilled water. The panels were returned to conditions of constant temperature and humidity, where they were allowed to remain until constant resistance values were obtained. These values are shown in the last column of Table III. Figures showing the original resistance before immersion are included for reference.

The data of Table III indicate that only the compositions of high pigment-volume ratio display any tendency to behave as metallic

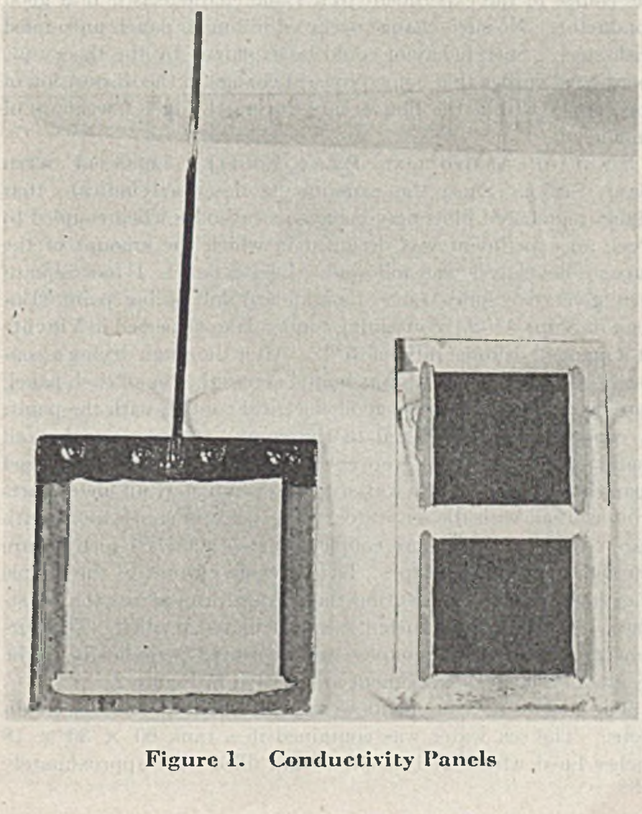

Figure 1. Conductivity Panels

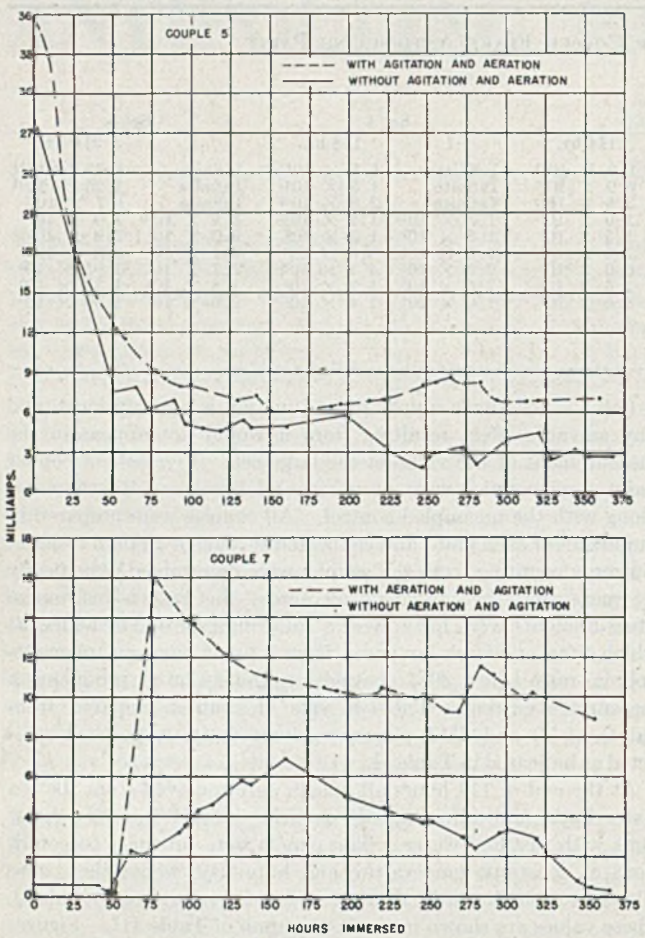

Figure 2. Galvanic Current from Copper-Steel Couple (*top*) and Copper Paint–Steel Couple (*bottom*)

cathodes. In the case of the couples producing measurable currents, the resistance in the plane of the film was reduced during the course of the experiment to a value characteristic of a good conductor. No such change occurred in similar panels uncoupled with steel. Such behavior could be explained by the theory (*4*) mentioned earlier that some physical change in the disposition of the copper within the film occurs during the first few hours of immersion.

Standard Antifouling Paint Coupled Directly with Bare Steel. Since the experiments described indicate that highly pigmented films may behave as cathodes when coupled to steel, an experiment was designed in which the amount of the current developed was followed. Lucite panels 1 foot square were given two spray coats of a standard antifouling paint (Bureau of Ships AF-23) containing copper flake dispersed in Vinylite at a pigment-volume ratio of 37%. After thorough drying a copper strip $^1/_2$ inch in width was bolted across the top of each panel, care being taken to ensure good electrical contact with the paint. A copper rod was soldered to the copper strip; after that all metal parts of the sytem were covered with one coat of aluminized spar varnish and heavily waxed to seal completely all metal parts from contact with the sea water. The painted panels along with bare copper controls were coupled to steel panels 1 inch square through a 10-ohm resistor. The galvanic current of the couple was determined by measuring the voltage drop across the resistance, from which the current was calculated readily. The current produced by the couples was measured periodically. The results of a typical experiment are plotted in Figure 2.

The current measurements were made under two sets of conditions. The sea water was contained in a tank 60 × 30 × 18 inches lined with cured neoprene and filled with approximately 150 gallons of artificial sea water prepared according to the following formula:

Constituent	% by Weight
Sodium chloride crystal	2.45–2.55
Magnesium chloride crystal ($MgCl_2.6H_2O$)	1.08–1.12
Calcium chloride crystal ($CaCl_2.2H_2O$)	0.155–0.165
Sodium sulfate, anhydrous	0.390–0.410
Distilled water	Balance

A gear pump having a capacity of 20 gallons per minute augmented by a Lightnin mixer was used to circulate the water from one end of the tank to the other. At a point just behind the output end of the circulatory system, a stream of air was injected into the water to ensure a continuous supply of dissolved oxygen. The circulating system was allowed to run continuously during one set of experiments and was discontinued during the other. The complete setup is illustrated in Figure 3.

Figure 2 shows the current produced by the copper-steel couples and the copper paint–steel couples with and without agitation of the sea water. The data for each couple show similar trends, except a time lapse up to 50 hours occurred in the case of the painted Lucite before an appreciable current was produced. This indicates that some penetration of the film by the solution is necessary before the resistance between individual particles of copper is reduced to a point where a measurable current can be produced. It is also significant that, in the case of the film of copper paint, larger current values were obtained than with the copper-steel couple; this might be explained by the fact that a larger effective surface area was available because of the flaky character of the copper pigment. The assumption that individual pigment particles in the dry film are in contact, and thus provide straight-line conductors throughout the plane of the paint film, would provide an immediate explanation for the production of current of the observed magnitude. However, such a hypothesis does not explain the time lapse required prior to the production of an appreciable current, nor can it be reconciled with the data of Table I. Again the theory (*4*) that paints containing copper submerged in sea water produce copper ion, which subse-

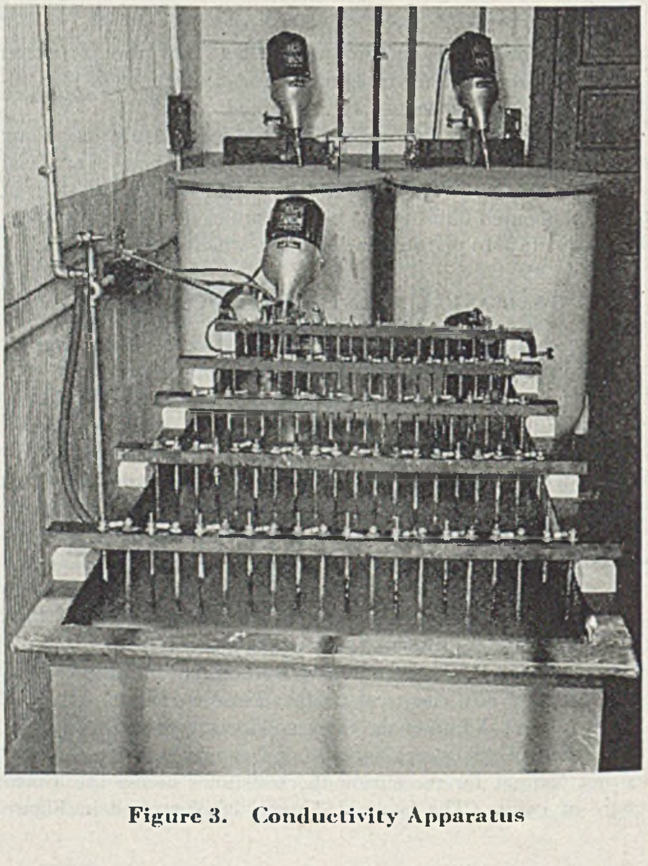

Figure 3. Conductivity Apparatus

quently plates out in or beneath the paint film in the form of metallic copper, offers an explanation of the time lapse before the paint film assumes the role of a good conductor.

Films of low pigment-volume ratio which showed high resistance to the passage of current developed the characteristic green or brownish color normally associated with films of this type immersed in sea water. Upon removal the films were firmly adhering and were removed in the form of a powder when scraped with a knife edge. On the other hand, films showing low electrical resistance, and which developed appreciable currents when coupled with steel, retained a bright metallic appearance, blistered, and thereby lost their adhesion to the Lucite. Uncoupled controls of high pigment-volume ratio behaved in exactly the same manner as did the coupled films of lower pigment concentration.

PERFORMANCE OF ANTIFOULING PAINTS

In order to establish the extent to which the observed data apply in a practical demonstration, a series of experimental paints was exposed at Miami Beach to determine the rate and extent of fouling which might show some correlation with conductivity data. For this study four pigments were selected as follows: (*a*) a high purity cuprous oxide (pyrochemical), (*b*) a proprietary copper pigment consisting of 85–87% metallic copper powder, the remainder being cuprous oxide, (*c*) a high purity copper flake, and (*d*) a copper powder analyzing above 99% metallic copper. Each sample of pigment was taken from a production batch. The pigments were dispersed in three matrices at pigment volume ratios of 12 and 36%. The composition of the matrices in weight % is shown in the following table:

	A	*B*	*C*
W. W. Rosin	87	75	75
Methyl abietate	12	20	5
Pliolite S-1	1	5	20

Three coats of each formulation were sprayed on panels of (*a*) wood, (*b*) steel primed with two coats of fast-dry anticorrosive primer (Navy Specification 52-P-18), and (*c*) primed steel on which a bare window 1-inch square was provided in the center of one side of the panel. The panels were exposed at the marine station of the Woods Hole Oceanographic Institution at Miami Beach, Fla. After 3 months the paints of 12% pigment-volume displayed no appreciable differences in their ability to prevent attachment of fouling (Table IV). These data describe the behavior of the pigments in matrix *A*. Corroborative evidence was obtained for matrices *B* and *C* but is not reproduced in this paper.

At the end of 3 months the panels of 12% pigment-volume were removed because of poor physical condition as manifested by severe checking and "alligatoring," shown subsequently to have resulted from the extremely low pigmentation. During the exposure of the samples inspections were made monthly; the paints were rated in terms of percentage of total surface area remaining free from fouling attachment. The efficiency of each pigment dispersed in matrix *A* at 36% pigment-volume is shown in Figure 4. Cuprous oxide demonstrates the highest degree of protection, all panels remaining perfectly clean (100% fouling resistance) for the full 8 months, whether applied to steel or wood. Figure 4 (top) shows that the copper pigment containing up to 15% cuprous oxide performs more efficiently over wood than over primed steel. Figure 4 (center and bottom) also demonstrates that a short life at high pigment-volume ratios may be expected for copper metal pigments applied to steel. This is in direct contrast to their behavior on wood, for which good performance is obtained over the total period of the experiment. Additional evidence substantially duplicating matrix *A* was obtained for the same pigments dispersed in matrices *B* and *C* (Table IV).

CONCLUSIONS

The data indicate that, under certain conditions, matrices pigmented with copper flake and copper powder at reasonably high

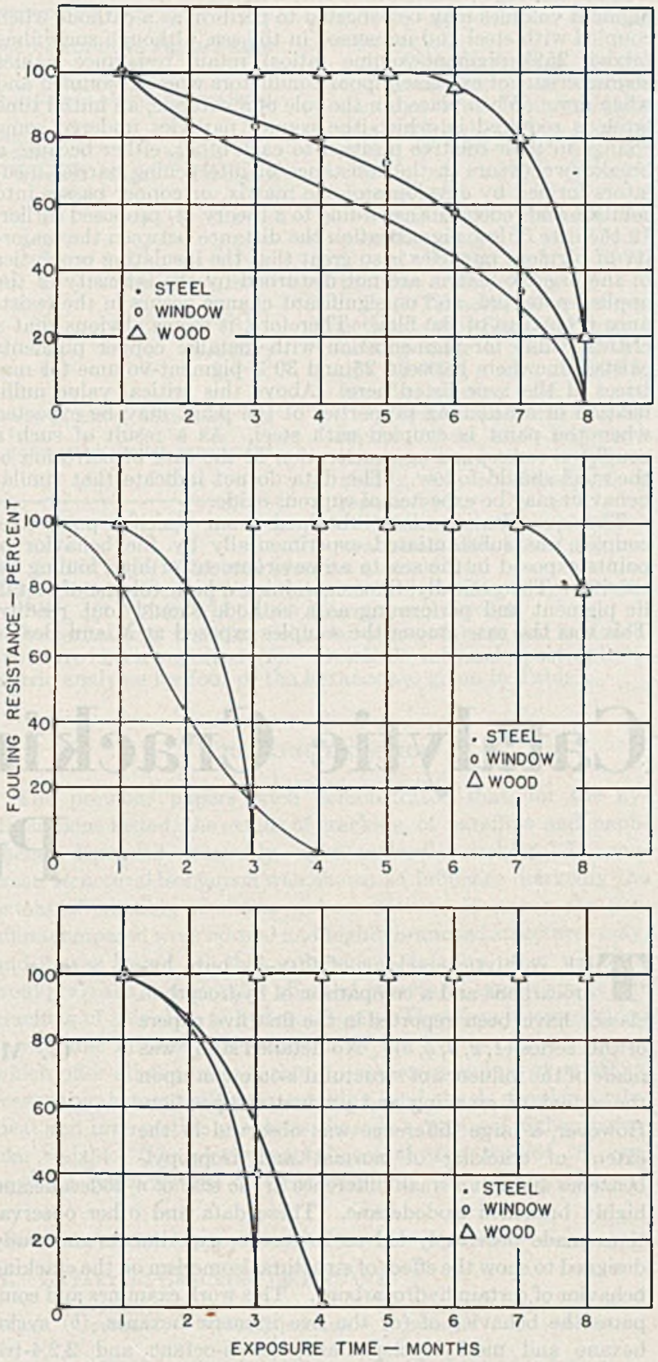

Figure 4. Antifouling Efficiency of Copper Pigments (*top*), Copper Flake (*center*), and Copper Powder (*bottom*) Dispersed in Matrix *A*

Table IV. Performance of 12% Pigment-Volume Paints in 3 Months

Panel No.	Pigment	Panel Material	Fouling Resistance by Months, % Protection 1	2	3
2	Cuprous oxide	Steel	100	91	100
23		Window	100	91	100
24		Wood	100	91	100
3	Copper pigment	Steel	100	88	100
24		Window	100	85	92
25		Wood	100	100	100
5	Copper flake	Steel	100	89	100
26		Window	100	100	100
47		Wood	100	100	100
6	Copper powder	Steel	100	100	100
27		Window	100	93	100
48		Wood	100	100	100

pigment volumes may be expected to perform as a cathode when coupled with steel and immersed in the sea, although such films (above 25% pigment-volume ratios) retain resistance values characteristic of extremely poor conductors when uncoupled and when dry. When placed in the role of a cathode, an initial time lapse is required in which the copper particles undergo some change in their relative position to each other, either because a breakdown occurs in the resistance of intervening barrier insulators formed by envelopes of the matrix, or copper passes into solution and redeposits according to a theory (*4*) proposed earlier. In the case of low pigmentation the distance between the majority of pigment particles is so great that the insulating properties of the organic matrix are not disturbed by the intensity of the applied potential, and no significant change occurs in the resistance properties of the film. Therefore, it seems obvious that a critical value for pigmentation with metallic copper pigments exists somewhere between 25 and 30% pigment-volume for matrices of the type listed here. Above this critical value nullification of antifouling properties of the paint may be expected when the paint is coupled with steel. As a result of such a couple, a corresponding acceleration in the rate of corrosion of the steel should follow. The data do not indicate that similar behavior may be expected of cuprous oxide.

The quantitative data obtained from specific paint-steel couples was substantiated experimentally by the behavior of paints exposed in the sea to an environment of high fouling intensity. Theoretically, films containing a high volume of metallic pigment and performing as a cathode should foul readily. This was the case among the samples exposed at Miami Beach. Similarly, less highly pigmented formulations (with metallic copper) perform equally well whether applied to steel or wood. Finally, cuprous oxide paints are apparently equally effective whether used over wood or metal, irrespective of pigment concentration.

ACKNOWLEDGMENT

The cooperation of Charles M. Weiss, Jr., of the Woods Hole Oceanographic Institution is gratefully acknowledged for exposing and reading the panels for the fouling tests at Miami Beach. Acknowledgment is due to E. F. Carlston and Scott Ewing of the Bureau of Ships for their interest and suggestions in the course of this investigation.

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Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Ill.

Catalytic Cracking of Pure Hydrocarbons

• • *CRACKING OF STRUCTURAL ISOMERS*

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Cracking of six sets of isomeric hydrocarbons over a silica-zirconia-alumina catalyst was studied, with emphasis on the behavior of the hexanes. Some large differences in rate of cracking and product composition were observed within these sets, which can be correlated with the carbon atom groupings of the isomers. In particular, tertiary carbons enhance the crackability markedly, and quaternary carbons act in the opposite way. Comparison of a paraffin and naphthene of selected C_{10} structure provides added information on cracking behavior.

THE catalytic cracking of fifty-six pure hydrocarbons and a comparison of hydrocarbon classes have been reported in the first five papers of this series (*1, 2, 3, 4, 5*). No detailed study was made of the influence of structural isomerism upon the extent of cracking and product composition. However, a large difference was observed in the extent of cracking of normal and isopropylbenzenes and but a small difference in the case of *n*-dodecane and highly branched isododecane. These data and other observations made previously led us to further experiments and study designed to show the effect of structural isomerism on the cracking behavior of certain hydrocarbons. This work examines and compares the behavior of (*a*) the five isomeric hexanes, (*b*) cyclohexane and methylcyclopentane, (*c*) *n*-octane and 2,2,4-trimethylpentane, (*d*) *n*-propylbenzene and isopropylbenzene, (*e*) three isomeric butylbenzenes reported earlier (*4*), (*f*) *n*-dodecane and isododecane reported in the first paper (*1*), and (*g*) Decalin and 2,7-dimethyloctane, a naphthene and paraffin of 10 carbon atoms each.

EXPERIMENTAL PROCEDURE

Definitions and terminology are the same as given in the first paper (*1*) except for the "percentage decomposed" or "extent of cracking" which now includes the hydrogen in the coke, as well as carbon, gas, and liquid boiling below the original, all summed on a no-loss weight basis. Hydrogen and carbon were determined by the burning of the catalyst deposit in an oxygen-nitrogen atmosphere, conversion of carbon monoxide formed to carbon dioxide over copper oxide, and absorption and weighing of the water and carbon dioxide produced. A different lot of U.O.P. cracking catalyst, type B, of slightly higher activity was used. This catalyst gives results similar to those obtained with the synthetic silica-alumina catalysts currently employed on a large scale in the petroleum industry.

Modifications in the original procedure (*1*) follow: Reaction products from the vertical catalyst tube were led directly to a still kettle cooled by solid carbon dioxide. Uncondensed gases passed through a meter to a 255-liter holder containing saturated magnesium sulfate brine. At the end of each process period the system was purged directly with 2.8 liters of nitrogen into the gas holder. For the experiments with Decalin and 2,7-dimethyloctane, 57 cc. of catalyst were used in a type 302 steel tube with an inside diameter of 1.58 cm., as described previously (*1*). Hexanes and octanes were cracked in a steel tube of 2.66 cm. i.d., with 209 and 90 cc. of catalyst, respectively. Methylcyclopentane and cyclohexane were cracked in a steel tube of 4.08 cm. i.d., with 200 cc. of catalyst. In the larger tubes silica chips

Table I. Infrared Analyses of Hexane Feed Stocks and of Liquid Products from Their Catalytic Cracking

(Temperature, 550° C.; process period, 60 minutes; LHSV, 0.5. Liquid product is C_6 and above, but material above C_6 was less than about 1%.)

	n-Hexane		2-Methylpentane[a]		3-Methylpentane		2,3-Dimethylbutane		2,2-Dimethylbutane	
	Feed	Product	Feed	Product	Feed	Product[b]	Feed	Product	Feed	Product
Hexane, wt. %										
n-Hexane	91.2	93.7	...	0	0.4	1.6	0.2	1	0.0	0.0
2-Methylpentane	3.4	2.2	90	90–95	13.4	12.8	4.8	8	1.3	2.5
3-Methylpentane	2.6	2.7	10	5–10	84.8	83.4	1.3	7	2.0	0.0
2,3-Dimethylbutane	1.2	1.0	...	1	1.4	2.2	92.2	83	0.3	0.5(1[c])
2,2-Dimethylbutane	1.6	0.4	...	0	0.0	0.0	1.5	1	96.4	97.0(93[c])
Bromine number	0.2	4.2	0.3	6.6	0.2	...	0.2	9.3	0.3	5.2

[a] Estimated values.

[b] From the run giving 27.1% conversion. The analysis of the product from the run at 23.7% conversion was also close to that of the feed, and bromine number was 1.0.

[c] Estimates for the run at 9.9% conversion. The detailed analysis is from an unreported similar experiment that gave a poor material balance.

were used to hold the catalyst in place; type 302 steel fillers served this purpose in the 1.58 cm. i.d. tube. The electric heater was model M32045 of the Hevi-Duty Electric Company, 62 cm. long and 7.6 cm. i. d., with four independent 220-volt units totaling 5.4 kilowatts. These were automatically controlled by a Celectray (C. J. Tagliabue Manufacturing Company), guided by four iron-constantan thermocouples incased in a stainless steel sheath which was set in a longitudinal groove in the Mechanite heat distribution block surrounding the catalyst tube. All experiments were made at atmospheric pressure.

Ultraviolet absorption was used for analyzing C_6 to C_8 aromatics and an infrared spectrophotometer for the hexanes. Liquid products were distilled in precision columns, usually of about ten theoretical plates, at 10 to 20 reflux ratio. Cut points were: C_6, 42-74° C.; C_7, 74-99° C.; C_8, 99-125° C. Olefin contents were computed from bromine numbers.

Properties and sources of hydrocarbons follow, with compounds arranged in order of increasing branching in sets of increasing molecular weight:

Cyclohexane (Eastman Kodak Company) was washed with concentrated sulfuric acid and distilled to a boiling range of 80–81° C., d_4^{20} 0.7826, n_D^{20} 1.4262, bromine number 0.5.

Methylcyclopentane from distillation of a California petroleum fraction had a boiling range of 71.8–71.9° C., d_4^{20} 0.7477, n_D^{20} 1.4095, bromine number 0.2.

n-Hexane (Shell Oil Company, Inc.) had a boiling range of 68.0–69.0° C., d_4^{20} 0.6613, n_D^{20} 1.3766, bromine number 0.2.

2-Methylpentane from hydrogenation of 2-methylpentenes had a boiling range of 59.6–66.0° C., d_4^{20} 0.6603, n_D^{20} 1.3730, bromine number 0.3. Analysis showed 10% 3-methylpentane (Table I).

3-Methylpentane was a distillation fraction of hydrogenated, catalytically cracked gasoline from Standard Oil Company of New Jersey (Louisiana Division). After treatment with silica gel it had d_4^{20} 0.6619, n_D^{20} 1.3755, bromine number 0.2, and analysis (Table I) indicated the presence of 13.4% 2-methylpentane.

2,3-Dimethylbutane from the alkylation of isobutane with ethylene had a boiling range of 56.5–57.3° C., d_4^{20} 0.6603, n_D^{20} 1.3732, bromine number 0.3.

2,2-Dimethylbutane from the isomerization of methylpentanes with aluminum chloride catalyst had a boiling range of 48.5–48.9° C., d_4^{20} 0.6542, n_D^{20} 1.3710, bromine number 0.3.

n-Octane from Eastman had a boiling range of 124–126.2° C., d_4^{20} 0.7025, n_D^{20} 1.3978, bromine number 0.16.

2,2,4-Trimethylpentane (isooctane) from Shell Oil had a boiling range of 98.6–99.4° C., d_4^{20} 0.6935, n_D^{20} 1.3925, bromine number 0.04.

Properties and cracking behavior of *n*- and isopropylbenzenes and the butylbenzenes have already been reported (*4*).

Decalin from Eastman, after treatment with silica gel, had d_4^{20} 0.8837, n_D^{20} 1.4755, and bromine number 0.4.

2,7-Dimethyloctane from Eastman had a boiling range of 158–160° C., d_4^{20} 0.7248, n_D^{20} 1.4089, bromine number 2.4.

Properties and cracking behavior of *n*-dodecane and isododecane have been reported (*1*). Detailed infrared spectrophotometric analyses for four of the hexanes are given in Table I.

CRACKING BEHAVIOR

The previous papers cited demonstrated that, for the hydrocarbons tested, the extent of cracking of paraffins and naphthenes depended primarily upon molecular weight. In contrast, structural isomerism was shown to influence markedly the extent of cracking of olefins and aromatics. However, the paraffins compared were normal and highly branched structures only, and it was stated (*1*) that subsequent data on other paraffins would reveal a considerable effect of structural isomerism on the cracking of this class of hydrocarbons. Therefore it was decided to examine in detail the behavior of the five isomeric hexanes, which offer all the basic carbon-to-carbon groupings of paraffins, reasonable susceptibility to cracking, and much simpler analytical and interpretive problems than do systems of higher molecular weight. The eleven naphthenes already studied (*3*) represent a wide variety of structures and demonstrate the pre-

Table II. Catalytic Cracking of Hexanes

Hydrocarbon	*n*-Hexane	2-Methylpentane	3-Methylpentane		2,3-Dimethylbutane	2,2-Dimethylbutane
Experimental conditions						
Temperature, ° C.	550	550	550	550	550	550
LHSV	0.52	0.45	0.50	0.49	0.49	0.49
Flow rate, moles/l./hr.	3.9	3.4	3.8	3.8	3.7	3.7
Process period, min.	60	45[a]	60	60	60	60
Gaseous product						
Moles/mole charge	0.296	0.492	0.620	0.510	0.638	0.249
Volume %						
H_2	9.4	9.1	8.8	7.8	7.7	10.1
CH_4	12.5	6.7	16.0	9.6	12.0	36.7
C_2H_4	12.7	7.3	16.3	7.9	6.5	12.0
C_2H_6	6.8	3.8	7.5	5.6	0.8	4.6
C_3H_6	32.2	40.7	31.6	40.3	41.2	18.8
C_3H_8	16.9	19.4	12.9	15.1	16.6	3.9
C_4H_6	0.4	0.0	0.0	0.0	0.0	0.0
Iso-C_4H_8	1.3	1.2	0.7	1.7	1.4	2.3
n-C_4H_8	2.2	2.0	1.0	2.1	2.5	2.6
Iso-C_4H_{10}	3.1	7.0	3.7	6.5	6.6	3.2
n-C_4H_{10}	1.5	1.0	0.7	1.5	1.2	0.3
C_5H_{10}	0.5	0.8	0.4	0.5	0.6	0.6
C_5H_{12}	0.5	1.0	0.4	1.4	2.9	4.9
Material balance, wt. % of charge						
Gas (including C_5)	13.0	24.3	25.6	24.2	30.8	9.3
Remaining product	82.1	73.8	69.6	79.5	67.4	87.6
Coke	0.1	0.2	0.3	0.5	0.5	0.3
Loss	4.8	1.7	4.5	−4.2	1.3	2.8
% decomposed, no-loss basis	13.8	24.9[a]	27.1	23.7	31.7	9.9

[a] The shorter process period implies somewhat severer cracking, but not enough difference to affect the relative results materially.

Table III. Catalytic Cracking of Naphthenes and Paraffins

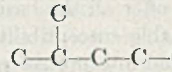
Hydrocarbon	Cyclohexane	Methylcyclopentane	n-Octane	Iso-octane	Decalin	2,7-Dimethyl octane
Experimental conditions						
Temperature, ° C.	550	550	550	550	500	500
LHSV	0.50	0.50	0.61	0.60	2.1	2.6
Flow rate, moles/l./hr.	4.6	4.5	3.7	3.6	13.5	13.3
Process period, min.	60	60	30	30	60	60
Gaseous product						
Moles/mole charge	0.350	0.582	0.967	1.216	0.725	0.746
Volume %						
H_2	48.7	30.0	12.3	11.5	21.3	3.2
CH_4	10.9	16.2	10.1	19.9	49.6[a]	3.3
C_2H_4	6.8	7.5	9.8	3.8	5.1	3.2
C_2H_6	2.5	2.5	6.1	1.8	...	0.5
C_3H_6	10.5	16.6	19.2	19.7	24.0[b]	36.8
C_3H_8	13.5	14.1	15.2	6.1	...	8.5
C_4H_6	0.0	0.0	0.0	0.2	...	0.0
Iso-C_4H_8	0.2	1.0	4.5	6.8	...	7.3
n-C_4H_8	1.1	1.7	6.6	7.5	...	10.1
Iso-C_4H_{10}	4.5	8.6	10.5	20.4	...	24.0
n-C_4H_{10}	1.3	1.8	5.7	2.3	...	3.1
Material balance, wt. % of charge						
Gas	8.3	18.3	30.3	38.4	20.5	24.4
Liquid below feed range	10.6	8.1	7.8	6.4	30.5	20.9
Feed range	63.8[c]	54.5			36.5	
Liquid above feed range	12.1	15.8	56.9	50.3	10.9	53.0
Hydrogen in coke	0.1	0.1	0.2	0.2	0.1	0.1
Carbon in coke	1.9	1.9	2.4	3.0	1.1	0.8
Loss	3.2	1.3	2.4	1.7	0.4	0.8
Boiling range of product considered as feed, ° C.	79-85	69-73	>120	>96	184-200	>152
% decomposed, no-loss basis	21.6	28.8	41.7	48.8	52.4	46.6

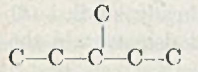
[a] Saturates in gas.
[b] Total olefins above C_2.
[c] Excluding benzene.

dominant influence of molecular weight over that of structure. Further study of this hydrocarbon class was directed primarily at a more exact determination of some small differences previously noted and their relation to structural isomerism.

Hexanes. The five isomeric hexanes were cracked at 550° C. and 0.5 LHSV (liquid hourly space velocity) with the results shown in Table II. The effect of structure is clearly demonstrated by the following approximate extents of cracking, in per cent by weight:

C—C—C—C—C—C 14


25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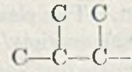
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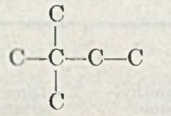
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Compared with the normal isomer, tertiary carbon groupings accelerate cracking and quaternary groupings decelerate it. As discussed later, this provides a qualitative explanation of the rather similar rates of cracking of n-dodecane and isododecane previously noted (*1*). The latter compound has one tertiary and two quaternary groups, which have opposite effects.

Examination of the gas analyses demonstrates that the chief products of hexanes cracking on a molar basis are propane and propylene, except for 2,2-dimethylbutane which not unexpectedly gives much methane. The surprising result is the predominance of C_3 in the gas from 3-methylpentane, since no simple, direct fission can produce C_3. Furthermore, the entire gas analysis resembles those for n-hexane and 2-methylpentane fairly closely. It will be noted that the experiment was repeated for verification. This problem is reviewed later in the text.

The liquid products were composed almost entirely of hexanes similar in composition to the starting materials. Table I gives infrared analyses. Isomerization was negligible except in the case of 2,3-dimethylbutane, which had 15% 2- and 3-methylpentanes in the liquid product compared with 6% in the feedstock. Assuming only 2,3-dimethylbutane cracked, the concentration of original 2- and 3-methylpentanes in the 67.4% product would be 9% at most; the remaining 6% would require isomerization of 4% of the feedstock, a minimum figure. On the basis of equal cracking of all components, 6% (by weight of charge) isomerization is indicated. It is concluded that direct isomerization of hexanes is of small importance.

The amounts of olefins in the liquid products were low, ranging from 2 to 5 weight per cent. Traces of benzene and toluene were found in some of the runs.

Cyclohexane and Methylcyclopentane. These two naphthenes were cracked previously (*3*) at 500° C. and 1.5 LHSV, and decomposed 6 and 9 weight per cent, respectively, on a no-loss basis. To magnify the cracking, these tests were repeated at 550° C. and 0.5 LHSV with the results shown in Table III. The percentages decomposed to lower boiling materials and coke were 22 and 29, respectively, verifying the greater susceptibility of methylcyclopentane, which contains a tertiary carbon atom. The chief product of molecular fission in both cases was propane-propylene.

The data in Table III, and the liquid product yields given in Table IV, show that there was also considerable formation of higher boiling material and some isomerization. The percentage decomposed, as defined, does not fully portray the reactivity of these compounds; thus, isomerized material and benzene are counted as part of the "decomposed" in the case of cyclohexane but not in the case of methylcyclopentane, because of the boiling point relations. If we include the higher boiling materials and the benzene formed, but not the isomerized C_6 naphthenes, the percentages reacted on a no-loss basis are 26.0 for cyclohexane and 42.8 for methylcyclopentane. These figures are derived from the following breakdown of products, given in weight per cent on a no-loss basis:

	Cyclohexane	Methylcyclopentane
Gas and lower aliphatics	10.3	26.8
Isomerized naphthene	8.1	2.0 (estd.)
Unchanged naphthene	65.9	55.2
Benzene	1.1	0.1
Remaining higher boiling	12.5	13.9
Coke	2.1	2.0
	100.0	100.0

The modified calculation again shows the methylcyclopentane to be more reactive. The appreciable formation of higher boiling products from the naphthenes is in contrast to the very slight formation of such materials from the paraffins. For the sake of consistency and because of the practical interest in lower boiling products, we shall continue to use the percentage decomposed as defined above in discussing the reactivities of various hydrocarbons, although bearing in mind the additional reactivity of naphthenes which leads to higher boiling products. Refractive indices show that these higher boiling materials, especially above 150° C., are rich in aromatics.

n-Octane and 2,2,4-Trimethylpentane. In the first paper (*1*) n-heptane and 2,2,4-trimethylpentane (iso-octane) provided

Table IV. Yields of Liquid Products from Catalytic Cracking of Cyclohexane and Methylcyclopentane

(Temperature, 550° C.; LHSV, 0.5; process period, 60 minutes)

Hydrocarbon	Cyclohexane	Methylcyclopentane
Product, wt. % of charge		
C_5	0.2	0.7
C_6 aliphatics[a]	1.4	7.4
Lower boiling C_6 naphthenes	7.9	0.0
Benzene	1.1	0.1
Feed boiling range	63.8[b]	54.5
Above feed to 150° C.	6.5	8.1[b]
150–254° C.	4.6	7.2
Above 254° C.	1.0	0.4
Olefin content, wt. %		
Below feed boiling range	14	18
Feed range and above	3	4

[a] Total 42–69° C. product.

[b] Excluding benzene.

data for the comparison of structural isomers, since a small interpolation along the curve for normal paraffins indicated that *n*-octane should crack to the extent of about 5% while iso-octane was 8.5% decomposed. In view of the great difference in structure, the similarity in cracking rates was considered noteworthy. The present tests under somewhat more severe conditions, 550° C. and 0.6 LHSV, provide a better comparison and serve to confirm the earlier results. As Table III shows, the weight percentages decomposed of *n*- and iso-octane were about 42 and 49, respectively. Compared with the two- to threefold differences in rates observed among the isomeric hexanes, *n*- and iso-octane show similar susceptibilities to cracking. In the hexane series tertiary carbon groupings favored cracking and quaternary groupings did the reverse. Iso-octane contains one of each type, and it is concluded that they act in compensating fashion to yield the observed results. The gas analyses show that iso-octane produces larger quantities of methane and C_4 hydrocarbons than *n*-octane, which may be associated with the particular structure of iso-octane.

Decalin and 2,7-Dimethyloctane. In a comparison of hydrocarbon classes (*4*), it was concluded that naphthenes crack considerably faster than normal paraffins. Approximate rate ratios of 2 to 3 were assigned for the C_{10} to C_{18} range of compounds. The explanation of this behavior may be sought both in the intrinsic properties of a cyclic structure and in the types of carbon groupings common to both aliphatic and alicyclic hydrocarbons. To explore this question, Decalin (decahydronaphthalene) and 2,7-dimethyloctane, each containing two tertiary carbon atoms, were cracked at 500° C. and about 13.4 moles per liter per hour, with the results shown in Table III. The extents of cracking were 52.4 and 46.6 weight per cent, respectively, a similarity quite at variance with the rate ratios just cited. In contrast, *n*-decane has a predicted extent of cracking of only 10% under these conditions (*1*, Figure 2). A comparison of the distribution of carbon groupings in these compounds follows (primary, secondary, tertiary, and quaternary groupings are designated as P, S, T, and Q): *n*-decane, 2P, 8S; 2,7-dimethyloctane, 4P, 4S, 2T; Decalin, 8S, 2T. This comparison indicates that the presence of tertiary groupings has such an important influence upon the cracking rate of paraffins that certain isomers will crack as readily as naphthenes of the same carbon number. The near equality in rates of cracking does not mean that the products are the same; they may be radically different, as Table V shows.

Higher boiling products were formed from Decalin in appreciable amounts but were not included in the percentage decomposed. If they are included, the total percentage reacted becomes 63.3. As noted under cyclohexane, this basis of computation is not further used in the present discussion.

Butylbenzenes. Normal, secondary, and tertiary butylbenzenes were cracked (*4*) at 400° C. and about 2 LHSV to the extents of 13.9, 49.2, and 80.4 weight per cent, respectively. The chief reaction was the removal of the entire butyl group from the aromatic ring. Here the greatest cracking again occurred with all the paraffinic carbon atoms in a tertiary grouping. However, the paraffinic carbon atom linked to the ring in *tert*-butylbenzene also may be viewed as quaternary, since all four valences are occupied by carbon. Therefore, an important categorical distinction must be observed in classifying the carbon groupings encountered in aromatic compounds with respect to catalytic cracking, which requires that only the paraffinic carbon atoms be counted in assigning the groupings. Thus, the butylbenzenes have the following distributions of carbon groupings: normal, 2P, 2S; secondary, 2P, 2S; tertiary, 3P, 1T. In addition, the grouping of the carbon atom attached to the aromatic ring must be taken into account, which in this case is P, S, and T, respectively, following standard nomenclature for substituted alkanes. The observed rates of cracking then fall in the same order as would be predicted from the results on other hydrocarbons presented here.

Propylbenzenes. Further confirmation of these relations is obtained from the results of cracking normal and isopropylbenzenes at 500° C. and 1.9 LHSV (*4*), which decomposed 43 and 84 weight per cent, respectively. The alkyl carbon atoms have the same grouping in both compounds—namely, 2P, 1S; however, the groupings attached to the ring are P and S, respectively, which again demonstrates the large differences in cracking rate produced by the type of linkage in these structural isomers.

Table V. Analysis of Liquid Products from Catalytic Cracking of Decalin and 2,7-Dimethyloctane

(Temperature, 500° C.; process period, 60 minutes)

Hydrocarbon	Decalin	2,7-Dimethyloctane
LHSV	2.1	2.6
Product, wt. % of charge		
42–99° C.	15.4	8.7
99–152° C.	8.2	1.7
Analysis of cuts, wt. %		
42–99° C.		
Olefins	15.3	40.4
Naphthenes	57.8	59.6[a]
Paraffins	19.8	
Benzene	5.6	
Toluene	1.5	
99–152° C.		
Olefins	9.8	88.0[a]
Naphthenes and paraffins[a]	27.4	
Benzene	0.5	0.0
Toluene	31.0	6.0
Ethylbenzene	5.0	0.0
o-Xylene	7.0	0.6
m-Xylene	12.9	3.8
p-Xylene	6.4	1.6

[a] By difference.

n-Dodecane and Isododecane. The catalytic cracking of these materials was studied in some detail (*1*). At 500° C. the extents of cracking were 18 and 13% and at 550° C. were 34 and 32%, respectively. The somewhat larger losses of material in the runs at 500° C. lead us to place more reliance on the runs at 550° C. The isododecane was obtained from the hydrogenation of tri-isobutene from the cold-acid polymerization of isobutene, and is considered to be chiefly 2,2,4,6,6-pentamethylheptane. This structure contains 7P, 2S, 1T, and 2Q carbon groupings, and the results indicate that compensating influences are at work which reduce its rate of cracking even below that of *n*-dodecane. It is also evident that a highly branched paraffin cracks no more readily than the normal isomer unless the carbon groupings are of a particular type. In isododecane the two quaternary groupings appear completely to offset the favorable influence of the tertiary grouping. It seems difficult at present to assign any general quantitative significance to the relative numbers of primary and secondary groupings with respect to the rate of cracking. Compounds containing large numbers of primary groupings tend to produce more methane than the normal isomers, which indicates a definite effect upon product composition.

TABLE VI. SUMMARY OF DATA ON STRUCTURAL ISOMERISM

Hydrocarbon	Carbon Groupings	Extent of Cracking, Wt. %	Conditions
Cyclohexane	..., 6S	22	A
Methylcyclopentane	1P, 4S, 1T	29	A
n-Hexane	2P, 4S	14	A
2-Methylpentane	3P, 2S, 1T	25	A
3-Methylpentane	3P, 2S, 1T	25	A
2,3-Dimethylbutane	4P, ..., 2T	32	A
2,2-Dimethylbutane	4P, 1S, ..., 1Q	10	A
n-Octane	2P, 6S	42	A'
Iso-octane	5P, 1S, 1T, 1Q	49	A'
n-Decane	2P, 8S	10[a]	B
2,7-Dimethyloctane	4P, 4S, 2T	47	B
Decalin	..., 8S, 2T	52	B
n-Dodecane	2P, 10S	34	C
Isododecane	7P, 2S, 1T, 2Q	32	C
n-Propylbenzene	1P, 1P, 1S	43	B
Isopropylbenzene	2P, $\underline{\text{1S}}$	84	B
n-Butylbenzene	1P, $\underline{\text{1P}}$, 2S	14	D
sec-Butylbenzene	2P, $\underline{\text{1S}}$, 1S	49	D
tert-Butylbenzene	3P, $\underline{\text{1T}}$	80	D

Conditions	Temp., ° C.	LHSV	Moles/Liter/Hour	Process Period, Min.
A	550	0.5	3.4– 4.6	60
A'	550	0.6	3.6– 3.7	30
B	500	1.9–2.6	13.3–13.8	60
C	550	3.1–3.2	13.6–14.1	60
D	400	1.9–2.1	12.3–13.2	60

[a] Estimated from Figure 2 of the first paper (*1*).

EFFECT OF STRUCTURAL ISOMERISM

A number of consistent relations between structural isomerism and extent of cracking have been demonstrated for several groups of isomeric hydrocarbons. It would be useful if these findings could provide a basis for generalizations covering a wide range of molecular weights and types for at least the paraffins and naphthenes. Aside from the alterations in relative rates of cracking of any two hydrocarbons introduced by change of experimental conditions, the diagrams for the effect of molecular weight on the cracking of normal paraffins (*1*, Figure 2) and of naphthenes (*3*, Figure 4) indicate that these relations are not simple functions and are different for the two hydrocarbon classes. Thus, additional correlation factors would be required for the computation of the relative extents of cracking of either two members of a homologous class or of any given paraffin-naphthene pair.

The clearest point established in these experiments is the accelerating influence of a tertiary carbon atom in paraffins, naphthenes, and alkyl groups attached to aromatic rings, upon the extent of cracking (Table VI).

The effect of a quaternary grouping appears to be definite for 2,2-dimethylbutane, although some doubt arises from the circumstance that the largest group attached to the quaternary carbon has only two carbon atoms. All prior work indicates that fragments smaller than three carbon atoms are removed with difficulty.

In the cases of iso-octane and isododecane, this difficulty does not arise, and it appears that the presence of a tertiary grouping offsets the effect of the quaternary. The concurrent changes in the number of primary and secondary carbons seem to be of less importance.

The series *n*-decane, 2,7-dimethyloctane, and Decalin strikingly illustrates the influence of tertiary groups. Comparison of the two latter shows that the presence of much primary carbon in 2,7-dimethyloctane has little effect.

The relations among the alkyl aromatics tested are particularly regular. Here, the type of paraffinic carbon grouping attached to the benzene ring (underlined in Table VI) determines the extent of cracking, increasing in the order primary, secondary, tertiary. The contrast between primary and secondary paraffinic carbon in these compounds may be ascribed to the fact that cracking predominantly occurs at only one linkage in the molecule, at which point the grouping of the attached paraffinic carbon is of prime importance.

Among the petroleum naphthenes as a class, only cyclopentane and cyclohexane are lacking in tertiary groups (all higher homologs contain at least one, except in the special cases of geminate substitution); linked and condensed ring naphthenes usually contain several. For this reason, it is difficult to make an estimate of the influence of ring structure alone upon the cracking of naphthenes. The results on the hexanes and 2,7-dimethyloctane clearly show that certain paraffins may crack about as well as naphthenes of the same carbon number. From a practical standpoint the preferred position of naphthenic cracking stocks in refinery operations (*4*) remains rather generally true because of the large proportion of normal isomers found in the paraffinic portion of most of the more abundant petroleums.

The effect of structural isomerism upon the nature of the cracked products varies in importance according to circumstances. However, examination of the size and structure of a hydrocarbon in the light of present knowledge can lead to useful predictions of cracking behavior. For example, certain structural units tend to persist in the products of catalytic cracking, particularly if they are bound in the original molecule by a linkage unusually susceptible to cracking. Thus, both normal and isopropylbenzenes yield largely benzene and propylene. Secondary and tertiary butylbenzenes show greatly different ratios of normal to isobutene in the cracked gas, despite the possibility of isomerization. Similarly, methylcyclopentane and iso-octane show a higher ratio of iso- to normal butane than do their isomers. Decalin, with a hexahydroaromatic structure, produces far more aromatics than a paraffin of the same carbon number. Aromatic rings are very stable and, regardless of the isomerism occurring in attached groups, tend to preserve their original structures, and lose only the more easily removed substituents. A large number of methyl groups in highly branched structures encourages the production of methane, although 2,3-dimethylbutane appears to be an exception. Other examples of persistence of structural units may be found in prior papers of this series. Thus, di- and tri-isobutenes revert primarily to the monomer isobutene (*5*); *n*-octenes yield more normal than isobutene. However, some of these differences may be markedly reduced if severe cracking conditions are imposed, particularly with respect to the ratio of iso to normal aliphatics which is especially susceptible to the temperature of cracking.

The cracking of 3-methylpentane to much C_3 and relatively little C_4 or C_2 is of particular interest. Most of the C_3 derived from 3-methylpentane is believed to arise during the primary cracking reaction and not from the subsequent cracking of larger fragments such as C_4 or C_5. Therefore, rearrangement of 3-methylpentane during the cracking reaction must take place to account for the observed C_3 production. It is further indicated that isomerization of 3-methylpentane independently of the cracking reaction is negligible, since the composition of the recovered hexanes is almost identical with that of the feedstock within the limits of analytical accuracy.

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Extrusion Properties of High Polymers with Included Crystalline Filler

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The rate of flow-stress curves for three types of crystalline filler in several high polymer binders was obtained by using an experimental extrusion press as a viscometer. With one exception, the high polymer systems studied exhibited exponential-type flow with pressure. The exception showed plastic flow. Addition of crystalline filler to the binders above 50% by weight caused a rapid increase in the apparent viscosity and tended to emphasize the exponential shape of the flow curves. Fine fillers gave the greatest increase in apparent yield point and in apparent viscosity, and the closest approach to theoretical density. Anomalous low viscosities obtained with fillers bearing —N—NO_2 and —O—NO_2 groups in Paraplex binders gave indication of the presence of a surface-active phenomenon around the filler particles. With increase of filler content the viscous volume of the flow segment tended to decrease in size, and the amount of decrease was in the order of increasing molecular weight of the polymer binder. It also appeared from the relative change in viscous volume that the real resistance to flow on addition of filler was in the fluid phase.

MANY high polymer materials, and materials consisting of high polymer and fillers, exhibit non-Newtonian flow, so that in most cases they cannot be characterized by a single viscosity coefficient. This necessitates the determination of the flow-stress curve over the range of stresses under consideration rather than the use of standard flow assessing methods which consider the rate of flow at one pressure only.

The causes of non-Newtonian flow have been discussed by Kauzmann and Eyring (*1*), and they conclude that this type of flow occurs either when a change of structure or of flow mechanism appears, or when the energy supplied in pushing the unit of flow into an empty hole is of the order of kT. The first alternative leads to what the authors define as thixotropy and plastic flow. Thixotropy on this model occurs when cross-linking bonds are breaking and re-forming at a given equilibrium rate, imposing a retarding force on the material. However, with faster rates of shear the rate of breaking increases until finally no bonds remain between any two moving planes, and the flow is again Newtonian. This definition is to be distinguished from the more general one which defines thixotropy simply as a decrease in shearing force with increasing rates of shear. In the case of plastic flow, increasing rates of shear promote the re-formation of bonds so that the equilibrium is independent of the shear rate, and a state arises where a constant retarding force is acting. If the non-Newtonian flow is due to the fact that the energy required to push a flow unit into an empty hole is of the order of kT, then the application of transition state theory results in the hyperbolic sine relation of Eyring (*3*, *4*).

It is considered that the work described here may be of technical interest, since the published literature of the flow of heterogeneous systems seems to be confined largely to particles in a low viscosity medium, such as clays or paints. High polymers mixed with crystalline fillers apparently have not been extensively described in the literature.

EXPERIMENTAL PROCEDURE

The rates of extrusion of a number of high polymers and high polymer–filler combinations were measured by extruding the material through a small die in an experimental press (Figure 1). The press was jacketed and heated by a steam-water mixture, and its temperature could be regulated within 1° C. The pressures measured were those on the ram rather than those directly at the die. However, as pointed out by Nason (*2*), who used a similar type of apparatus, friction losses in the cylinder head are apt to be negligible, and most of the shearing occurs in the die. The materials tested were extruded at different pressures, the amount extruded being determined by weighing. In these experiments the times of extrusion were approximately the same. The density of the extruded material was also obtained in order to allow conversion to volume units.

The range of materials investigated is given in Table I. This table is arranged in order of increasing filler content in each family of binders, in order to bring out fundamental relations between both fillers and binders.

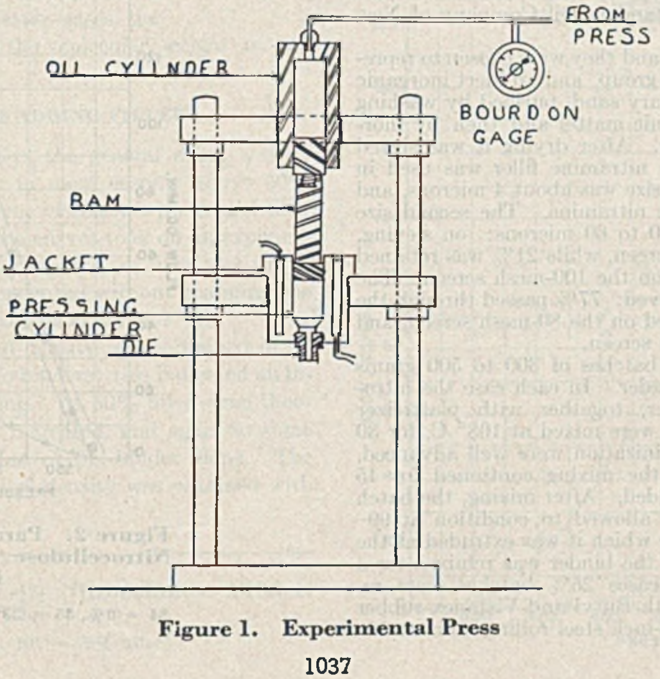

Figure 1. Experimental Press

MATERIALS

The properties and nature of the materials used are briefly as follows: Paraplex is a condensed dibutyl sebacate manufactured by The Resinous Products and Chemical Company. In the experiments described in this paper, type G-25 was used. The polyvinyl acetate used was type V $1^1/_2$ manufactured by Canadian Resins and Chemical Company Ltd. N.C.1 refers to a propulsive soluble nitrocellulose manufactured by

Table I. Properties of Binder-Filler Systems Studied

Chemical Composition								Physical Properties					
										Apparent viscosity in poises at rates of flow of			
Batch No.	Filler, %	Type of filler	N.C., %	Type of N.C.	Paraplex, %	Polyvinyl acetate, %	Others, %	Theoretical density, %	Apparent yield point	10 cc./min.	50 cc./min.	100 cc./min.	λA, Cu. Cm.
84	..	....	20	1	80	..	....	91.2	120	6,910	6,910	6,910	....
84R	..	....	20	1	80	..	....	...	150	4,140	4,140	4,140	....
84R2	..	....	20	1	80	..	....	90.6	150	3,040	3,040	3,040	....
115	..	....	20	1	80	..	....	93.2	160	4,240	4,240	4,240	....
81	..	....	20	5	80	..	....	93.2	210	46,100	18,000	...	1.5×10^{-20}
88	..	....	20	1	..	68	Dibutyl phthalate, 12	92.8	210	32,900	...	14,000	1.0×10^{-20}
88A	..	....	20	1	..	60	Dibutyl phthalate, 20	92.8	210	24,300	...	13,400	9.1×10^{-21}
111	..	....	..	...	..	..	Butyl rubber, 100	100	400	33,300	...	4,060	2.1×10^{-20}
113	..	....	..	...	..	..	Vistonex rubber, 100	100	700	34,000	...	6,670	2.7×10^{-20}
84	..	....	20	1	80	..	....	91.2	120	6,910	6,910	6,910	....
85	25	Nitramine	15	1	60	..	....	88	120	5,070	5,070	5,070	....
86	50	Nitramine	10	1	40	..	....	90.5	120	7,000	7,000	7,000	....
87	75	Nitramine	5	1	20	..	....	91.4	120	28,200	...	...	....
115	..	....	20	1	80	..	....	93.2	160	4,240	4,240	4,240	....
100	50	Sand	10	1	40	..	....	94.9	150	8,770	...	3,330	2.4×10^{-20}
101	75	Sand	5	1	20	..	....	91.0	300	24,400	...	6,670	2.6×10^{-20}
115	..	....	20	1	80	..	....	93.2	160	4,240	4,240	4,240	....
102	50	Nitrate	10	1	40	..	....	90.7	120	5,640	5,640	5,640	....
104	75	Nitrate	5	1	20	..	....	93.0	500	25,000	...	...	2.9×10^{-20}
103	80	Nitrate	4	1	16	..	....	95.2	4000	About 23×10^6	...	...	....
115	..	....	20	1	80	..	....	93.2	160	4,240	4,240	4,240	....
117	25	Fine nitramine	15	1	60	..	....	91.7	120	3,690	3,690	3,690	....
105	50	Fine nitramine	10	1	40	..	....	98.5	240	18,800	...	6,960	1.6×10^{-20}
106A	75	Fine nitramine	5	1	20	..	....	94.5	900	52,000	...	...	1.7×10^{-20}
106	75	Fine nitramine	5	1	20	..	Incorporated with acetone	94.0	550	25,000	...	5,200	2.6×10^{-20}
81	..	....	20	5	80	..	....	93.2	210	46,000	18,000	...	1.5×10^{-20}
82	25	Nitramine	15	5	60	..	....	93.2	210	38,800	12,900	...	1.4×10^{-20}
83	50	Nitramine	10	5	40	..	....	96.0	170	46,500	22,000	...	1.3×10^{-20}
43B	75	Nitramine	5	5	20	..	....	93.0	210	64,800	22,400	...	1.2×10^{-20}
88	..	....	20	1	..	68	Dibutyl phthalate, 12	92.8	210	32,900	...	14,000	1.0×10^{-20}
89	25	Nitramine	15	1	..	51	Dibutyl phthalate, 9	87.0	170	46,000	...	12,800	1.0×10^{-20}
88A	..	....	20	1	..	60	Dibutyl phthalate, 20	92.8	210	24,300	...	13,400	9.7×10^{-21}
89A	50	Nitramine	10	1	..	30	Dibutyl phthalate, 10	90.0	140	50,700	23,400	...	9.5×10^{-21}
90	75	Nitramine	5	1	..	15	Dibutyl phthalate, 5	91.5	210	70,000	...	...	8.3×10^{-21}
111	..	....	..	...	..	..	Butyl rubber, 100	100	400	33,300	...	4,070	2.1×10^{-20}
112	75	Nitramine	..	...	..	..	Butyl rubber, 25	86	400	56,400	...	...	1.9×10^{-20}
113	..	....	..	...	..	..	Vistanex rubber, 100	100	700	34,000	...	6,670	2.7×10^{-20}
114	75	Nitramine	..	...	..	..	Vistanex rubber, 25	86.0	700	88,200	...	...	1.1×10^{-20}
120	80	Nitramine	..	...	..	..	Low molecular weight Vistanex rubber, 20	..	..	....	...	...	1.6×10^{-20}
115	..	....	20	1	80	..	....	93.2	160	4,240	4,240	4,240	....
116	25	Nitramine	15	1	60	..	....	90.8	150	3,130	3,130	3,130	....
117	25	Fine nitramine	15	1	60	..	....	91.7	120	3,690	3,690	3,690	....

the displacement process; its nitrogen content was 12.2% and its intrinsic viscosity, $\log_e (\eta_{\text{rel.}})/c$, in *n*-butyl acetate at a concentration of 0.05 gram per 100 ml., was 3.3. N.C.5 refers to a blasting soluble nitrocellulose manufactured by the mechanical process; its nitrogen content was 12.2%, and its intrinsic viscosity in *n*-butyl acetate was 10.7%. The Butyl rubber used was type GR-1-50 obtained from Polymer Corporation Ltd., and the Vistanex rubber, type B-120, molecular weight 120,000, was obtained from The Standard Oil Company of New Jersey.

Three types of fillers were used, and they were chosen to represent a nitramine group, a nitrate group, and an inert inorganic group. The last named was ordinary sand, purified by washing with chromic acid to remove organic matter and then by thorough washing with distilled water. After drying it was sieved through an 80-mesh screen. The nitramine filler was used in two sizes. In the first the crystal size was about 4 microns, and this material is referred to as fine nitramine. The second size contained crystals ranging from 10 to 60 microns; on sieving, 67% passed through a 200-mesh screen, while 21% was retained on the 200-mesh screen and 12% on the 100-mesh screen. The third, the nitrate filler, was also sieved; 77% passed through the 80-mesh screen, 17.5% was retained on the 80-mesh screen, and 4.5% was retained on the 60-mesh screen.

These materials were mixed in batches of 300 to 500 grams in a small brass sigma-bladed kneader. In each case the nitrocellulose and other high polymer, together with plasticizer where polyvinyl acetate was used, were mixed at 108° C. for 30 minutes. When mixing and gelatinization were well advanced, the filler was added slowly and the mixing continued for 45 minutes after all filler had been added. After mixing, the batch was transferred to the press and allowed to condition at 99–100° C. for 30 to 60 minutes, after which it was extruded at the same temperature. In most cases the binder was remixed for a binder-filler batch, but in some cases 25% batches were reincorporated with more filler. With Butyl and Vistanex rubber incorporation was carried out on 8-inch steel rolling mills at 60–100° C. The rolled batches were then conditioned in the press and extruded.

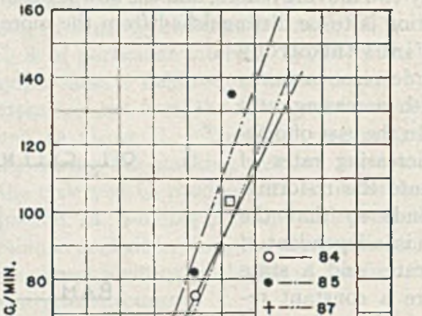

Figure 2. Paraplex–Low Viscosity Nitrocellulose Binder, Nitramine Filler

84 = 0%, 85 = 25%, 86 = 50%, 87 = 75% filler

RESULTS

The data obtained were analyzed by plotting the rate of flow in cc. per minute against pressure (Figures 2–9). From these curves the apparent viscosities at rates of flow of 10, 50, and 100 cc. per minute were obtained by applying the Poiseuille equation. With the apparent yield points, these are listed in Table I along with the per cent theoretical densities (actual density divided by theoretical density), the theoretical density being calculated by assuming additivity of constituent densities.

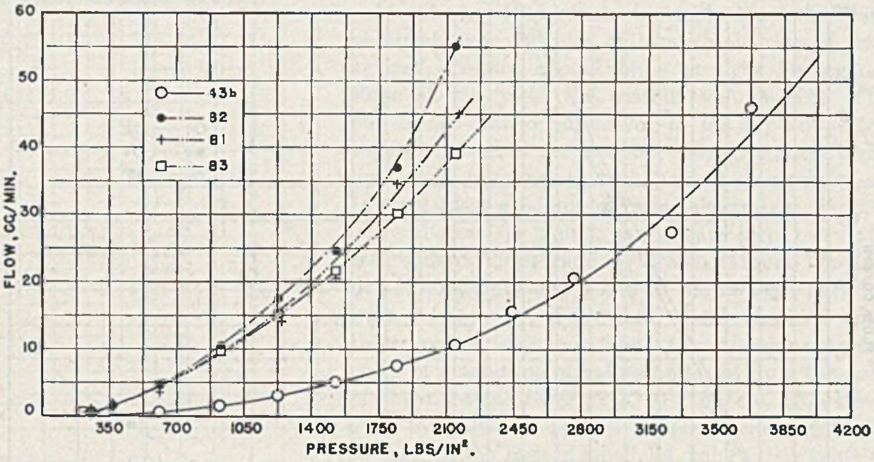

Figure 3. Paraplex–High Viscosity Nitrocellulose Binder, Nitramine Filler

81 = 0%, 82 = 25%, 83 = 50%, 43B = 75% filler

FLOW PROPERTIES OF BINDERS

Four batches of binder 84 are shown in Table I (84, 84R, 84R2, and 115). With polymeric materials it is known that mixing time, moisture content, maturing time, and several other factors markedly influence the viscosity of the resulting gel. The reproducibility of different batches was therefore within the usual limits for this material in semiplant manufacture. However, in order to minimize any effect from different batches, the same batch of binder was used throughout each family of curves. Duplication of flow reading on any one batch was possible within ±3%.

The first section of Table I lists the various binders used for this work. A comparison of their properties given in the table and the figures showed that, with nitrocellulose of low intrinsic viscosity (batches 84 and 115), plastic flow was obtained, and the rate of flow was linearly dependent on pressure. When the nitrocellulose was changed to that of high intrinsic viscosity (batch 81), the flow curve was no longer linear but appeared to be exponential with pressure. Batches 88 and 88A differed only in that the latter had less polyvinyl acetate and more dibutyl phthalate. The effect of this change altered merely the slope of the flow pressure curve and not its general shape. With rubber binders (batches 111 and 113) the exponential-type curve was again apparent; in these latter cases the slopes of the curves varied with the molecular weight of the components used.

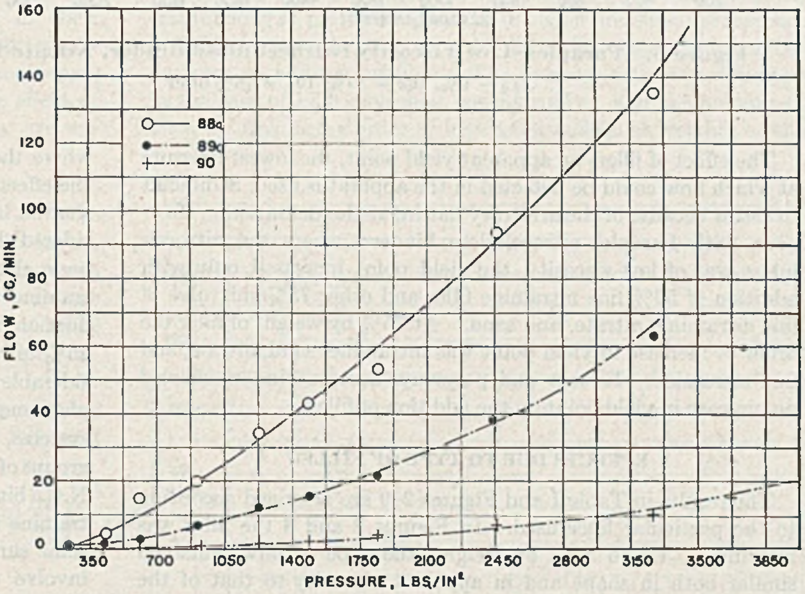

Figure 4. Gelva-Nitrocellulose Binder, Nitramine Filler

88A = 0%, 89A = 50%, 90 = 75% filler

GENERAL EFFECTS OF ADDING FILLER

When filler was added to binders, the general effect was an increase in the apparent viscosity in most cases. Above 50% filler the rate of increase in apparent viscosity with added filler became marked, and in all cases the curves took on an exponential form. At high concentrations the effect of filler was to decrease the rate of climb of the exponential without changing the general characteristic form of the curves (Figures 2–9).

Decreases in per cent theoretical density were obtained in all cases on the addition of 25% filler to binders; this indicated an increase in air inclusion during mixing. At 50% filler some theoretical densities decreased, others increased, and again in some cases no change occurred from that of the binder alone. The highest value for per cent theoretical density was obtained with fine nitramine filler.

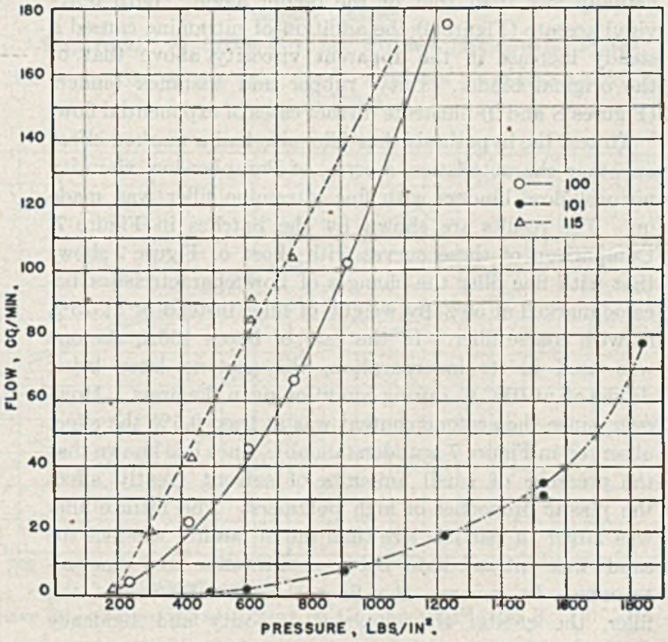

Figure 5. Paraplex–Low Viscosity Nitrocellulose Binder, Sand Filler

115 = 0%, 100 = 50%, 101 = 75% filler

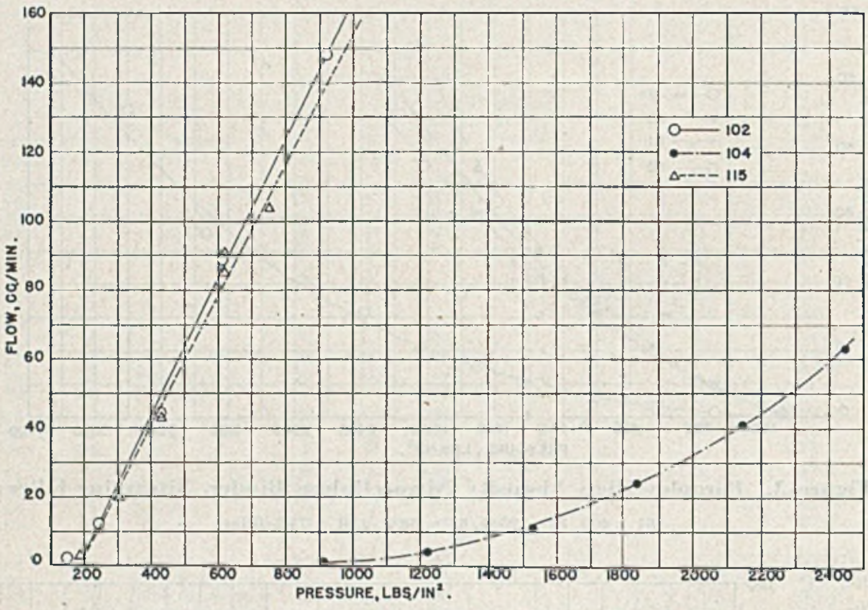

Figure 6. Paraplex–Low Viscosity Nitrocellulose Binder, Nitrate Filler

115 = 0%, 102 = 50%, 104 = 75% filler

The effect of fillers on apparent yield point, the lowest pressure at which flow could be detected in the apparatus used, is difficult to assess because of the arbitrary nature of the definition. However, with Paraplex-nitrocellulose binders, where the nitrocellulose was of low viscosity, the yield point increased only with addition of 50% fine nitramine filler and other 75% mixtures of fine nitramine, nitrate, and sand. At 75% by weight of filler the order of increase in yield point was nitramine, sand, nitrate, and fine nitramine. Rubber and polyvinyl acetate binders showed no increase in yield point on the addition of filler.

EFFECTS DUE TO TYPE OF FILLER

The results in Table I and Figures 2–9 are arranged according to the particular filler used. In Figures 2 and 3 the filler was nitramine. Up to 50% by weight, the type of flow remained similar both in shape and in apparent viscosity to that of the binder alone—that is, plastic with low viscosity nitrocellulose in Figure 2, exponential in Figure 3. In fact the apparent viscosity of the batch with 25% filler was actually less than that of the binder alone. With polyvinyl acetate (Figure 4) the addition of nitramine caused a steady increase in the apparent viscosity above that of the original binder. Butyl rubber and Vistanex binders (Figures 8 and 9) illustrate further cases of exponential flow.

To test the hypothesis that filler size had a marked effect on other characteristics, a series of Paraplex-low viscosity nitrocellulose binders with fine nitramine filler was made up. The results are shown by the batches in Figure 7. Comparison of these curves with those of Figure 2 shows that with fine filler the changes of flow characteristics became marked at 50% by weight of filler instead of at 75% as with coarse filler. In the case of batch 106A, acetone was used in its incorporation, the acetone later being driven off at 100° C. during conditioning in the press. However, since the acetone content was at least 0.5% the effect observed in Figure 7 is understandable, since it is known that the presence of small amounts of solvent greatly affect the plastic properties of high polymers. The nitrate filler was larger in particle size than the nitramine, whereas the sand was intermediate between nitramine and fine nitramine. In general, the finer the particle size of the filler, the greater the apparent viscosity and tendency toward an exponential type of curve.

Figures 5 and 6 show curves of sand and nitrate filler with the Paraplex-nitrocellulose binder. As has been pointed out, the apparent viscosities tended to increase with increasing amounts of filler in all batches except those with Paraplex binders at low filler contents (sand was not run at 25%). At 25 to 50% filler the shape of the curve and the apparent viscosities were similar to, or in some cases even less than, that of the binder alone, as opposed to the curves for sand, which at 50% were different in shape and significantly higher in viscosity (Figure 5). With nitrate filler the plastic flow characteristics at 50% by weight were possibly due in part to the large size of the nitrate particles. In the case of the nitramine the decrease in per cent theoretical density in some cases might account for some of the lack of increase in viscosity, since viscosity is inversely proportional to the free volume of the material. However, since the same phenomenon occurred in the case of binder 81 with nitramine filler (Figure 3) where there was no decrease in density at 25 or 50%, and since the effect was not present in the polyvinyl acetate binders which showed large decreases in per cent theoretical density, it is considered that some other effect was acting. Anomalous viscosities have also been obtained when 0.5% lecithin was added to nitramine binder systems. With Vistanex-nitramine a small reduction in apparent viscosity resulted, whereas with Paraplex and 25% nitramine the same addition at 100° C. resulted in a considerable increase in viscosity. This indicated that a surface phenomenon could modify the rate of flow in nitramine binder systems, and it is probable that with —N—NO_2 and —O—NO_2 groups of fillers some surface phenomenon is acting with Paraplex N.C. binders. The difficulty of extracting Paraplex from nitramine in solvent analysis has provided additional evidence of some surface phenomenon. The interaction might, for instance, involve coiling of the nitrocellulose chains. Polyvinyl acetate

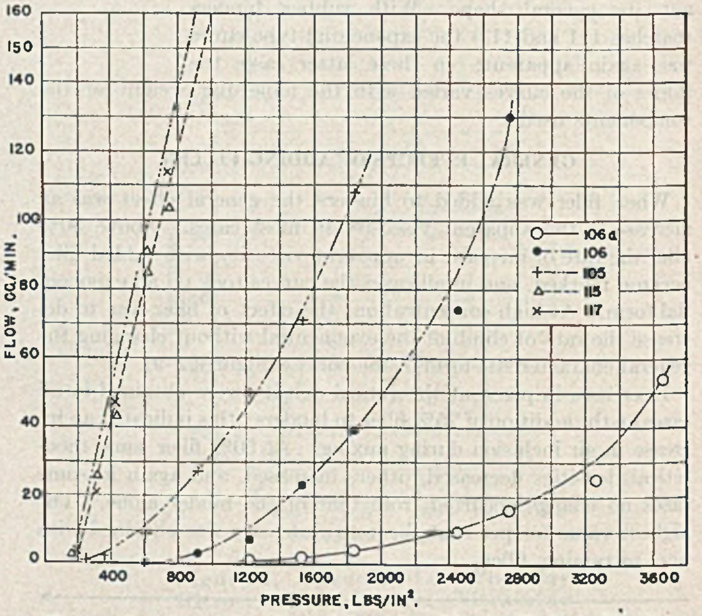

Figure 7. Paraplex–Low Viscosity Nitrocellulose Binder, Fine Nitramine Filler

115 = 0%, 117 = 25%, 105 = 50%, 106A = 75%, 106 = 75% filler + solvent

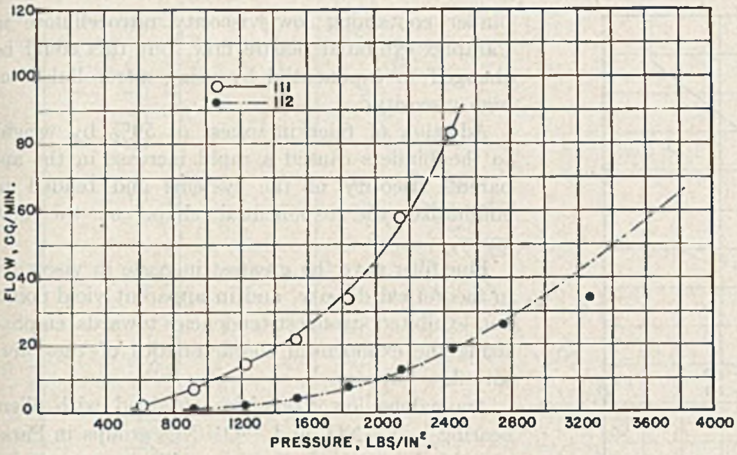

Figure 8. Butyl Rubber Binder, Nitramine Filler

111 = 0%, 112 = 75% filler

and synthetic rubber binders showed no anomalies in their viscosities except with lecithin. A carefully prepared series consisting of Paraplex N.C. binder and 25% fine filler and coarse filler is shown in batches 115, 116, and 117. Both the effect of particle size and the anomalous decrease in viscosity are apparent.

INTERPRETATION OF EXPONENTIAL FLOW

No evidence of thixotropic breakdown was obtained in the press, either from the appearance of any hysteresis in going from low to high and back to low extrusion pressures, or from a change of flow rate with time at a given pressure; consequently it should be possible to apply Eyring's explanation to the cases where non-Newtonian types of flow other than plastic were noted.

From considerations based on transition state theory, Eyring (*3, 4*) predicted that the rate of extrusion is given by the following expression:

$$\frac{dV}{dt} = \frac{k'\lambda 2\pi R^2}{\lambda' B}\left(\cosh BR - \frac{2}{BR}\sinh BR + \frac{4}{(BR)^2}\sinh^2\frac{BR}{2}\right)$$

where $B = \dfrac{P\Delta\lambda}{4LKT}$

$k' = \dfrac{kT}{h}e^{-\frac{\Delta F}{kT}}$

$\dfrac{dv}{dt}$ = volume rate of flow, cc./sec.

h Planck constant

k = Boltzmann constant

λ' = distance between moving layers of the material, cm.

λ = distance between equilibrium positions on the potential energy surface—that is, distance a flow unit jumps in going from one equilibrium position to another, cm.

ΔF = free energy of activation for the process

A = cross section of flow unit, sq. cm.

R = radius of die, cm.

L = length of parallel in die, cm.

P = pressure, dynes/sq. cm.

T = temperature, ° Kelvin

In the case of large pressures this becomes

$$\frac{dv}{dt} = \frac{4\pi\,(kT)^2R^2L}{h\,\lambda'\,AP}\,e^{-\frac{\Delta F}{kT}}\,e^{\frac{P\lambda\,AR}{4\,LKT}}$$

If this hypothesis can be applied to the data obtained, then the plot of logarithmic rate of flow against pressure should be a straight line whose slope should yield the viscous volume λA. The plot of non-Newtonian curves, of the type of which Figures 10 and 11 are samples, showed that straight lines were obtained at high pressures as predicted. In most cases a falling off from the straight line occurred below 600 pounds per square inch, but since good straight lines could be drawn through the last five or six points, the slopes of the straight portions were determined. The values of λA obtained from these slopes are given in Table I, and they are in the order of magnitude of values obtained from the data of Sheppard and Sweet, 2×10^{-19} cu. cm. (*4*). However, the values of Table I are of critical magnitude, so that, in the case of small λA values, the value of BR in Eyring's equation is of the order of 0.5 or less at pressures of 400 to 500 pounds per square inch. Thus in these cases, approximating the hyperbolic functions to exponentials leads to a falling off from the linear log (rate of flow) *vs.* pressure relation until higher pressures are reached.

Table I shows that the values of λA either remain the same or decrease on addition of filler. The decrease was most apparent in the case of high molecular weight rubber, and the amount of decrease was in the order of increasing molecular weights of the

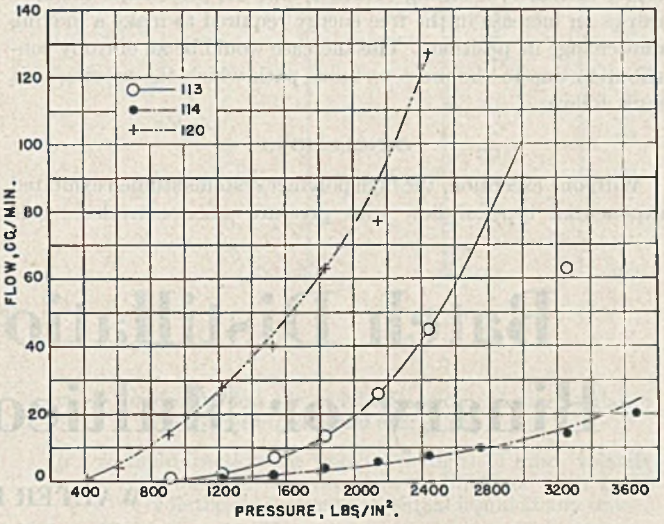

Figure 9. Vistanex Rubber Binder, Nitramine Filler

113 = 0%, 114 = 75% filler, 120 = 75% with low molecular weight Vistanex

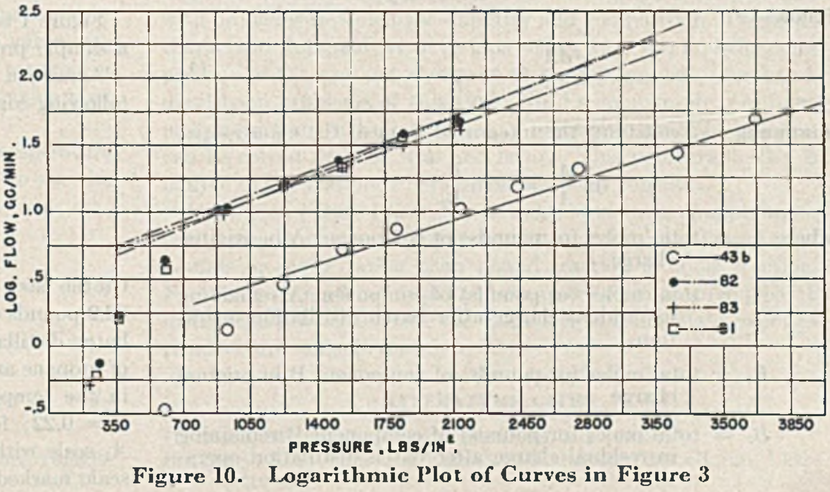

Figure 10. Logarithmic Plot of Curves in Figure 3

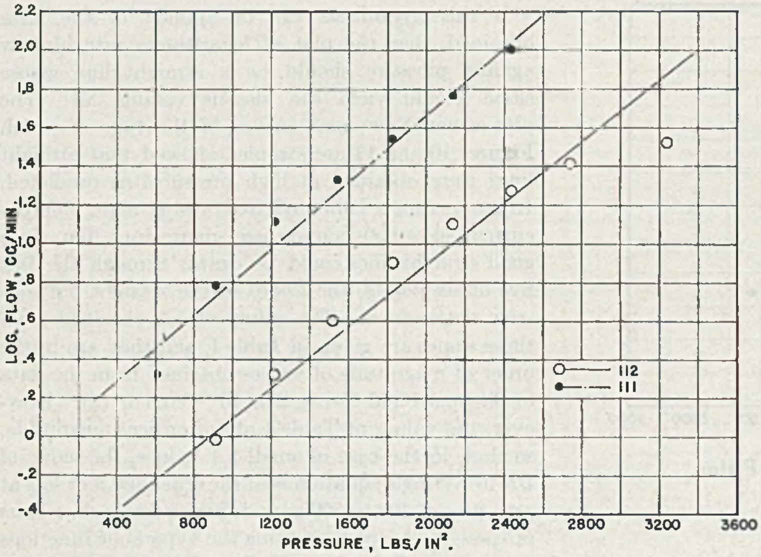

Figure 11. Logarithmic Plot of Curves in Figure 8

binder. This decrease was interpreted as a reduction in the size of flow segment of the binder molecule in the presence of large amounts of filler. The fact that λA does not decrease markedly with addition of large amounts of filler, while the apparent viscosity increases, is strong evidence that the presence of the filler causes an increase in the free energy required to make a moving unit change its position. This increase would be an entropy contribution due to the more tortuous path which the moving unit must follow.

CONCLUSIONS

With one exception, the high polymer systems studied exhibited exponential type of flow with pressure when extruded. One binder containing low viscosity nitrocellulose in Paraplex exhibited plastic flow, but this could be changed to exponential by using nitrocellulose of high viscosity.

Addition of filler in excess of 50% by weight to the binders caused a rapid increase in the apparent viscosity of the systems and tended to emphasize the exponential shape of the flow curve.

Fine filler gave the greatest increase in viscosity, in theoretical density, and in apparent yield point, and exhibited strongest tendencies towards emphasizing the exponential characteristics of the pressure-flow curves.

Anomalous low viscosities obtained with fillers bearing —N—NO$_2$ and —O—NO$_2$ groups in Paraplex binders gave indication of the presence of a surface-active phenomenon around the filler particles.

With increase of filler content the viscous volume of the flow segment tended to decrease in size, and the amount of decrease was in the order of increasing molecular weight of the polymer binder. The order of size of the change in viscous volume indicated that resistance to flow when filler was added might be in the fluid phase.

ACKNOWLEDGMENT

The authors wish to thank D. C. Rose of the Canadian Armament Research and Development Establishment for arranging and facilitating publication of this paper.

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Batch Distillation Nomograph for Binary or Multicomponent Mixtures

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Monsanto Chemical Company, St. Louis, Mo.

FOR dealing with multicomponent mixtures in a simple batch distillation problem, the Rayleigh equation is written as follows (*2*):

$$\frac{-dA}{-dB} = \alpha_{AB}\frac{A}{B} \qquad (1)$$

Assuming α_{AB} constant, the integrated form of the equation is:

$$\ln\frac{A_1}{A_2} = \alpha \ln\frac{B_1}{B_2} \qquad (2)$$

where A_1 = total moles (or pounds) of component A in original charge

A_2 = total moles (or pounds) of component A remaining in residual charge after batch distillation operation

B_1 = total moles (or pounds) of component B in original charge

B_2 = total moles (or pounds) of component B remaining in residual charge after batch distillation operation

α = relative volatility of A to B, K_A/K_B (or if Raoult's law applies $\alpha = P_A/P_B$)

Figure 1 is a nomograph of Equation 2. To illustrate its use, a sample problem (*2*) is illustrated.

Assume a mixture of propane, butane, and pentane, of the following composition:

Component	Weight %
C_3	8.0
C_4	65.6
C_5	26.4
	100.0

On the basis of 100 pounds of this original mixture, consider that 32.2 pounds of butane are to be left in the residual liquid after a batch distillation process. It is desired to calculate the amount of propane and pentane in the residual liquor. Average α values in the temperature ranges under consideration are for C_4/C_3, $\alpha = 0.22$; for C_4/C_5, $\alpha = 4.3$. Connect the point 65.6 on the A_1 scale with 32.2 on the A_2 scale and continue the line to the scale marked C. Connect the point on the C scale with the α

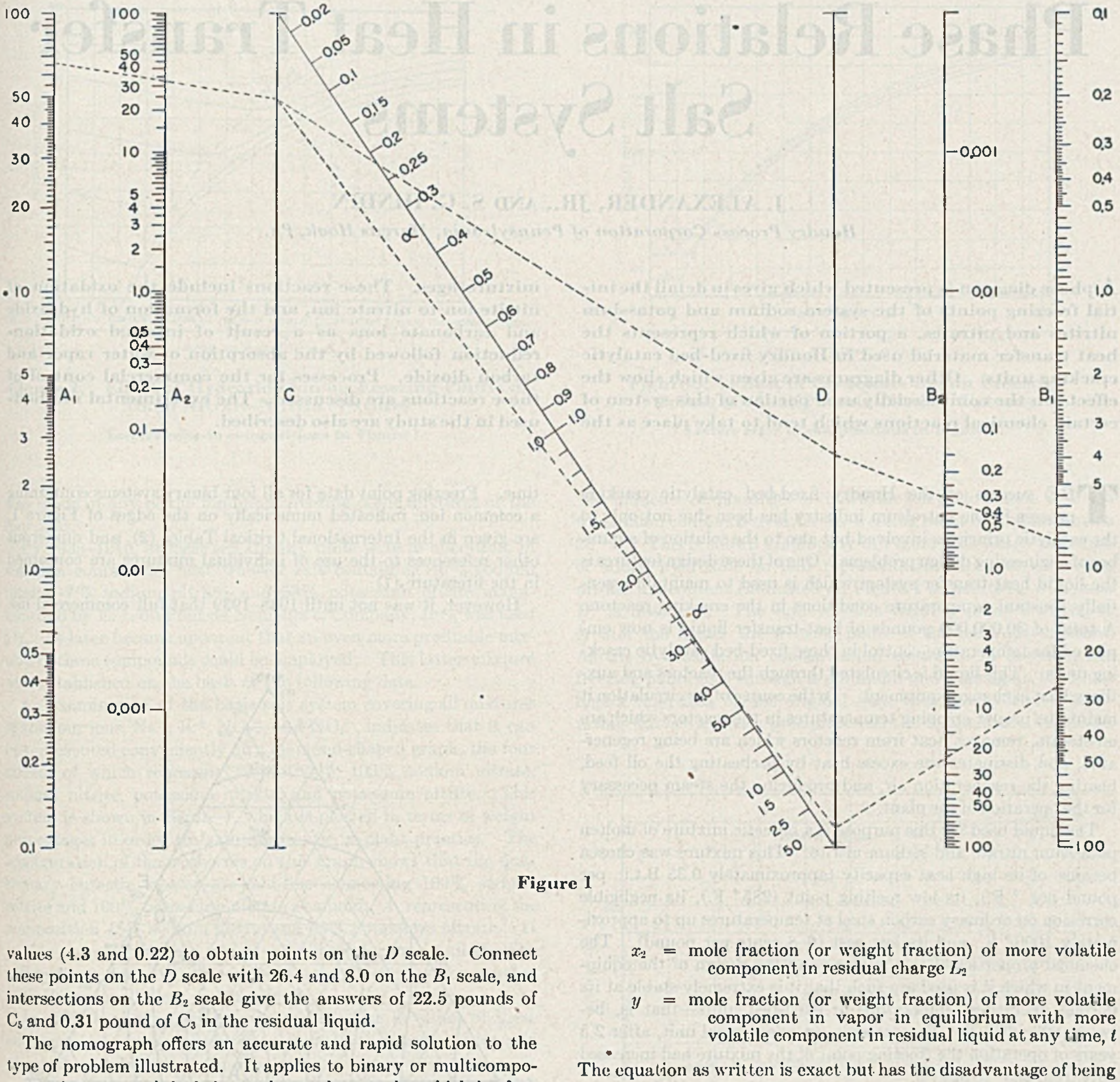

Figure 1

values (4.3 and 0.22) to obtain points on the D scale. Connect these points on the D scale with 26.4 and 8.0 on the B_1 scale, and intersections on the B_2 scale give the answers of 22.5 pounds of C_5 and 0.31 pound of C_3 in the residual liquid.

The nomograph offers an accurate and rapid solution to the type of problem illustrated. It applies to binary or multicomponent mixtures, and deals in total pounds or moles which is often advantageous in that a conversion to weight fraction or mole fraction is eliminated. A limitation to the use of the nomograph is the fact that it applies only over a range where α remains fairly constant. For mixtures where wide variations in α values are obtained, a stepwise solution is required. The range covered in each step must be small enough so that a constant α value may be used.

For batch distillations of binary mixtures over temperature ranges involving wide variations in α, it is advisable to use the exact form of the Rayleigh equation (*2*):

$$\ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y - x} \qquad (3)$$

where L_1 = moles (or pounds) of original charge

L_2 = moles (or pounds) of residual charge after $L_1 - L_2$ have been distilled off

x_1 = mole fraction (or weight fraction) of more volatile component in original charge L_1

x_2 = mole fraction (or weight fraction) of more volatile component in residual charge L_2

y = mole fraction (or weight fraction) of more volatile component in vapor in equilibrium with more volatile component in residual liquid at any time, t

The equation as written is exact but has the disadvantage of being time consuming since, in general, a graphical determination of the area under the curve $1/(y-x)$ *vs.* x must be made. A trial-and-error solution is required when the nomograph is used to deal with problems in which the quantity and composition of original charge and the quantity of residual charge are set, and the composition of the residual charge is to be determined. For batch distillation problems of this type, Nord's nomograph (*1*) of the integrated form of Equation 3 may be used so that the problem can be solved without trial and error. This nomograph also is limited to applications where α remains fairly constant.

In general, Figure 1 has the particular advantage of applying to multicomponent as well as binary mixtures and of dealing in total pounds or moles rather than pound fraction or mole fraction. Furthermore, it offers a rapid and accurate means of solving batch distillation problems where the variations in α are slight over the temperature range in question.

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Phase Relations in Heat Transfer Salt Systems

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A phase diagram is presented which gives in detail the initial freezing points of the system sodium and potassium nitrites and nitrates, a portion of which represents the heat transfer material used in Houdry fixed-bed catalytic cracking units. Other diagrams are given which show the effects on the commercially used portion of this system of certain chemical reactions which tend to take place as the mixture ages. These reactions include the oxidation of nitrite ion to nitrate ion, and the formation of hydroxide and carbonate ions as a result of internal oxidation-reduction followed by the absorption of water vapor and carbon dioxide. Processes for the commercial control of these reactions are discussed. The experimental methods used in the study are also described.

THE success of the Houdry fixed-bed catalytic cracking process in the petroleum industry has been due not only to the catalytic principles involved but also to the solution of a number of engineering design problems. One of these design features is the liquid heat-transfer system which is used to maintain essentially constant temperature conditions in the cracking reactors. A total of 30,000,000 pounds of heat-transfer liquid is now employed for temperature control in these fixed-bed catalytic cracking units. This liquid is circulated through the reactors and auxiliary heat exchange equipment. In the course of its circulation it maintains proper cracking temperatures in the reactors which are on-stream, removes heat from reactors which are being regenerated, and dissipates the excess heat by preheating the oil feed, heating the regeneration air, and producing the steam necessary for the operation of the plant.

The liquid used for this purpose is a eutectic mixture of molten potassium nitrate and sodium nitrite. This mixture was chosen because of its high heat capacity (approximately 0.35 B.t.u. per pound per ° F.), its low melting point (285° F.), its negligible corrosion on ordinary carbon steel at temperatures up to approximately 1000° F., and its low cost (6-8 cents per pound). The chemical properties of this mixture and the design of the equipment in which it is used are such that it is extremely stable at its normal operating temperature in fixed-bed units—that is, between 800-900° F. For example, in one typical unit, after 2.5 years of operation the freezing point of the mixture had increased only from 285° to 324° F.

The salt systems have been designed to prevent, within practical limits, contact between air or other gases and the molten salt. However, under operating conditions certain chemical reactions normally take place slowly which, if allowed to continue, ultimately affect the utility of these systems by raising the freezing points beyond practical limits, or by forming insoluble materials which settle out in the systems. The survey described in this paper was made primarily as an aid to the detection, evaluation, and control of these reactions. It was limited by practical considerations to a determination of the initial freezing points, which are defined here as the temperatures at which the first solid phase appears. This was done because it is the absence or presence of solid matter in these mixtures which determines their usefulness as heat transfer media. All data are given in ° F. because of the fact that the primary application of such data is in connection with commercially operated plants in this country.

PHYSICAL AND CHEMICAL BEHAVIOR OF SYSTEM

The use of mixtures of the nitrates and nitrites of sodium and potassium for heat-transfer purposes has been known for some time. Freezing point data for all four binary systems containing a common ion, indicated numerically on the edges of Figure 1, are given in the International Critical Tables (*2*), and numerous other references to the use of individual mixtures are contained in the literature (*1*).

However, it was not until 1938-1939 that full commercial use

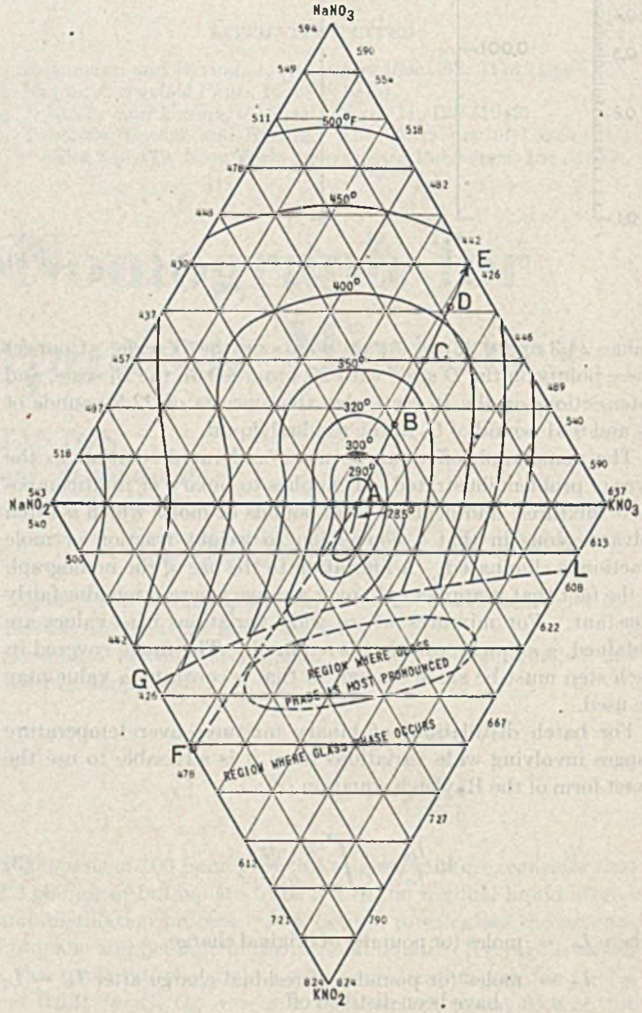

Figure 1. Freezing Points of Alkali Nitrate-Nitrite Mixtures with Compositions Given in Weight Per Cent

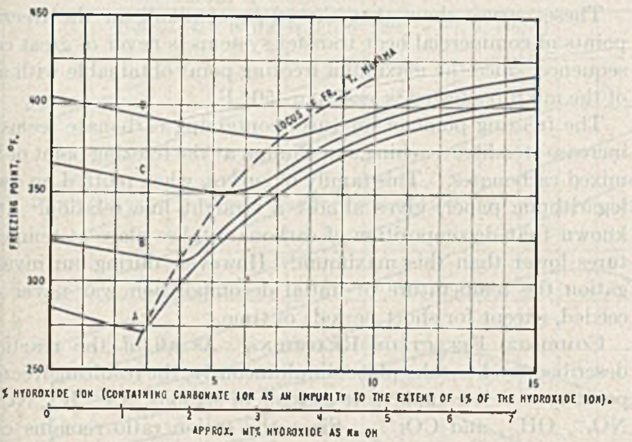

Figure 2. Effect of Hydroxide Ion on Freezing Points of Alkali Nitrate-Nitrite Mixtures

Letters refer to compositions in Figure 1.

was made of any of the minimum freezing point mixtures of the four ions.

By 1939–1940, at least ten Houdry units were in operation, in which a commercial heat transfer salt containing 40% sodium nitrite, 7% sodium nitrate, and 53% potassium nitrite manufactured by E. I. du Pont de Nemours & Company, Inc., was used (*1*). It later became apparent that an even more profitable mixture of these compounds could be employed. This latter mixture was established on the basis of the following data.

An examination of the basic salt system covering all mixtures of the four ions, Na^+, K^+, NO_2^-, and NO_3^-, indicates that it can be represented conveniently on a diamond-shaped graph, the four apexes of which represent, respectively, 100% sodium nitrate, sodium nitrite, potassium nitrate, and potassium nitrite. This system is shown in Figure 1, which is plotted in terms of weight percentages in order to facilitate its use in plant practice. The configuration of the isotherms on this graph shows that the quaternary eutectic crosses the mid-line connecting 100% soduim nitrite and 100% potassium nitrate at a point, *A*, representing the composition 45% sodium nitrite and 55% potassium nitrate. It is this eutectic mixture which was chosen for use in all Houdry salt systems since 1941, because of its simple composition coupled with its unusually low melting point.

In use, three chemical reactions take place in either of these commercial mixtures which tend to change their composition and physical properties.

OXIDATION OF NITRITE. The nitrite ion is oxidized to nitrate ion, usually through contact with air, according to the simple equation:

$$2NO_2^- + O_2 \longrightarrow 2NO_3^-$$

This reaction results in the formation of mixtures which are represented by points located on the line *AE* (Figure 1). Line *FAE* represents all salts having a constant Na^+-K^+ mole ratio of 1.20. As the composition shifts in the direction of increasing sodium nitrate concentration, a correspondingly increasing freezing point occurs until a maximum of approximately 430° F. is reached at the point where all nitrite has been converted to nitrate.

The maximum allowable freezing point in a given plant is dependent on the pressure and degree of superheat of the steam available for use in the storage-tank heating coils. In most plants it has proved desirable to hold the freezing point below 350° F.

FORMATION OF HYDROXIDE ION. Hydroxide ion is formed as a result of the internal oxidation-reduction of small amounts of nitrite ion with the simultaneous absorption of water vapor.

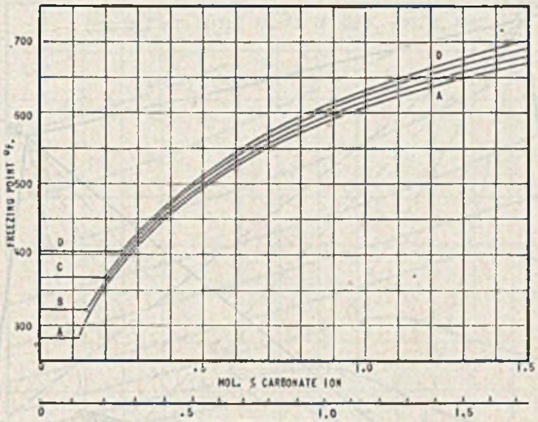

Figure 3. Effect of Carbonate Ion on Freezing Points of Alkali Nitrate-Nitrite Mixtures

Letters refer to compositions in Figure 1.

The influence of quantities of hydroxide ion up to 5 mole % of the total anion content is to lower the freezing point by amounts up to 20° F. This is shown graphically in Figure 2, in which the effect of added hydroxide on four representative mixes of increasing nitrate ion content (indicated on Figure 1 as points *A*, *B*, *C*, and *D*) is described. The limit of this freezing point lowering is greater the higher the freezing point of the basic salt mixture. As the hydroxide ion concentration continues to increase, the freezing point goes through a minimum and rises again to values higher than that of the original salt, with the hydroxide separating out as a glassy precipitate at the temperature indicated.

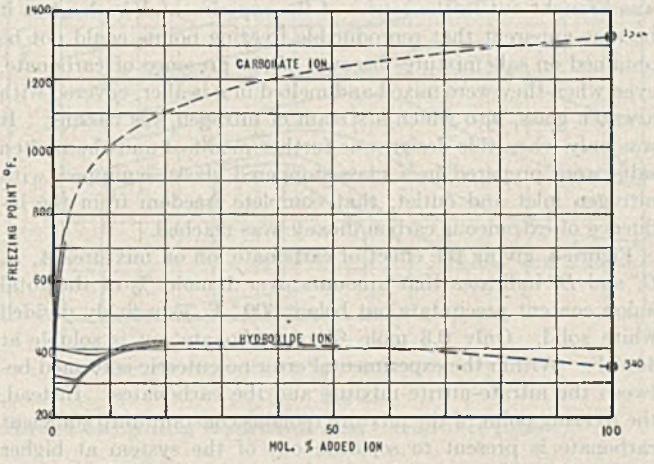

Figure 4. Comparison of Influences of Hydroxide and Carbonate Ions on Freezing Points of Alkali Nitrate-Nitrite Mixtures

The curves in Figure 2 are slightly high in the 8–15% hydroxide region because of the presence of about 1% carbonate in the alkali used for making up the experimental mixes. (The extent of this error can be estimated from Figures 7–10, in which the dotted lines represent the minimum amount of carbonate present for a given alkali concentration.) The weight % scales in Figures 2 and 3 are average scales. The exact conversion factors for mole % to weight % vary slightly with changing composition of the basic salt mixture.

In plant practice the concentration of hydroxide has never yet exceeded that corresponding to the minimum melting point. However, the presence of alkali undoubtedly increases the rate of

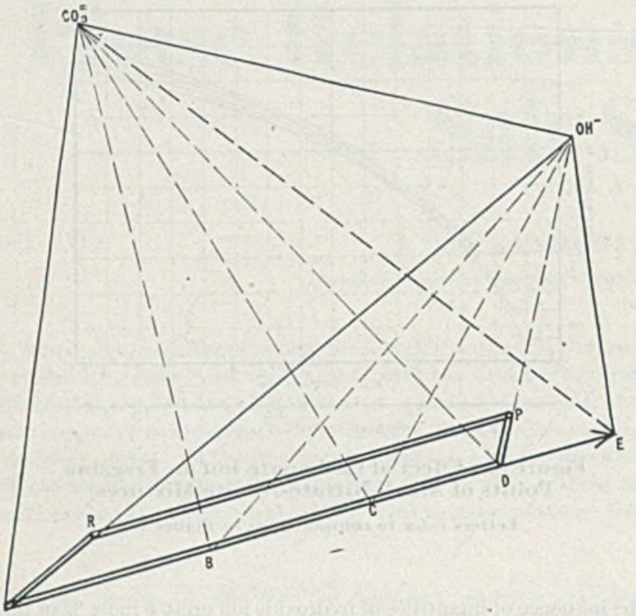

Figure 5. Tetrahedron Representing Alkali Nitrate-Nitrite Mixtures Containing Hydroxide and Carbonate Ions

Letters refer to compositions in Figure 1. Na^+-K^+ ratio = 1.20

absorption of acid gases such as carbon dioxide as mentioned below.

Formation of Carbonate Ion. Carbon dioxide, if present in the atmosphere above the molten salt, is absorbed readily by the free alkali, forming carbonates which are insoluble in the salt system. This case of absorption of carbon dioxide was brought out in the course of the experimental work when it became apparent that reproducible freezing points could not be obtained on salt mixtures because of the presence of carbonate, even when they were mixed and melted in a beaker, covered with a watch glass, into which a stream of nitrogen was passing. It was only when this design was further modified and the molten salts were prepared in a glass-stoppered flask, equipped with nitrogen inlet and outlet, that complete freedom from the influence of extraneous carbon dioxide was reached.

Figure 3, giving the effect of carbonate ion on mixtures *A*, *B*, *C*, and *D*, indicates that amounts over 1 mole % of the total anion content precipitate out below 600° F. as a finely divided white solid. Only 0.3 mole % of carbonate ion is soluble at 400° F. Within the experimental error no eutectic is formed between the nitrate-nitrite mixture and the carbonates. Instead, the freezing point of the mixture remains constant until sufficient carbonate is present to separate out of the system at higher temperatures. It is probable, however, that a eutectic mixture is actually formed. This can be deduced from the behavior of the binary systems sodium nitrate–sodium carbonate, and potassium nitrate–potassium carbonate, as given in the International Critical Tables (*2*).

Since there are sections of the salt systems which operate at temperatures of 550–600° F., it is advisable that carbonate concentrations be maintained below 0.5 mole % so as avoid carbonate precipitation in quiet spots of the heat exchange equipment.

Ultimate Effect of Hydroxide and Carbonate Ions on Freezing Points. Figure 4 indicates roughly the limits of the influence of the two mentioned ions on heat transfer systems. This graph was constructed by extrapolating the experimental data toward the freezing point figures for 100% sodium hydroxide–potassium hydroxide and 100% sodium carbonate–potassium carbonate (Na^+-K^+ mole ratio 1.20) obtained from the International Critical Tables.

These curves show that the effect of alkali on the freezing points of commercial heat transfer systems is never of great consequence, since the maximum freezing point obtainable with any of the mixtures tested is less than 450° F.

The freezing point of mixtures containing carbonate seems to increase steadily, reaching a maximum at the freezing point of the mixed carbonates. This family of curves, when plotted on semilogarithmic paper, gives almost a straight line relation. It is known that decomposition of carbonate takes place at temperatures lower than this maximum. However, during our investigation the temperature of initial decomposition was never exceeded, except for short periods of time.

Combined Effect of Reactions. As all of the reactions described tend to take place simultaneously, the resulting freezing point system is complex; it consists of six ions, Na^+, K^+, NO_2^-, NO_3^-, OH^-, and CO_3^{--}. Since the cation ratio remains constant throughout these changes, the system can be represented as a regular tetrahedron, one edge of which indicates the nitrate-nitrite ratio expressed in terms of the freezing point of the hydroxide- and carbonate-free salt, while the opposite edge connects points representing 100 mole % OH^- and 100 mole % CO_3^{--}. Figure 5 is a diagrammatic sketch of this tetrahedron resting on its edge *AE*. This edge corresponds to the line similarly represented in Figure 1. As all the information of practical interest is included in the section of this tetrahedron *ADPR*, this section has been distorted and replotted on three-dimensional rectangular coordinates in Figure 6, in order to make it more legible. It is given in only enough detail to show the trends involved. Figure 7 represents four planes of this figure, which give the same data in a form in which they may be read quantitatively. In these graphs the weight % scales are exact.

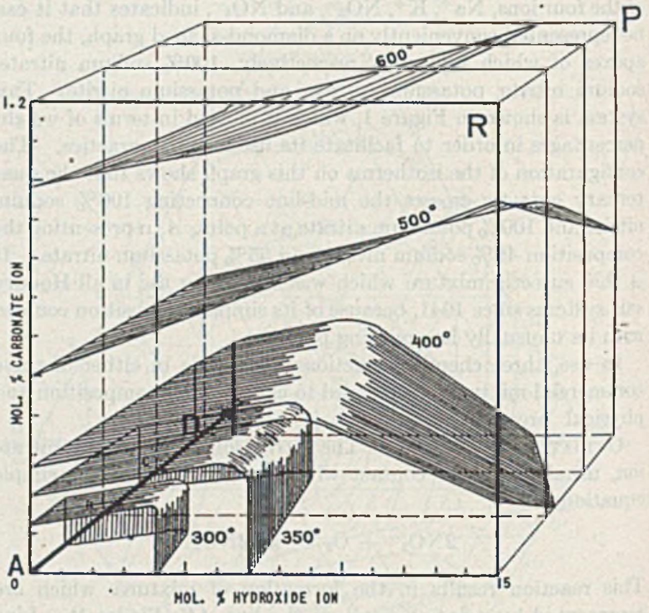

Figure 6. Freezing Points of Alkali Nitrate-Nitrite Mixtures Containing Hydroxide and Carbonate Ions for Section *ADPR* in Figure 5

Conclusions which may be drawn from these graphs are: (*a*) Very generally, the effects of added hydroxide and carbonate are independent of each other. (*b*) More specifically, low concentrations of carbonate have the effect of raising the freezing point of mixtures containing over 10% hydroxide ion. High concentrations of carbonate cause precipitates to form well above the freezing points of mixtures containing only hydroxide. However, minimum freezing points are still present at successively higher hydroxide concentrations. (*c*) Low concentrations of hydroxide lower the initial freezing points of mixtures containing

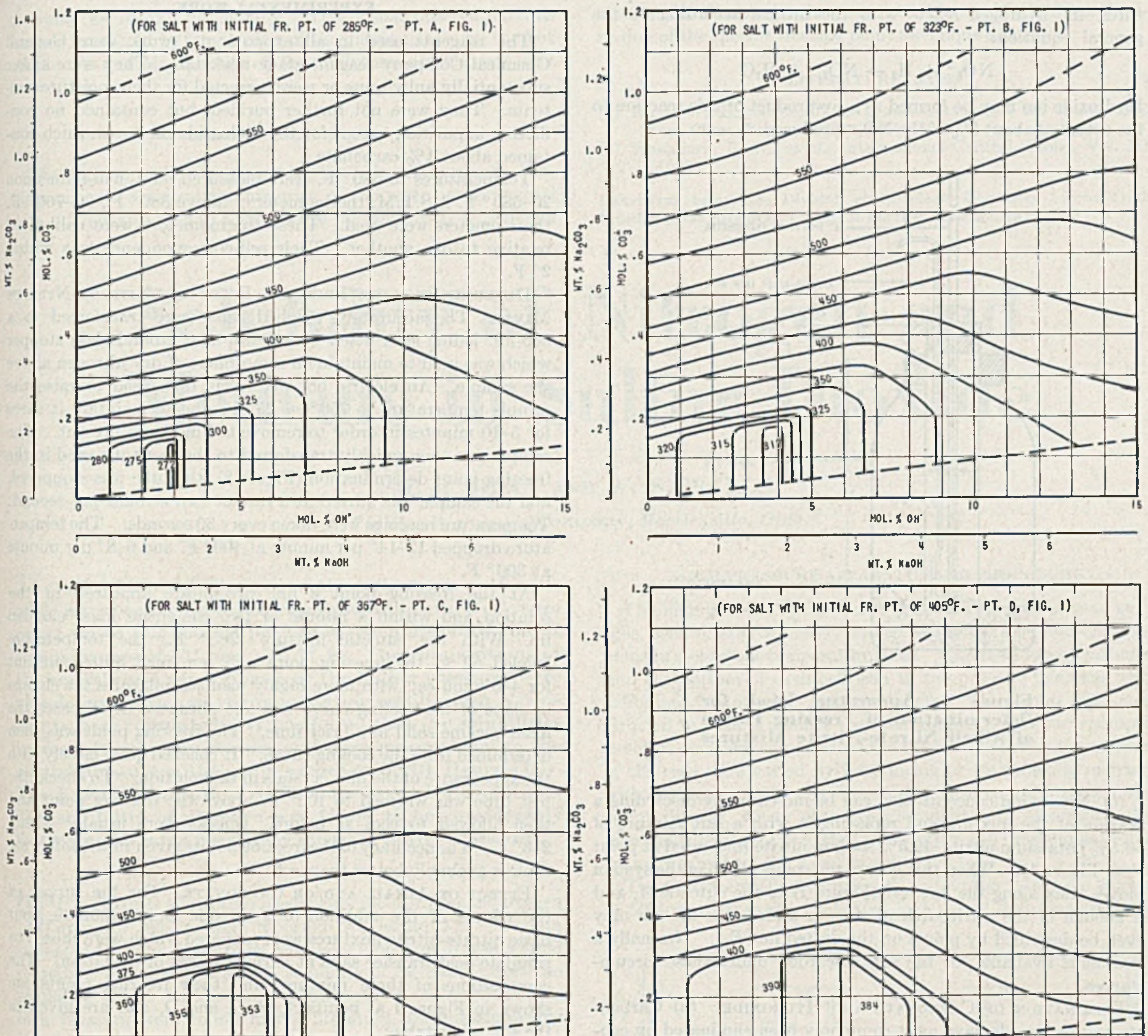

Figure 7. Freezing Points of Alkali Nitrate-Nitrite Mixtures Containing Hydroxide and Carbonate Ions

small amounts of carbonate but do not materially affect the solubility curves of carbonate. High concentrations of hydroxide lower the solubility of the carbonate and tend to eliminate the constant temperature portions of the carbonate solubility curves.

Mixtures Containing Over 20% Excess KNO_2. As an interesting sideline to this freezing point investigation, our experimental work has shown that the majority of that portion of the basic salt system containing more than 20% excess potassium nitrite (region of Figure 1 below the dotted line *GL*) has the peculiar property of solidifying slowly as a transparent glass without ever undergoing a sharp transition from liquid to solid state. This phenomenon is present to varying extents in different portions of this area. For example, on the edges connecting sodium nitrite and potassium nitrite and potassium nitrite and potassium nitrate, respectively, freezing points are obtainable, but odd viscosity effects are experienced in the temperature region above the freezing points. The center of the disturbance seems to be within the dotted elipse, and in this section it is virtually impossible to obtain a freezing point by the method used in this paper.

PLANT CONTROL OF SALT COMPOSITION

The commercial control of the reactions described in the previous section and the commercial reconditioning of salts which have deteriorated beyond the desirable point proved to be comparatively simple. A brief summary of methods which are commercially usable for these purposes is as follows:

Methods for Freezing Point Reduction. (*a*) The reduction of nitrate to nitrite ion may be accomplished by passing a portion of the salt through an absorption tower in which it is brought into contact with hydrogen. At plant operating temperatures, the hydrogen reacts with the nitrate according to the general equation:

$$NO_3^- + H_2 \rightarrow NO_2^- + H_2O$$

Hydroxide ion may be formed as a by-product of this reaction to the extent of about 5% of the NO_2^- produced.

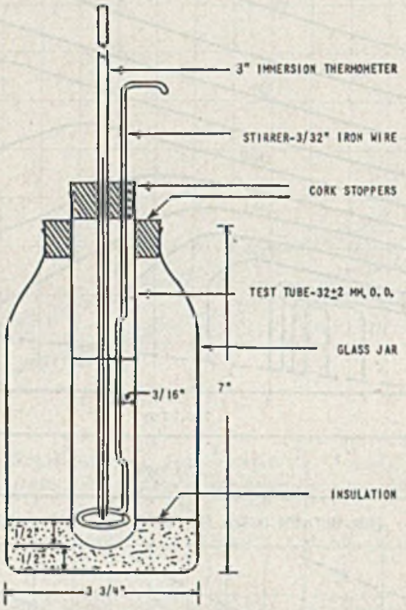

Figure 8. Apparatus Used for Determination of Freezing Points of Alkali Nitrate-Nitrite Mixtures

(*b*) Nitrite ion concentration can be increased by discarding a portion of the mixture and replacing it with a salt mixture of 50.5% potassium nitrite-49.5% sodium nitrite (indicated at point *F* on Figure 1). When this occurs the composition of the system moves back along the line *AE* (Figure 1) to the eutectic *A*, and if enough of the nitrite-rich mixture is added, the system may even be described by points on the dotted line *FA*. Normally a market is available for the salt discarded under these circumstances.

ELIMINATION OF CARBONATE AND HYDROXIDE. (*a*) Carbonate and hydroxide have most commonly been eliminated by conversion to nitrate. This is accomplished by adding concentrated nitric acid to the salt system, usually in a liquid-filled absorption tower. Additional nitrate thus accumulated should then be reduced to nitrite by one of the means previously mentioned. This reduction to nitrite is not necessary when carbonate and hydroxide are converted to a mixture of nitrate and nitrite by reaction with gaseous nitrogen dioxide. This latter method has not been applied commercially until recently because nitrogen dioxide has not been available in large quantities.

(*b*) Carbonate concentrations may be reduced to approximately 0.3 mole % CO_3^{--} by taking advantage of the low solubility of carbonate in heat transfer salt. This is accomplished by cooling a side stream of salt from the main salt system in a conventional exchanger, allowing the carbonate to settle in a properly designed tank following the cooler and then withdrawing this precipitate.

(*c*) Carbonate may also be eliminated from the salt system by precipitation with calcium nitrate and subsequent filtering in a separate unit. In this method it is necessary to take into solution the total batch of salt being treated by the addition of approximately 10% water. Calcium nitrate is added to the mixture, and the precipitated calcium carbonate is filtered out in a gravel filter. The wet salt is returned to the system by injection in small quantities into the main salt storage tank.

EXPERIMENTAL WORK

The reagents used in all experimental work were General Chemical Company reagent-grade materials. They were either substantially anhydrous or were corrected for their moisture contents. They were not further purified, but contained no conflicting impurities, except for the hydroxide mixtures which contained about 1% carbonate.

Temperatures to 580° F. were measured on 3-inch-immersion 20–580° F. A.S.T.M. thermometers; above 580° F., 20–760° F. thermometers were used. These thermometers were calibrated relative to one another. Their self-correspondence was within 2° F.

DETERMINATION OF FREEZING POINT OF NITRATE-NITRITE MIXES. The accurately weighed salts were transferred to a 500-ml. iodine flask fitted with a two-inlet ground-glass stopper which was used to maintain an atmosphere of dry nitrogen above the sample. An electric hot plate was then used to raise the sample temperature to 750° ± 25° F. and to maintain it there for 5–10 minutes in order to remove the moisture present. The sample was then quickly transferred to the test tube used in the freezing point determination (Figure 8), the tube was stoppered, and the sample was stirred at a rate of two strokes per second. Temperature readings were taken every 30 seconds. The temperature dropped 12–14° per minute at 400° F. and 6–8° per minute at 300° F.

At the freezing point a fine precipitate appeared in the solution, and within a minute or two the entire mass clouded up. With the eutectic mixture (285° F.) the temperature leveled off at the freezing point and remained quite constant for 4–5 minutes; with more highly oxidized mixtures the change in slope of the cooling curve was less abrupt. In all cases the mass became solid in a brief time. The freezing point was then determined from the cooling curve. It checked quite closely with the appearance of the first crystals in the solution. To check, the test tube was warmed to 100° F. above the freezing point and then allowed to cool as before. Checks were usually within 2–3° F. The accuracy of the freezing points given in the following table is probably better than ±5° F.

EFFECT OF ALKALI AND/OR CARBONATE. For the survey of the effects of the addition of hydroxide and carbonate, four basic nitrate-nitrite mixtures were prepared which were chosen to simulate heat transfer salts at various stages of oxidation. The compositions of these mixtures and their freezing points are shown in Figure 1 at points *A*, *B*, *C*, and *D*, and are given in the following table:

	Freezing Point, ° F.	Composition, % by Wt.		
		KNO_3	$NaNO_3$	$NaNO_2$
Mixture *A*	285	55.0	45.0	0.0
Mixture *B*	323	53.2	29.7	17.1
Mixture *C*	367	51.9	17.9	30.2
Mixture *D*	405	50.9	8.3	40.8

The mole ratio of sodium to potassium is essentially constant in these mixtures and equals 1.20.

Accurately weighed amounts of hydroxide and/or carbonate were added to each of the four basic mixes, hydroxide being added as a sodium hydroxide–potassium hydroxide mixture and carbonate as a sodium carbonate–potassium carbonate mixture (Na^+-K^+ mole ratio 1.20). In preparing mixes containing both ions, the carbonate impurities in the alkali were taken into consideration. The resulting mixes were melted and transferred to the freezing point apparatus as described. A slightly different technique of measurement was required, however, because of the fact that no appreciable change in the slope of the cooling curve was noticed except with high hydroxide concentrations. The point at which carbonate or small amounts of hydroxide produced a solid phase had to be noted visually with the temperatures dropping at 10-12° per minute. This visual observation was further hampered by the etching of the glass surfaces by the hot alkali. As a result, the data on these mixtures are accurate only to ±10° F.

ACKNOWLEDGMENT

The authors wish to acknowledge the help of Charles S. Pennington, who obtained the majority of the recent experimental data. They also wish to acknowledge the work of I. W. Mills of the Sun Oil Company, who contributed to the original standardization of the specific freezing point technique described.

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Solubility of Nitrogen and Methane in Sulfur Dioxide

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The solubilities of nitrogen and methane in sulfur dioxide have been determined experimentally over a pressure range up to 515 pounds per square inch absolute and at temperatures of 83° and −25.7° F. The compositions of the equilibrium vapor phases at the higher pressures were also determined, and the vaporization equilibrium *K* constants were computed. It was found that the solubilities increased with temperature and were proportional to the partial pressure of the gas in accordance with Henry's law. The Kuenen absorption coefficients were also computed. The solubility of nitrogen was found to be considerably less than the value previously reported in the literature.

THE Kuenen absorption coefficients for nitrogen and oxygen in sulfur dioxide were reported by Dornte (*1*). The data indicated the solubilities to be relatively large, and it was desired to make a comparison with the solubility of methane. Since no solubility values for methane or nitrogen in sulfur dioxide at high pressure were found in the literature, the measurements reported here were made over a range of pressures up to 515 pounds per square inch absolute. Several experiments, in which the gas partial pressure was 1 atmosphere, were carried out in order to obtain solubilities for comparison with those computed from the high pressure data.

MATERIALS USED

The nitrogen and oxygen used were the regular water-pumped grades of the Air Reduction Company. Orsat analyses indicated that the nitrogen contained less than 0.1% oxygen and that the oxygen was 99.7% pure. The gases were used as received, except they were dried under pressure with dehydrated calcium sulfate as the desiccant.

The methane used was obtained from Phillips Petroleum Company. A low temperature fractional analysis showed it to be free of noncondensable gases. Specifications furnished with the material stated that it contained only a trace of carbon dioxide and that the major impurity, ethane, was present at a concentration of approximately 0.5%.

The sulfur dioxide was a product of the Virginia Smelting Company and of refrigeration grade. Specifications furnished with the material stated that it was water-free and was at least 99% sulfur dioxide. An Orsat analysis of the vapor phase in the container showed it to be 99.6% acid gas. It was used as received.

HIGH PRESSURE APPARATUS AND PROCEDURE

The high pressure apparatus (Figure 1) consisted of twin steel cells, each of approximately 240-cc. capacity, mounted on trunnions in a constant temperature bath. The steel tubing fastened into the bottom of each cell lead to the pressure gage and to a calibrated piston-type mercury pump. The pump was constructed in such a manner that the volume of mercury pumped could be continuously measured to 0.1 cc. The effective volumes of the cells were varied by introducing or withdrawing mercury with the pump. One cell was employed to contain the gas and sulfur dioxide, where they were brought into equilibrium by vigorous shaking of the cell. The other cell was employed in taking a sample of the vapor phase.

The pressure was measured with a Bourdon tube type of gage of 500-pound capacity calibrated in 5-pound divisions and esti-

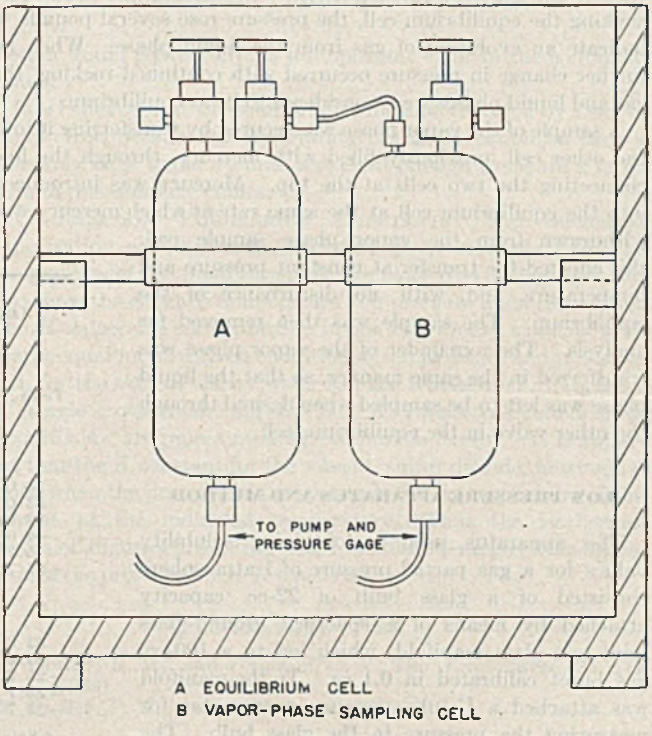

Figure 1. Equilibrium Apparatus

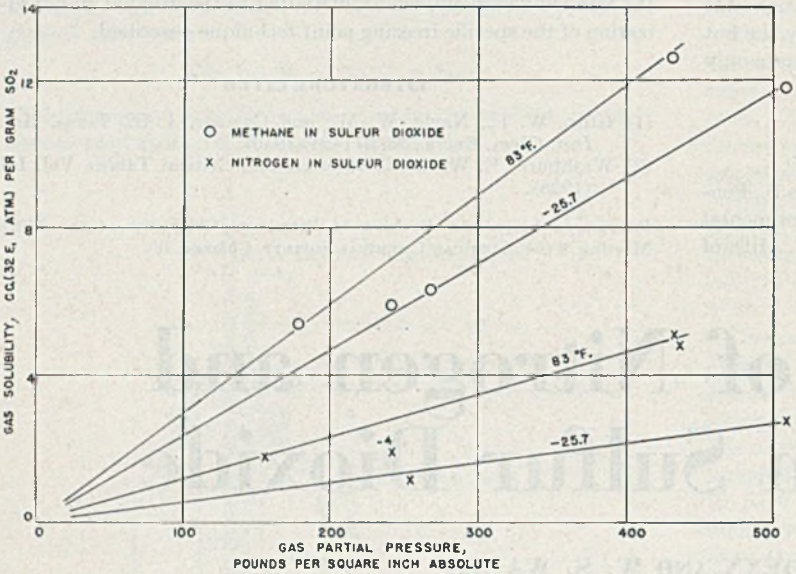

Figure 2. Solubility of Nitrogen and Methane in Sulfur Dioxide

mated to the nearest pound. Bath temperatures were measured with calibrated mercury-in-glass thermometers graduated in 0.2° F. divisions. The low temperature was maintained by the intermittent addition of dry ice to an ethylene glycol–water mixture.

Analyses of the phase samples were carried out with conventional Orsat gas analysis equipment using aqueous potassium hydroxide solution as reagent.

The experimental procedure consisted of charging a known weight of sulfur dioxide into the evacuated equilibrium cell, followed by sufficient nitrogen or methane to raise the pressure to within a few pounds of the desired experimental pressure. The pressure was then raised 50 to 100 pounds above the experimental pressure by introducing mercury into the equilibrium cell with the pump, rocking the cells vigorously by hand for several minutes, then withdrawing mercury from the cell to lower the pressure to the experimental pressure. It was observed that, upon shaking the equilibrium cell, the pressure rose several pounds to indicate an evolution of gas from the liquid phase. When no further change in pressure occurred with continued rocking, the gas and liquid phases were considered to be at equilibrium.

A sample of the vapor phase was secured by transferring it into the other cell, previously filled with mercury, through the line connecting the two cells at the top. Mercury was introduced into the equilibrium cell at the same rate at which mercury was withdrawn from the vapor phase sample cell; this effected the transfer at constant pressure and temperature and with no disturbance of the equilibrium. The sample was then removed for analysis. The remainder of the vapor phase was transferred in the same manner, so that the liquid phase was left to be sampled when desired through the other valve in the equilibrium cell.

LOW PRESSURE APPARATUS AND METHOD

The apparatus used in obtaining solubility values for a gas partial pressure of 1 atmosphere consisted of a glass bulb of 22-cc. capacity attached by means of a spherical ground-glass joint to a glass manifold, which led to a 100-cc. gas buret calibrated in 0.1 cc. To the manifold was attached a U-tube mercury manometer for measuring the pressure in the glass bulb. The spherical ground-glass joint allowed the bulb to be shaken vigorously without detaching it from the manifold. The method comprised condensing a known weight of sulfur dioxide (12 to 19 grams) into the evacuated bulb. The bulb was immersed in a constant temperature bath, and the methane, nitrogen, or oxygen added from the buret to a partial pressure of 1 atmosphere. The bulb and contents were then vigorously agitated to dissolve the gas. The decrease in pressure which occurred when gas went into solution was compensated for by intermittent additions of more gas. When no further decrease in pressure could be obtained with continued agitation, the decrease in gas volume in the buret was noted, and a correction (approximately 16 cc.) was applied to compensate for the gas remaining in the vapor phase over the sulfur dioxide.

To demonstrate that the method would give dependable solubility values, the solubility of nitrogen in carbon tetrachloride at 77° F. and 1 atmosphere partial pressure was found to be 0.15 cc. per gram and checks the value of 0.15 cc. per gram derived from the measurements reported by Frolich (*2*). It is believed that the error in the low pressure solubilities reported here is no more than 0.1 cc. per gram.

RESULTS

The high pressure work was carried out at two temperatures, 83° and −25.7° F., with varying total pressures up to 515 pounds per square inch absolute. The compositions of the coexisting vapor and liquid phases are given in Table I together with the calculated vaporization equilibrium *K* constants and the calculated partial pressures of the components. The partial pressures were calculated from the total pressure and the vapor-phase composition. The solubilities of the gases in sulfur dioxide are expressed as cubic centimeters of gas (32° F., 1 atmosphere) in 1 gram of sulfur dioxide.

Solubility Data. The solubilities were plotted against the gas partial pressures in Figure 2 to show that the solubilities were proportional to the pressure in accordance with Henry's law. The Kuenen absorption coefficients (cubic centimeters of gas at 32° F. and 1 atmosphere in 1 gram of sulfur dioxide per atmosphere of partial pressure) were computed from the curves of Figure 2 and listed in Table III.

The Kuenen absorption coefficients for methane, nitrogen, and oxygen in sulfur dioxide determined in the low pressure apparatus

Table I. Experimental Data for Nitrogen–Sulfur Dioxide and Methane–Sulfur Dioxide Systems

Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Phase Compn., Mole %				Vaporization Equil. Const., $K = y/x$		Partial Pressure, Lb./Sq. In. Abs.		Soly., Cc./G.[a]
		Liquid phase		Vapor phase						
		Nitrogen–Sulfur Dioxide System								
		N_2	SO_2	N_2	SO_2	N_2	SO_2	N_2	SO_2	N_2
83.0	515	1.43	98.57	84.3	15.7	59	0.159	434	81	5.1
83.0	515	1.34	98.66	84.9	15.1	63	0.153	437	78	4.8
83.0	225	0.51	99.49	69.3	30.7	136	0.309	156	69	1.8
−4.0	253	0.55	99.45	95.8	4.2	174	0.042	242	11	1.9
−25.7	515	0.78	99.22	98.9	1.1	127	0.011	509	6	2.8
−25.7	262	0.33	99.67	97.2	2.8	295	0.028	255	7	1.2
		Methane–Sulfur Dioxide System								
		CH_4	SO_2	CH_4	SO_2	CH_4	SO_2	CH_4	SO_2	CH_4
83.0	515	3.48	96.52	83.9	16.1	24	0.167	432	83	12.6
83.0	253	1.52	98.48	70.8	29.2	47	0.297	179	74	5.4
−25.7	515	3.26	96.74	98.7	1.3	30	0.013	508	7	11.8
−25.7	275	1.76	98.24	97.9	2.1	56	0.021	269	6	6.3
−25.7	249	1.65	98.35	97.2	2.8	59	0.028	242	7	5.9

[a] Solubility, cc. gas (32° F., 1 atmosphere) in 1 gram sulfur dioxide.

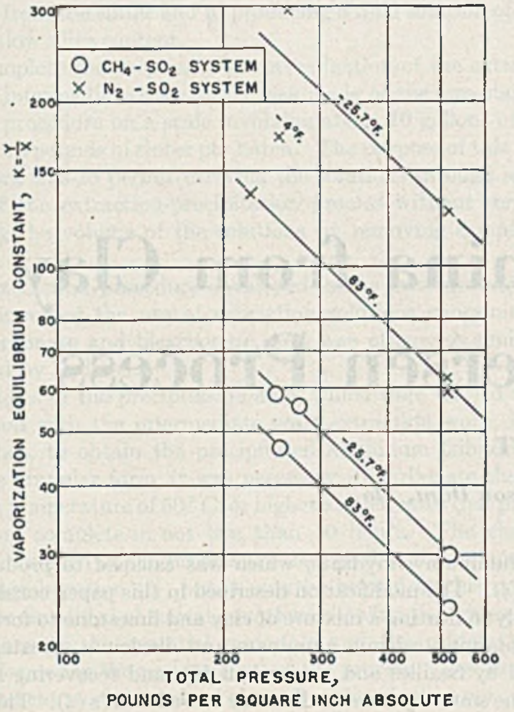

Figure 3. Vaporization Equilibrium Constants for Nitrogen and Methane in Sulfur Dioxide

are given in Table II. The accuracy of the coefficients is not so good as the coefficients computed from the high pressure measurements. The primary purpose in making the low pressure measurements was to show that coefficients obtained using two different methods check in magnitude. A comparison made in Table III between Kuenen absorption coefficients for nitrogen and oxygen found in this work and those reported by Dornte (*1*) show a great difference in values. In this low pressure work the volume of the liquid phase was approximately 10 cc., and that of the vapor phase approximately 17 cc., whereas Dornte used only 1 cc. of sulfur dioxide in the liquid phase with a vapor phase of 116 cc. By utilizing here a relatively larger volume of sulfur dioxide and a smaller vapor volume than those used by Dornte, the corrections necessarily made for the nitrogen or oxygen in the vapor phase were reduced to a point where the uncertainty in the correction would create only an unimportant error in the solubility values.

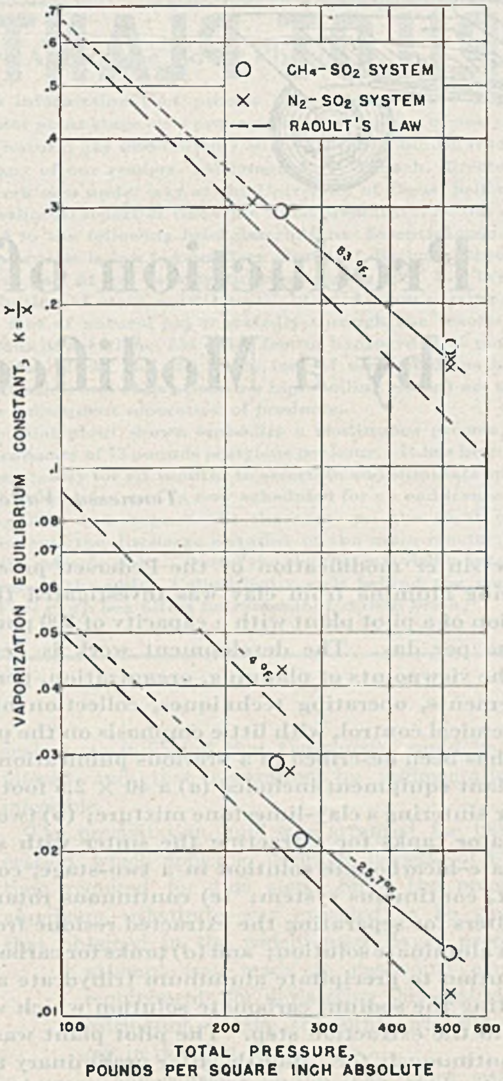

Figure 4. Vaporization Equilibrium Constants for Sulfur Dioxide Solvent

Table II. Solubilities of Methane, Nitrogen, and Oxygen in Sulfur Dioxide at One Atmosphere Partial Pressure

Temp., ° F.	Gas	Solvent	Soly., Cc./G.[a]
−25.7	Nitrogen	Sulfur dioxide	0.03
−25.7	Nitrogen	Sulfur dioxide	0.05
−25.7	Nitrogen	Sulfur dioxide	0.11
		Average	0.06
−25.7	Oxygen	Sulfur dioxide	0.18
−25.7	Oxygen	Sulfur dioxide	0.17
−25.7	Oxygen	Sulfur dioxide	0.14
		Average	0.16
−25.7	Methane	Sulfur dioxide	0.35
77	Nitrogen	Carbon tetrachloride	0.15

[a] Solubility, cc. gas (32° F., 1 atmosphere) in 1 gram sulfur dioxide.

Table III. Comparison of Kuenen Absorption Coefficients

Source	Absorption Coefficient, Cc./G. SO_2[a] Nitrogen	Oxygen −25.7° F.	Methane
Dornte (*1*)	22.3	10.1	...
Low pressure work	0.06	0.16	0.35
High pressure work	0.077	...	0.435
		83° F.	
High pressure work	0.169	...	0.435

[a] At 32° F. and 1 atmosphere.

It is believed that the solubility coefficients reported by Dornte are in error, because the uncertainty in the correction for such a relatively large vapor volume was great enough to create a large error in the solubility values.

Vaporization Equilibrium Constants. The calculated vaporization equilibrium *K* constants given in Table I for the components of the binary systems are plotted as in Figures 3 and 4 to show the effect of temperature and pressure upon the values. The *K* values for sulfur dioxide in the two binary systems were nearly equal for any given condition of temperature and pressure, and, for the sake of clarity, their loci are represented in Figure 4 by single isothermal curves. The *K* values calculated from Raoult's law are represented by the broken curves. It is apparent that the *K* constant for the solvent, sulfur dioxide, must equal unity when the pressure of the system is the vapor pressure of the solvent at the indicated temperature. Thus the isothermal curves of Figure 4 are extrapolated, within the range of the figure, toward the pressure where *K* equals unity.

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(2) Frolich, P. K., *et al.*, *Ibid.*, 23, 548 (1931).

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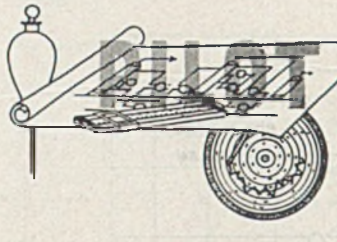

PILOT PLANTS

Production of Alumina from Clay by a Modified Pedersen Process

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A lime-sinter modification of the Pedersen process for producing alumina from clay was investigated through operation of a pilot plant with a capacity of 300 pounds of alumina per day. The development work is described from the viewpoints of planning, organization, personnel requirements, operating techniques, collection of data, and chemical control, with little emphasis on the process, which has been described in a previous publication. The pilot plant equipment included (*a*) a 40 × 2.5 foot rotary kiln for sintering a clay-limestone mixture; (*b*) two trains of agitator tanks for extracting the sinter with sodium carbonate–bicarbonate solution in a two-stage, countercurrent, continuous system; (*c*) continuous rotary vacuum filters for separating the extracted residue from the sodium aluminate solution; and (*d*) tanks for carbonating the solution to precipitate aluminum trihydrate and regenerating the sodium carbonate solution which was recycled to the extraction step. The pilot plant was operated continuously for 2 months after preliminary tests of each unit, and adequate data were obtained for design of an industrial scale plant and estimation of investment and production costs. Optimum conditions for pilot plant operation were accurately predicted by small scale tests, and alumina recovery in the pilot plant was comparable to that of small scale tests.

AT THE request of the War Production Board in October 1942 the Chemical Engineering Department of the Tennessee Valley Authority undertook investigations to determine the feasibility of producing alumina, suitable for reduction in electrolytic aluminum cells, from clay by a lime-sintering, soda-ash leaching process.

The development of an economical process was particularly desirable at that time because the supply of bauxite of suitable grade for alumina production by the commercially used Bayer process was jeopardized by rapid depletion of domestic deposits and wartime difficulties of importing bauxite. The process described in this paper was selected for development because the required raw materials, limestone and clay, were abundant and cheap, and because small amounts of critical materials would be required for plant construction, as compared with amounts needed for acid processes.

The original Pedersen process consisted in smelting together bauxite, lime, iron ore, and coke to produce iron (a by-product) and a low-silica calcium aluminate slag (*3*). The slag was leached with dilute (3 to 8%) sodium carbonate solution, and the resulting sodium aluminate solution was carbonated to regenerate the sodium carbonate for re-use in the leaching step and to precipitate aluminum trihydrate, which was calcined to produce alumina (*4*). The modification described in this paper consisted essentially in heating a mixture of clay and limestone to form a sinter containing calcium aluminate and dicalcium silicate, as described by Seailles and Dyckerhoff (*5*), and recovering alumina from the sinter by a method similar to Pedersen's (*4*). This modification was necessary to adapt the process to the use of high-silica raw materials, such as clay.

The present paper is a description of the pilot plant and methods used in its operation and control; little emphasis is given to the process, which has been described in a previous publication (*1*).

SMALL SCALE TESTS

A series of laboratory scale tests were made to obtain data for design of the pilot plant, to indicate suitable operating conditions, and to serve as a basis for deciding what problems should be investigated in the pilot plant. Tests were made of the sintering step by heating $^1/_4$- to 1-pound batches of briquetted mixtures of calcium carbonate and clay in an electrically heated laboratory furnace. The results showed that the "soluble" alumina content of the lime-clay sinter was 90 to 95% of the total alumina when the calcium carbonate and clay had been intimately mixed and accurately proportioned to provide 2 moles of calcium oxide per mole of silica, plus 1.6 moles of calcium oxide per mole of alumina, and the mixture had been heated at least 1 hour within the temperature range 1360° to 1400° C. (The term "soluble" alumina is used in this paper to designate the amount of alumina extracted from sinter by a test procedure that was designed to give the maximum extraction obtainable with dilute sodium carbonate solution.)

Laboratory scale single-extraction studies made in glassware on a scale involving about 20 grams of sinter and 200 ml. of extracting solution (usually 3% sodium carbonate) showed that it was desirable to agitate the slurry vigorously during extraction and to separate the residue from the solution promptly after extraction. Maximum extraction was obtained in the temperature range 45° to 65° C., with extraction time in the range of 15 to 30 minutes and a proportion of sodium carbonate solution to sinter such that 1.6 or more moles of sodium carbonate were supplied per mole of alumina. Although it was possible to obtain maximum alumina extraction by a single extraction procedure, the silica content of the resulting solution was high (about 2% based on Al_2O_3). Solutions of low silica content (less than 0.1% based on Al_2O_3) could be obtained by single extraction with smaller proportions of sodium carbonate solution, but this resulted in alumina extraction of only 75% of the maximum. Further tests indicated that a two-stage countercurrent extraction procedure would be effective in obtaining nearly complete extraction of the soluble alumina from the sinter and in producing a final solution of satisfactorily low silica content.

To complete the prepilot plant investigation of the extraction step, an intermediate scale study was made of the two-stage extraction procedure on a scale involving about 10 gallons of solution and 18 pounds of sinter per batch. The purpose of this larger scale work was to permit carrying the solutions through several cycles of the extraction-precipitation process without seriously depleting the volume of the solutions by removing samples for analysis.

The extraction procedure developed in the intermediate scale studies involved the use of extracting solutions containing sodium carbonate and bicarbonate, and was otherwise similar to that used by Pedersen.

In studies of the precipitation step, which were carried out in connection with the intermediate scale extraction work, it was found that, to obtain the precipitated aluminum trihydrate in desirable granular form, it was necessary to carbonate the solution at a temperature of 50° C. or higher at such rates that precipitation was complete in not less than 10 hours. The chemical changes involved in the process are discussed in some detail in a previous publication (*1*), but it may be helpful at this point to introduce simplified chemical equations showing the approximate proportions of the essential materials and the principal compounds formed in the various steps of the process. The clay used in the present work contained about 2 moles of silica per mole of alumina, and the sintering reaction is represented as follows:

$$\underset{\text{clay}}{3(Al_2O_3\cdot 2SiO_2)} + \underset{\text{limestone}}{17CaCO_3} = \underset{\text{sinter}}{5CaO\cdot 3Al_2O_3 + 6(2CaO\cdot SiO_2)} + 17CO_2$$

Since the dicalcium silicate of the sinter is inert, it may be omitted from the extraction reaction; the over-all reaction of the two-step extraction process as carried out in the pilot plant is approximately as follows:

$$\underset{\text{sinter}}{5CaO\cdot 3Al_2O_3} + \underset{\text{extracting soln.}}{3Na_2CO_3 + 2NaHCO_3} = \underset{\text{extraction soln.}}{6NaAlO_2 + 2NaOH} + \underset{\text{residue}}{5CaCO_3}$$

The precipitation step reaction may be represented by the following equation:

$$\underset{\text{extraction soln.}}{6NaAlO_2 + 2NaOH} + 9H_2O + 5CO_2 = \underset{\text{regenerated extracting soln.}}{3Na_2CO_3 + 2NaHCO_3} + \underset{\text{aluminum trihydrate}}{6Al(OH)_3}$$

THE PILOT PLANT

The purpose of constructing and operating the pilot plant was to determine the feasibility of carrying out the process in equipment that would be adaptable to industrial scale production and to provide data for designing a full scale plant and estimating production costs. It was particularly desirable to determine whether the process could be carried out in equipment of standard design which would be readily available for putting the process into full scale production with minimum delay, if an urgent wartime necessity developed.

A rotary kiln was used for the sintering step, because the requirements of the sintering operation appeared similar to those of portland cement production, in which the rotary kiln is widely used. Also, the rotary kiln is a standard and relatively simple type of equipment.

The extraction unit was designed for continuous flow, since it was believed that a continuous system would be better adapted to low cost production than a batch system. In this respect the design of the pilot plant differed from the previous work by Pedersen and the prepilot plant studies, in both of which a batch operation was used. Continuous rotary vacuum filters were used for separating the extraction residue from the solution, since small scale tests indicated that the slurries could be readily filtered and that separation by sedimentation was infeasible.

More About the Cover Photo . . .

The information that process investigations have reached the pilot plant stage on a process for manufacture of acetylene from natural gas undoubtedly will be of outstanding interest to many of our readers. Although E. P. Schoch, director of the work now under way at the University of Texas, believes a full technical report at this time to be premature, he has consented to the following brief description: Essential principle of the process is low temperature electrical discharge through natural gas, at gas temperatures averaging 300° F. Typical distribution of main constituents obtained upon passing 1000 cubic feet of natural gas repeatedly through the reactor are 9 pounds of acetylene, 534 cubic feet of hydrogen, 1.25 pounds of carbon black, and 665 cubic feet of unreacted methane. Dry filtration and absorption in a high boiling solvent are steps in the subsequent separation of products.

The pilot plant shown embodies a continuous process and has a capacity of 13 pounds acetylene per hour. It has been run intermittently for six months to ascertain and eliminate operational difficulties, and is now scheduled for an endurance run during July and August. In the scene on the front cover of this issue the discharge chamber of the main reactor unit is on the extreme right. One of the electrodes is visible entering the side of the unit. Cylindrical vessels behind the control board are cloth bag filters for removal of carbon black.

The precipitation unit was arranged for batch operation, which appeared desirable because of the long time required for this step. Since the precipitated aluminum trihydrate was expected to be similar to that obtained in the widely used Bayer process, no attempt was made to determine equipment requirements for dewatering this material, and calcination of the trihydrate was not carried out in the pilot plant.

The capacity of the pilot plant was based on the production and extraction of 1 ton of sinter per day (24 hours); this resulted in the production of 455 pounds of aluminum trihydrate (equivalent to 300 pounds of alumina) per day.

Figure 1 is a diagrammatic flow sheet of the pilot plant, which shows the quantities of the principal raw materials and products, and illustrates the types of equipment used. Limestone and clay were crushed, dried, ground, and mixed, and the mixture was sintered in a rotary kiln. The sinter disintegrated on cooling to a very fine powder which was extracted with sodium carbonate solution in a two-stage continuous-flow system. The slurries from the extraction trains were filtered by continuous rotary vacuum filters, the completely extracted residue was discarded, and the sodium aluminate solution was carbonated to precipitate aluminum trihydrate and to regenerate sodium carbonate solution for reuse in the extraction step.

Figure 2 is a photograph of the pilot plant. It shows the rotary kiln in the background; the extraction trains, filters, and solution storage tanks in the middle foreground; sinter storage bins at the left; and carbonation tanks for the precipitation step at the right. A floor plan (Figure 3) further clarifies the layout of equipment. The crushing, drying, and grinding equipment used to prepare limestone and clay mixtures are not shown in Figures 2 and 3, as they were located in another building.

Plan of Operation. There were two phases of pilot plant operation: (*a*) test runs of the individual units to work out operating techniques and correct any design defects, and (*b*) simultaneous operation of all units. The first run of the rotary kiln was scheduled early in the investigation to determine whether it would be a satisfactory type of equipment for the sintering step and to produce a sufficient quantity of sinter for use in the intermediate scale extraction studies. In this test run, the duration of which was 48 hours, no difficulties were encountered in operating the kiln on the limestone-clay mixture, and the soluble alumina content of the sinter was nearly as high (about 15%) as that produced in the laboratory work; it was concluded, therefore, that the rotary kiln would be satisfactory. Later, test runs of the kiln were made to determine the best procedure for preparing the kiln feed and to supply sinter for a test of the extraction unit. However, the sinter produced in these test runs was much lower in soluble alumina content than that made in the previous test run (11% as compared to 15%), and it was necessary to carry out additional laboratory studies to determine the cause. It was found that the presence of 1 to 2% magnesia in the limestone was the cause of the low soluble alumina content. Consequently, a supply of low-magnesia (about 0.5%) limestone was obtained, and a third series of test runs was made. In these runs sinter of up to 16% soluble alumina content was produced, and it was found that the use of dry-mixed limestone-clay kiln feed was preferable to wet-mixed or extruded feed. The duration of each of these test runs was 3 to 6 days, and the total time required was about 8 weeks.

In test runs of the extraction unit it was determined that solutions of the same silica and alumina contents were produced in the continuous pilot plant unit as in parallel experiments in the batch, intermediate scale extraction unit under identical conditions of retention time, temperature, and solution-sinter ratio. Erratic material balances in the pilot plant led to the discovery that deposition of alumina on the orifices used for metering the solutions to the extraction train rendered the flow rate determinations inaccurate. This difficulty was corrected by providing constant-level metering tanks that discharged through an orifice accessible for easy cleaning. The extraction unit test runs were each of about 5 hours' duration and required a total time of 1 week.

Solutions produced in the test runs of the extraction unit were carbonated in test runs of the precipitation unit; four tests of 10 to 30 hours' duration, which extended over a 1-week period, were made. Difficulty in maintaining steady combustion of fuel oil in the combustion chamber, which was used to supply flue gas for carbonation, was avoided by substituting carbon monoxide gas for fuel oil.

After completion of the preliminary test runs on the three pilot-plant units, the entire plant was operated for about 2 months. Operation was on a continuous basis 6 days per week except as temporarily interrupted by shutdowns for equipment repairs or changes. At the end of the 2 months, sufficient data had been obtained on the sintering step, and sufficient sinter was on hand to complete the work planned on extraction and precipitation; consequently the sintering unit was shut down, and operation of the extraction and precipitation units was continued for an additional month.

Personnel Requirements. Although the personnel assignment was flexible and varied depending on the phase of the work that was emphasized, the following description is typical of the period when the entire pilot plant was in operation.

The investigation was under the general supervision of a project leader who reported to the chief of the Process Development Division. The project leader was assisted by three engineers who exercised general supervision over the sintering, extraction, and precipitation units, respectively, and a fourth engineer who, with one or two assistants, was responsible for correlation and tabulation of data, coordination of sampling and analysis, preparation of reports, and special and small scale tests.

For operation of the pilot plant, each shift crew consisted of two chemical engineers, one control chemist, three operators, two assistant operators, and eight laborers. The engineers acted as shift supervisors and assistant shift supervisors, and they were responsible for maintaining operating conditions specified by the general supervisors; they also had supervisory responsibility for collection of data and samples, which was done by the operators.

A kiln operator controlled firing of the kiln, recorded data, and supervised weighing, sampling, and handling of the kiln charge and product, which was done by four laborers. A raw materials operator, assisted by two laborers, weighed and mixed limestone and clay, sampled the mixture, added limestone, clay, or recycled sinter when required, and remixed the material. The operation of the extraction and precipitation units was supervised by an operator and two assistant operators. One of the assistant operators recorded extraction unit data, weighed and charged sinter to the sinter feeders, and controlled rates and temperatures. The other assistant operator recorded data and controlled rates and temperatures for the precipitation unit, and made Orsat analyses of the flue gas used for carbonation. The laborers removed the extracted filter cake, filled the sinter storage bins, and assisted in handling the aluminum trihydrate from the precipitation unit.

The function of the control chemist is discussed under "Data, Sampling, and Chemical Control."

Professional personnel, constituting the supervisory group, were members of the Process Development Division by which the over-all engineering development was controlled. Trades and labor personnel were furnished by the Research Service Section, a unit which provides assistance in pilot plant design and construction, operators and laborers, various supplies, processing of requisitions, fabrication of laboratory equipment, and other services.

The personnel requirements were unusually high as compared with other pilot plant operations. This high personnel requirement resulted from the large amount of manual handling of materials, the use of unskilled personnel (caused by the wartime shortage of skilled personnel), and the urgency of completing the project in a relatively short time.

OPERATING TECHNIQUE

Clay containing 44% alumina and 51% silica (calcined basis) and limestone containing 99% calcium carbonate were crushed in a jaw crusher to −10 and −20 mesh, respectively, dried in a steam-heated pan drier (1500- to 2000-pound capacity), and ground in a ball mill (400-pound capacity) to 78 and 98% −200 mesh, respectively. The dried, ground materials were mixed in the proportions indicated earlier (small scale tests) in a rotating drum mixer that was equipped with flights and had a capacity of about 1 ton per batch. Each batch of approximately 1 ton was mixed for 1 hour; after ten of these batches had been made, a sample of the 10-ton batch was collected with a thief sampler from several locations in the pile, and was tested to determine whether it contained the proper proportions of limestone and clay for producing sinter of high soluble alumina content.

The test procedure consisted in mixing portions of the sample with added clay or limestone in a ball mill to prepare a series of mixtures containing 5 and 10% additional limestone and 5 and 10% additional clay. Briquets prepared from these test mixtures were sintered in an electrically heated laboratory furnace. The test mixture that produced sinter containing the highest percentage of soluble alumina was assumed to have the optimum proportion of limestone and clay, and, if this proportion was different from that of the 10-ton batch, a suitable amount of limestone or clay was added to it to give the indicated optimum proportion. After any necessary adjustment of the composition of the large batch had been made, it was intimately mixed in 300-pound batches in a ball mill which was equipped with 3-inch-diameter rubber-covered steel balls. This final mixing was found to be necessary for obtaining sinter of maximum soluble alumina content, even when no addition of clay or limestone was necessary. A probable explanation of the necessity of this type of mixing is that the clay particles tended to cohere into loosely agglomerated

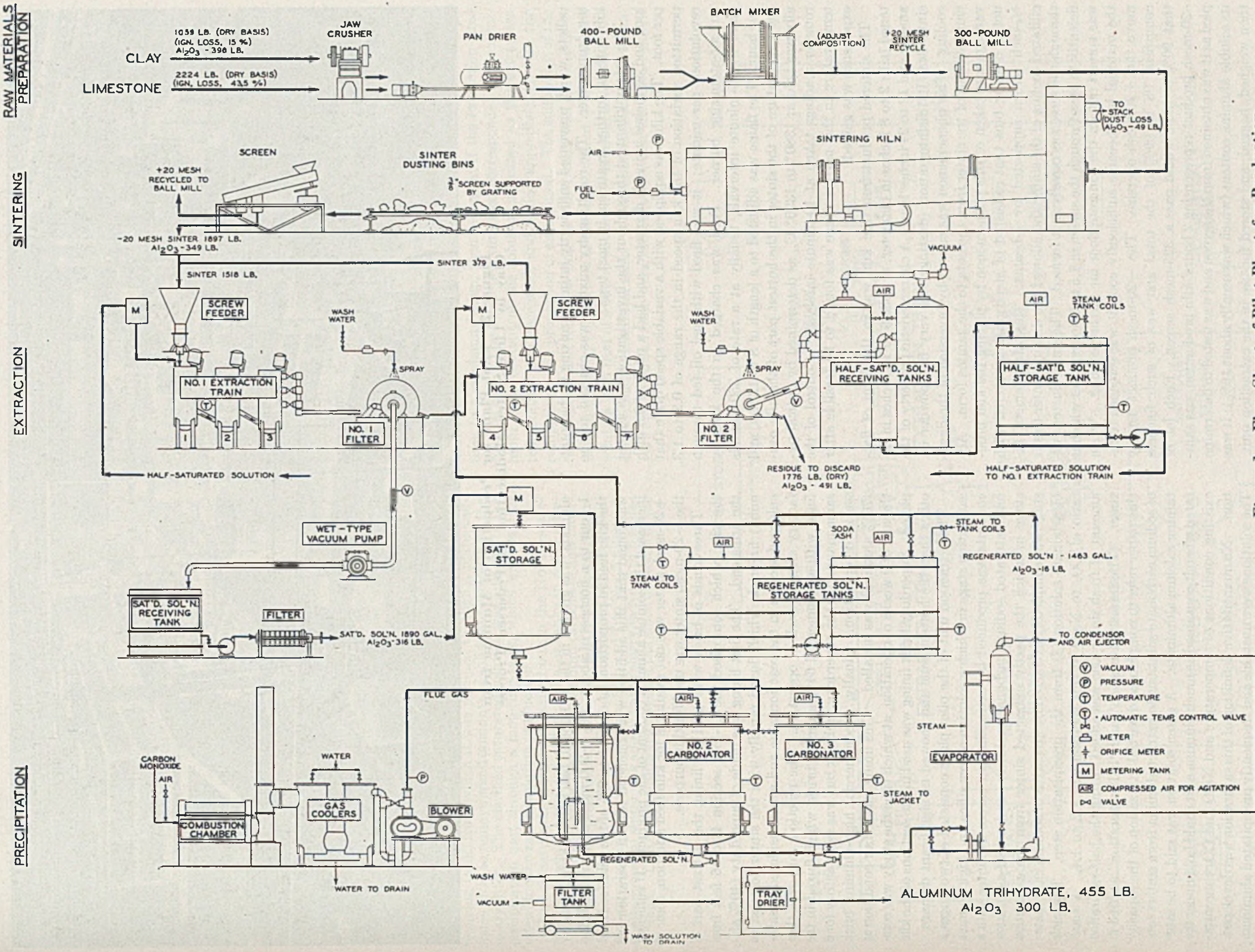

Figure 1. Flow Sheet of Pilot Plant for Production of Alumina from Clay by Modified Pedersen Process

(Quantities are based on 24 hours' operation)

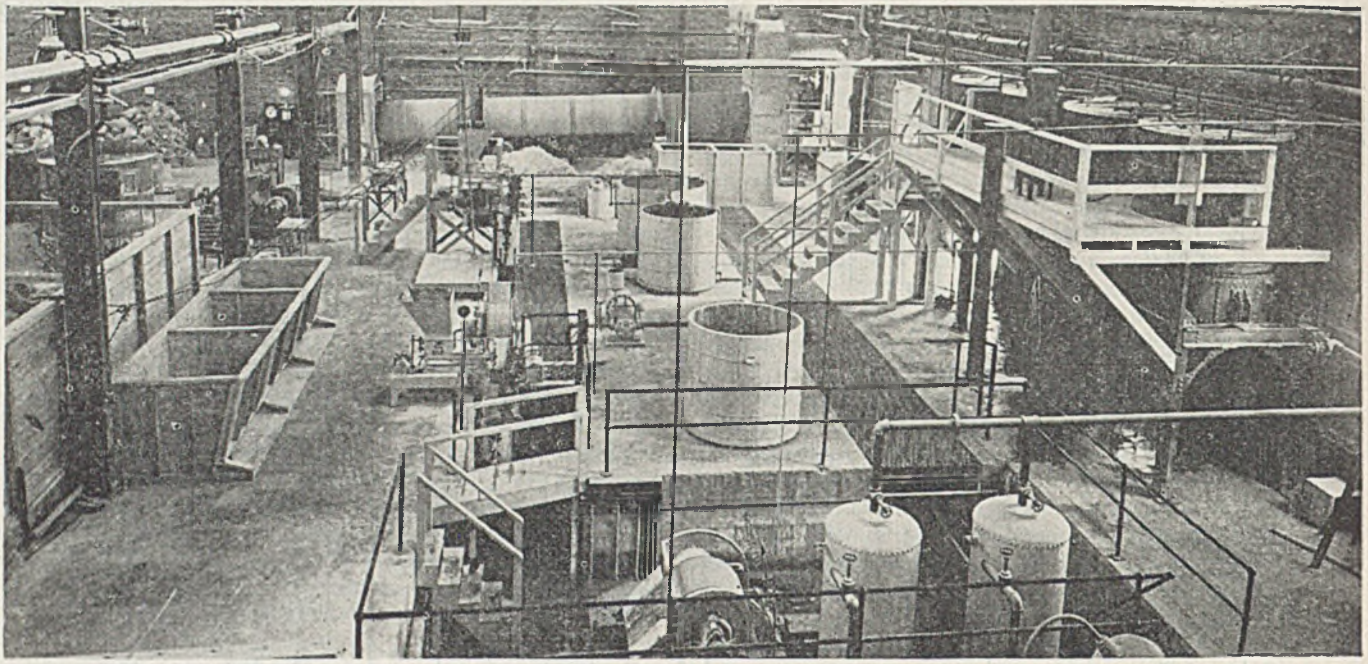

Figure 2. Pilot Plant for Production of Alumina from Clay by Lime-Sinter Modification of Pedersen Process

pellets, which prevented sufficiently intimate mixing in the rotating drum mixer. The resulting dry mixture was charged to the kiln without further treatment in most tests.

The rotary kiln used throughout the investigation was 40 feet long and 30 inches in inside diameter, and had a pitch of 0.5 inch per foot. The kiln was equipped with a variable speed drive that permitted variation of the kiln speed in the range of 0.2 to 1.3 revolutions per minute; it was fired with fuel oil fed through an air-atomizing burner. Feed was charged to the kiln by hand at 15-minute intervals, usually at a rate of 350 pounds per hour. The flame was adjusted to a length of 8 to 12 feet, and the temperature of the sinter in the hottest part of the kiln usually was held at 1380° to 1390° C., as determined by optical pyrometer readings taken at 10-minute intervals. Control of the temperature in this narrow range was found to be feasible after experience was gained.

The sintered product from the kiln was in the form of flattened balls 2 to 8 inches in diameter, or rolls 6 to 15 inches in diameter and 12 to 24 inches long. A characteristic property of the sinter was its disintegration (dusting) to a very fine powder on cooling. This phenomenon was caused by inversion of the dicalcium silicate of the sinter from the beta to the gamma form. Advantage was taken of this phenomenon by placing the kiln product in dusting bins that consisted of steel grating covered with $^3/_8$-inch screen supported by I-beams; this arrangement facilitated cooling of the sinter and allowed the dusting sinter to sift through the screen as rapidly as it formed. The sinter dusted sufficiently to pass through the screen in 1.5 to 3 hours, after which it was spread out on the concrete floor for further cooling. When the material had become sufficiently cool, it was screened to remove the +20-mesh oversize. The −20-mesh product usually comprised 98 to 99% of the total and was of such fineness that 90% or more would pass a 325-mesh screen. Each lot of −20-mesh product representing 2 hours' kiln production was sampled as it was obtained from the screen and was tested to determine its soluble alumina content (which was usually about 16%); it was then weighed, bagged, and stored for use in the extraction unit. The soluble alumina content was noted on a tag attached to each bag.

The +20-mesh sinter, which contained only about 10% soluble alumina, was ground in the 300-pound ball mill for approximately 1 hour to a fineness of about 70% −200 mesh and was added to the kiln feed in proportions of about 1 to 2% of the kiln feed. It was found that this addition was beneficial to kiln operation and increased the soluble alumina content of the product. If sufficient +20-mesh sinter was not available for kiln feed addition, some of the −20-mesh sinter was used for this purpose.

Three kinds of brick were used for lining the hottest part of the kiln, which comprised the 12-foot section 4 to 16 feet from the firing end. The first lining was made of superduty (40% alumina) firebrick, which fluxed rapidly with the sinter to form an enlarged section in the reaction zone and was considered unsatisfactory after 1 week of operation. The reaction zone was then lined with a commercial 64% alumina brick, which fluxed in the same manner as the superduty firebrick but was satisfactory for 6 weeks of operation. Finally, a commercial high-alumina brick (70% alumina) was installed. This lining was in fair condition at the end of 9 weeks of operation, at which time the study was completed. Superduty brick lining was used in the sections of the kiln other than the hottest zone and showed no significant damage.

The extraction unit of the pilot plant consisted of two stages, a saturation stage in which a solution of low silica and high alumina contents was produced by extracting an excess of sinter with a half saturated sodium carbonate solution, and a half-saturation stage in which the partly extracted sinter from the saturation stage was completely extracted by an excess of sodium carbonate-bicarbonate solution (*2*) from the precipitation step. The mole ratio of CO_2 to Na_2O in this solution was 1.2 to 1.4. A small amount of fresh sinter also was added during the half-saturation stage. (The terms "saturation" and "half-saturation" as used in this paper refer to complete and partial utilization of the capacity of sodium carbonate solutions to extract alumina from sinters containing calcium aluminate. A given solution was said to be saturated when it contained as much alumina as it could hold under the existing conditions of temperature and Na_2O and CO_2 concentration. No quantitative definition of this saturation was developed. The solutions were unstable and frequently precipitated aluminum hydroxide on standing (autoprecipitation). Half-saturated is similarly defined as containing approximately half as much alumina as the solution in question is capable of extracting.)

The saturation stage of the extraction was carried out in the No. 1 train (Figure 1), which consisted of three steel tanks arranged for series flow. Half-saturated solution was pumped from the storage tank to the metering tank, which was equipped with an adjustable overflow pipe for maintaining a constant head of solution above an orifice located in the bottom of the metering tank. Overflow from the metering tank was returned to the storage tank, and the metered solution entered No. 1 agitator tank. The sinter input was controlled by charging the desired weight of sinter to the sinter feeder hopper at 20-minute intervals and by adjusting the feeder to deliver the sinter to the No. 1 agitator tank at a constant rate. The sinter and half-saturated solution fed to the No. 1 agitator tank formed a slurry, which passed through No. 2 and No. 3 agitator tanks. The average time of retention of the slurry in the agitator tanks could be varied over a range of 3 to 1 for any given solution rate, by selection of one of three outlets on No. 3 agitator tank or by-passing No. 3 agitator tank. The temperature of the slurry was measured with a thermometer located in No. 2 agitator tank and was controlled by adjusting the temperature of the half-saturated solution by means of steam coils in the storage tank, from which the solution was pumped into the system.

The slurry overflowing from the No. 3 agitator tank passed through an inclined trough, made from 2-inch steel pipe, to the No. 1 rotary filter; there the saturated solution was separated from the partly extracted residue, and the residue was washed. The residue was then discharged into No. 4 agitator tank (half-saturation stage) for further extraction. Vacuum (usually 20 to 24 inches of mercury) for filtering was provided by use of a wet-type vacuum pump, which discharged the solution into a wood receiving tank, from which it was pumped through a plate-and-frame filter to remove small amounts of solids not removed by the rotary filter. The clarified saturated solution was pumped to the precipitation unit through a metering tank, which was used to determine the rate of solution production.

The half-saturation stage was carried out in the No. 2 extraction train, which consisted of four agitator tanks in series. Regenerated soda solution (containing sodium carbonate and bicarbonate) from the precipitation unit, and partly extracted residue from the No. 1 filter, entered No. 4 agitator tank and then passed successively through agitator tanks 5, 6, and 7 to No. 2 filter. A small amount of sinter was added to the slurry in No. 5 or 6 agitator tank. This sinter addition decreased the silica contents of the solution at this point and provided for better control of the silica content of the saturated solution. Equipment and procedure for controlling sinter and solution rates, temperature, and retention time were similar to those used in the No. 1 train. The filter was operated with a vacuum of 10 to 15 inches of mercury, which was supplied by a compressed air ejector, and the half-saturated solution (filtrate) was collected alternately in one of two receiving tanks. From the receiving tanks the solution was forced by compressed air at 30-minute intervals to a 1200-gallon storage tank, from which it was recycled to the No. 1 train.

The No. 1 filter had a 3-foot-diameter drum and a 1-foot face. The No. 2 filter had a 3-foot-diameter drum and a 2-foot face. The rate of rotation of No. 1 filter was 1.0 or 0.7 r.p.m., and that of the No. 2 filter was variable in the range of 0.20 to 0.36 r.p.m. The last-mentioned rates for each filter were the more satisfactory; when the rate was too slow the cake was so thick that it would slip off the drum; when the rate was too fast the cake was too thin for efficient washing. Wash water was supplied at the top of each drum through individually controlled spray nozzles, each of which had a capacity of about 0.1 gallon per minute. Three nozzles were used on the No. 1 filter and seven on the No. 2 filter.

Control of the retention time and temperature in the No. 1 extraction train (saturation stage) was particularly important because the silica content of the solution decreased with extraction time to a minimum value, then increased if the extraction time was too long. The extraction time that corresponded to the minimum silica content of the solution increased as the extraction temperature was decreased, and varied unpredictably with the composition and proportion of sinter used. The suitability of the temperature and retention time in No. 1 train was checked at 4-hour intervals by comparison of the silica content of the saturated solution with that of solution obtained by filtering a sample of the slurry from No. 2 agitator tank. It was assumed that the temperature and retention time were satisfactory when the silica content

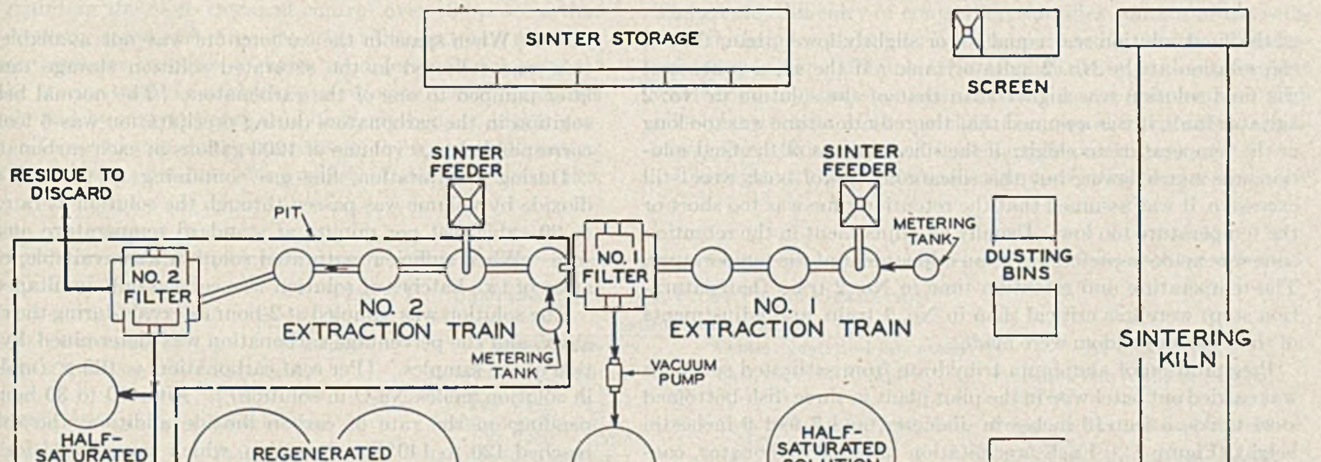

Figure 3. Floor Plan of Pilot Plant

TABLE I. DATA COLLECTED FOR PILOT PLANT OPERATION

Operation	Method of Determination	Frequency of Recording	Range or Usual Value	Remarks
Sintering				
Kiln feed[a], lb.	Platform scales	1 hr.	350	Batches weighed at 15-min. intervals and total wt. recorded hourly
Kiln product (−20 mesh), lb.	Platform scales	2 hr.	400	Weighed after dusting and screening in batches representing 2-hr. operation
Kiln product (+20 mesh), lb.	Platform scales	2 hr.	6	
Kiln speed[a], r.p.m.	Stop watch	8 hr.	0.5–1.25	...
Kiln retention time, hr.	Special test[b]	No schedule	1–3	[b]
Kiln stack gas temp., ° C.	Thermocouple	Continuous chart	640	...
Kiln hot-zone temp.[a], ° C.	Optical pyrometer	10 min.	1385	...
Oil rate, gal./hr.	Orifice meter	1 hr.	25	...
	Integrating meter	8 hr.	...	...
Primary air pressure, lb./sq. in.	Bourdon gage	1 hr.	8	...
Extraction				
No. 1 train (satn. step)				
Half-satd. soln. temp., ° C.	Thermometer	1 hr.	35–55	...
Half-satd. soln. vol., gal.	Calibrated tank	2 hr.	...	...
Half satd. soln. feed rate[a], gal./min.	Metering tank	1 hr.	1.4–2.5	...
No. 2 agitator temp.[a], ° C.	Thermometer	1 hr.	45	...
Sinter added to No. 1 agitator[a], lb.	Platform scales	1 hr.	100–170	Batches weighed at 20-min. intervals and total wt. recorded hourly
No. 1 filter speed[a], r.p.m.	Stop watch	No schedule	1.0–0.7	Varied by changing gear ratio
No. 1 filter vacuum, in. Hg	Manometer	1 hr.	20–24	...
Wash water rate[a], gal./min.	Orifice meter	1 hr.	0.0–0.45	...
	Integrating meter	2 hr.	...	...
Slurry retention time[a], min.	Calculated	4 hr.	15–50	Calcd. from slurry level in agitator tanks and soln. feed rate
Satd. soln. production rate, gal./min.	Metering tank	1 hr.	1.3–2.4	...
No. 2 train				
Regenerated soln. temp., ° C.	Thermometer	1 hr.	55	...
Regenerated soln. vol., gal.	Calibrated tank	2 hr.	...	...
Regenerated soln. feed rate[a], gal./min.	Metering tank	1 hr.	1.2–1.6	...
No. 5 agitator temp.[a], ° C.	Thermometer	1 hr.	50	...
Sinter added to No. 6 agitator[a], lb.	Platform scales	1 hr.	33–72	Batches weighed at 20-min. intervals and total wt. recorded hourly
No. 2 filter speed[a], r.p.m.	Stop watch	No schedule	0.20–0.36	Adjusted by variable speed drive
No. 2 filter vacuum, in. Hg	Manometer	1 hr.	10–15	...
Wash water rate[a], g.p.m.	Orifice meter	1 hr.	0.48–0.85	...
	Integrating meter	2 hr.	...	...
Slurry retention time[a], min.	Calculated	4 hr.	54–133	Calcd. from slurry level in agitator tanks and soln. feed rate
Precipitation				
Soln. vol., gal.	Calibrated tank	Each batch	1000	Measured before and after carbonation
Soln. temp.[a], ° C.	Thermometer	2 hr.	70	...
Flue gas rate, cu. ft./min.	Orifice meter	2 hr.	10–30	...
Flue gas temp.[a], ° C.	Thermometer	2 hr.	45–60	...
Flue gas pressure, lb./sq. in.	Bourdon gage	2 hr.	2.5	...
Carbonation time, hr.	Clock	Each batch	10–30	...
Product wt., lb.	Platform scales	Each batch	240–400	Weighed after drying 24 hr. at 150° C.

[a] Controlled variables.

[b] Kiln retention time was determined by adding iron oxide to a 100-lb. batch of kiln feed and observing time interval for maximum discoloration of product.

of the final solution was equal to, or slightly lower than, that of the solution at the No. 2 agitator tank. If the silica content of the final solution was higher than that of the solution in No. 2 agitator tank, it was assumed that the retention time was too long or the temperature too high; if the silica content of the final solution was much lower, but the silica contents of both were still excessive, it was assumed that the retention time was too short or the temperature too low. Usually an adjustment in the retention time was made in preference to an adjustment of the temperature. The temperature and retention time in No. 2 train (half-saturation step) were less critical than in No. 1 train, and adjustments of these factors seldom were made.

Precipitation of aluminum trihydrate from saturated solutions was carried out batchwise in the pilot plant in three dish-bottomed steel tanks, 5 feet 10 inches in diameter, and 7 feet 6 inches in height (Figure 1). Each precipitation tank, or carbonator, contained an air agitator consisting of a 1/2-inch pipe extending to a depth of 7 feet into the tank; compressed air from the plant supply was used for agitation. The solution in the carbonators was heated by steam jackets located around the walls near the bottom of the carbonators. The solution temperature was measured with gas-bulb thermometers protruding through the walls of the tanks. Each carbonator was provided with an adjustable-height decantation outlet of 1-inch pipe for the removal of liquid, and a 6-inch bottom outlet, fitted with a gate valve, for the removal of the trihydrate slurry. A fourth steel tank, identical in size to the carbonators, was used for storing saturated solution. The carbonators and the storage tank were fitted with tight wooden covers.

Saturated solution from the extraction unit—or from the desilication unit, when this step was included in the process—was collected in the carbonators and heated to 50° to 80° C. before carbonation. When space in the carbonators was not available, solution was collected in the saturated solution storage tank and later pumped to one of the carbonators. The normal height of solution in the carbonators during precipitation was 6 feet; this corresponded to a volume of 1200 gallons in each carbonator.

During precipitation, flue gas containing 10 to 30% carbon dioxide by volume was passed through the solution at rates of 10 to 30 cubic feet per minute at standard temperature and pressure. When sufficient saturated solution was available, carbonation of two batches of solution was carried out simultaneously.

The solution was sampled at 2-hour intervals during the carbonation, and the percentage carbonation was determined by titration of the samples. [Per cent carbonation = 100 × (moles CO_2 in solution/moles Na_2O in solution).] After 10 to 30 hours, depending on the rate of carbon dioxide addition, the solutions reached 120 to 140% carbonation, which was desired for use in the extraction step (2). Carbonation was then halted, and the precipitated aluminum trihydrate was allowed to settle for approximately 2 hours. The regenerated sodium carbonate solution was then decanted as completely as possible without disturbing the trihydrate and concentrated for use in the extraction unit by evaporation or by addition of sodium carbonate.

The mixture of aluminum trihydrate and residual sodium carbonate solution was flushed from the carbonators into a filter tank with water. The filter tank was a wooden tank 4 feet in diameter and 3 feet 8 inches in height that contained a filter cloth supported by a perforated steel plate. The tank was mounted on a hand truck so that it could be wheeled under the discharge of whichever carbonator was to be flushed out. After being washed three times in the filter tank, the trihydrate cake was dewatered by the application of vacuum supplied by an air ejector for at least 1 hour, and then dried in the tray dryer for approximately 24 hours at 150° C. The wash solution was discarded as a matter of convenience, although discarding in industrial practice would incur an uneconomical soda loss.

Desilication. Mention should be made of desilication investigations that were made in conjunction with the pilot plant but have not been included thus far in the description of the plant. Alumina produced in the pilot plant under carefully controlled conditions contained an average of 0.05% silica. To assure production of high grade alumina without the need of extreme accuracy in plant control, and to determine whether alumina containing less than 0.02% silica could be produced, a desilication step was included in the pilot plant during the latter part of its operation.

Laboratory scale tests showed that saturated solutions containing as much as 0.2% silica (Al_2O_3 basis) could be desilicated to less than 0.02% silica by agitating with lime for 30 minutes at 70° C.

In the pilot plant, twenty-six 250-gallon batches of saturated solution were successively agitated with a single 75-pound charge of lime in a steel tank; 97% of the silica was thereby removed from the solution. After each solution batch had been agitated with the lime for about 30 minutes, agitation was discontinued, the lime was allowed to settle for 30 minutes, and the solution was pumped to the precipitation unit through an 8-inch plate-and-frame filter. About 17% of the alumina was also precipitated by this treatment, but small scale tests indicated that this alumina precipitation might be reduced to about 4%. Operation of the desilication unit was continued for a sufficient length of time to establish the technical feasibility of this step, but no attempt was made to determine the best type of equipment for carrying it out.

DATA, SAMPLING, AND CONTROL

The principal data collected, the frequency of recording, and the usual range of values are shown in Table I. These data were recorded on standard forms provided for this purpose.

To maintain the close chemical control over the process that was necessary, speed was more important than extreme accuracy for some samples, whereas samples used for material balances over the process could be analyzed according to a less urgent time schedule and by conventional analytical methods of higher precision. To meet this dual requirement, a control laboratory was set up at the pilot plant for analysis of the control samples, and a control chemist was assigned to each shift. Volumetric methods of analysis were used in the control laboratory except for simple gravimetric procedures, such as ignition loss and moisture determinations. Other samples were analyzed by standard procedures in the central analytical laboratory.

The sampling system established for control of the pilot plant and for procurement of material balance data is shown in Table II. This table shows the constituents determined, the frequency of sampling, and the purpose of each sample.

RESULTS AND DISCUSSION

The conditions that were found suitable for production of sinter of maximum soluble alumina content in the pilot plant agreed closely with those defined by the laboratory scale work. The optimum temperature range was narrower in the pilot plant than in the laboratory because of mechanical difficulties caused by too much softening (fusion) of the sinter that occurred when the pilot plant kiln was operated in the upper portion (1390° to 1400° C.) of the temperature range that was optimum for small scale tests. The average proportion of soluble alumina in the sinter produced in the pilot plant during extended runs under optimum conditions was slightly less than that of sinter produced in the laboratory (87% as compared to 92% of the total alumina) probably because the time of heating at maximum temperature was not uniform. The nonuniformity of the total retention time in the kiln was determined in special tests in which a batch of kiln feed, colored by addition of iron oxide, was charged to the kiln preceded and followed by the regular kiln charge. The iron oxide color first appeared in the product 0.8 hour after charging, the deepest color occurred 2.2 hours after charging, and the last perceptible color was seen 4.7 hours after charging.

In general, the pilot plant extraction unit did not give solutions of so low a silica content as were obtained in the studies made on a smaller scale, although there were periods of several days of operation in the pilot plant when the silica content of the solutions was as low as those obtained from the small scale unit. The greater difficulty of controlling the silica content of the solutions in the pilot plant may have been caused by less exact chemical control. The alumina extraction efficiency in the pilot plant was about the same as was obtained in the laboratory. The pilot plant results of the precipitation step did not differ significantly from those obtained in the smaller scale work.

Throughout the developmental investigation major emphasis

Table II. Samples Taken for Pilot Plant Operation

Description of Sample	Frequency of Sampling	Constituents Determined: Control laboratory	Constituents Determined: Central analytical laboratory	Use of Analyses
Composite of limestone[a]	Each batch[b]	Ignition loss, moisture (mesh size: +100, −100 +200, −200 +325, −325)[c]	CaO, SiO_2, R_2O_3, MgO	Preparing kiln feed and material balance
Composite of clay[a]	Each batch[b]	Ignition loss (mesh size: +100, −100 +200, −200)[d]	CaO, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO	Preparing kiln feed and material balance
Composite of kiln feed[a]	Each batch[e]	Ignition loss, moisture	CaO, SiO_2	Controlling kiln feed composition
Sinter (as produced)	2 hr.	Soluble Al_2O_3	....	Evaluating results of kiln operation
Composite of sinter	Each kiln run[f]	Soluble Al_2O_3	CaO, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, ignition loss	Material balance
Composite of sinter bin	When bin refilled	Soluble Al_2O_3	CaO, SiO_2, R_2O_3, ignition loss	Calculating extraction efficiencies and material balance
Extraction residue from No. 2 filter[a]	Each shift	....	CaO, SiO_2, R_2O_3, MgO, ignition loss	Calculating extraction efficiencies and material balance
Regenerated soln. feed	4 hr.	Na_2O, % carbonation	Al_2O_3	Controlling operation of extraction unit and for material balance
Half-satd. soln. feed	4 hr.	Na_2O, Al_2O_3, SiO_2	....	
Half-satd. soln. product	8 hr.	Na_2O	Al_2O_3, SiO_2	
Satd. soln. slurry[g]	4 hr.	Na_2O, Al_2O_3, SiO_2	....	
Satd soln. filtrate	4 hr.	Na_2O, Al_2O_3, SiO_2	....	
Satd. soln. before carbonation	At start of carbonation	Na_2O	Al_2O_3, SiO_2	Material balance
Regenerated soln. produced	At end of carbonation	Na_2O	Al_2O_3, SiO_2	
Aluminum trihydrate[a]	After drying in tray dryer	(Mesh size: +20, −20 +200, −200 +325, −325)[b]	Ignition loss, SiO_2	
Satd. soln. being carbonated	4 hr.	Na_2O, % carbonation	....	Controlling progress of carbonation
Flue gas for carbonation	2 hr.	CO_2, O_2, CO	....	Controlling carbonation and determining CO_2 absorption efficiency

[a] Dried at 150° C. by the control laboratory.
[b] Each batch = 10 tons.
[c] Wet-screen analysis
[d] Dry-screen analysis.
[e] Sampled as fed, composited by shifts. Shift samples composited by batch.
[f] 2-hour sinter samples composited at end of each run.
[g] Filtered immediately; filtrate analyzed as indicated.

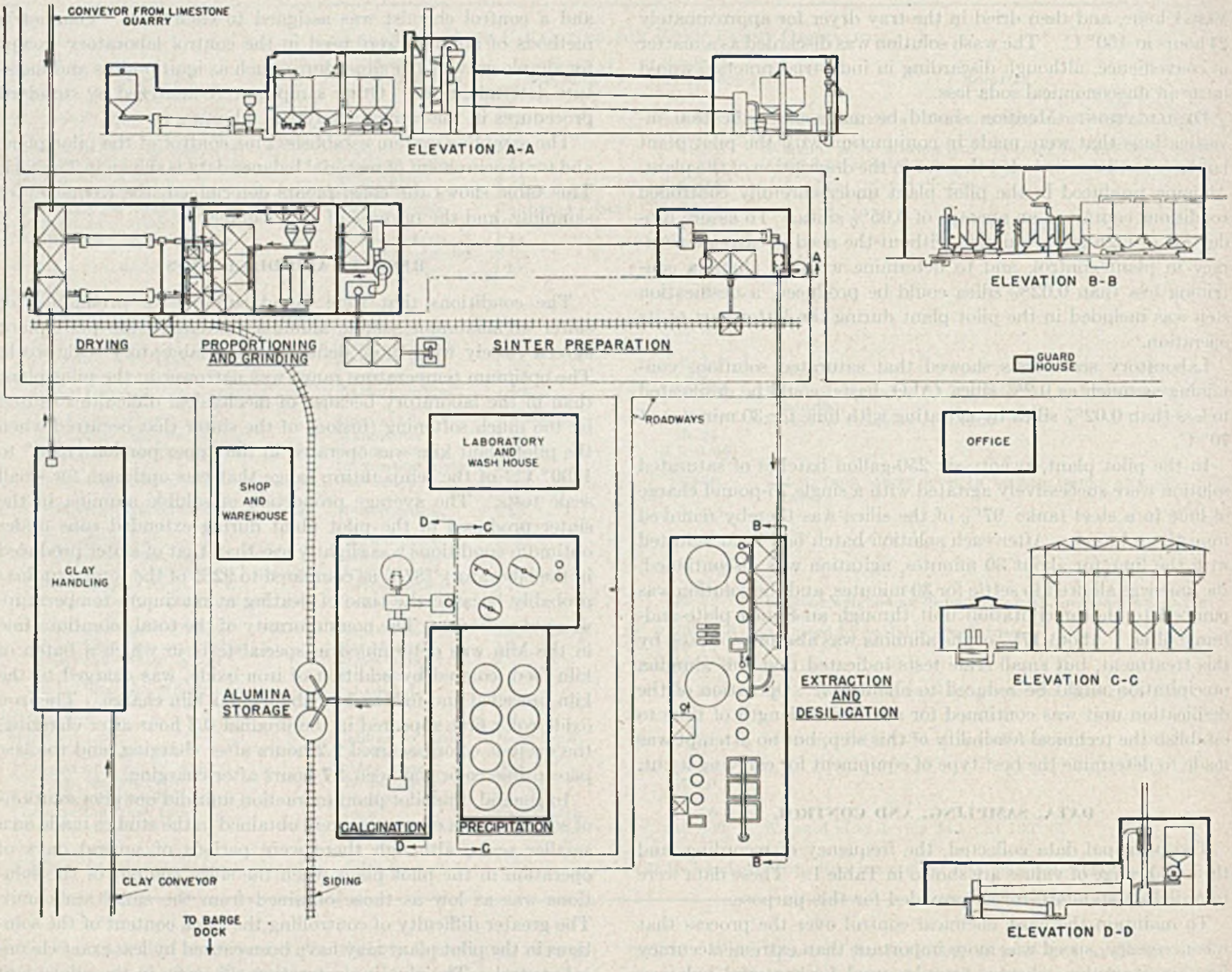

Figure 4. Layout of Proposed Demonstration Plant for Producing 50 Tons of Alumina per Day by Modified Pedersen Process

was placed on definition of basic engineering data required for carrying out the process. Such data would be applicable in the large scale production of alumina from clay by the lime-sinter modification of the Pedersen process, and it is believed that enough data were obtained so that little difficulty would be involved in applying the process to semiwork scale or full scale operation.

Detailed information was obtained on the preparation of raw materials for sintering, such as fineness and time of grinding, and mixing procedures. Sintering was studied from such standpoints as accuracy of temperature control and retention time in kiln. Extraction data included accuracy necessary in proportioning sinter and extraction solution, temperature control, agitation required, filtration and washing, and cement formation. Considerable desilication information was obtained. Studies of carbonation and precipitation produced data on time of precipitation, amount of carbon dioxide required, and settling rates of precipitate.

Estimates were made in considerable detail on construction and production costs for a plant having a capacity of 50 tons of alumina per day. A demonstration plant of this size was considered the next logical step in the development before design of a large scale plant. Based on economic conditions prevailing in 1944, the estimated investment for a 50-ton-per-day plant was about 4 million dollars, and the estimated cost of producing alumina in such a plant was about 47 dollars per ton. This does not include depreciation charges and assumes that the clay used would be of somewhat lower grade than that used in the pilot plant (39% as compared to 44% alumina, calcined basis). A layout of this plant is shown in Figure 4. A similar estimate indicated that the investment cost for a 160-ton-per-day plant would be 9 million dollars, and the production cost would be 35 dollars per ton of alumina.

ACKNOWLEDGMENT

The work described in this paper was carried out under the general supervision of R. L. Copson and J. H. Walthall of the Tennessee Valley Authority and John D. Sullivan and other members of the War Metallurgy Committee. Acknowledgment is made to the War Production Board, which financed the investigation; to L. I. Mitchell, E. E. Coll, D. O. Myatt, and other members of the technical staff of the Chemical Engineering Department of the Tennessee Valley Authority who aided in carrying out the experimental work; and to E. L. Newman and Julius Silverberg for assistance in the preparation of this paper.

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(3) Pedersen, H., Brit. Patent 232,930 (April 23, 1924).
(4) Pedersen, H., U. S. Patent 1,618,105 (Feb. 15, 1927).
(5) Seailles, J. C., and Dyckerhoff, W. R. G., *Ibid.*, 2,248,826 (July 8, 1941).

July's HEADLINES...

Events of Interest to Chemists, Chemical Engineers, and Executives∼∼*Reviewed by the Editors*

¶ July 1. American Institute of Chemists' committee on national legislation affecting chemists favors National Science Foundation bill, recommending proposed Federal Act to create Foundation include "To achieve permanent peace with all nations" as statement of purpose, Foster D. Snell, president, announces. Committee consists of: L. N. Markwood, Eduard Farber, and Gustav Egloff.∼∼John L. McMurphy, manager compound division, GE, announces completion of Pittsfield, Mass., magnesium oxide plant.∼∼American-Soviet Medical Society publication reports Russian cancer remedy, KR, is dissolving malignant growths on half of patients treated.∼∼Guatemala grants oil exploration rights in 2,000,000-acre area to Stapper Oil Co., Houston, Tex.∼∼International Rubber Study Group conference opens in Paris; discussion expected to include issue of over-production, and synthetic versus natural rubber.∼∼George W. Merck, president Merck & Co., Inc., reports promotions of R. T. Major to vice president and scientific director, J. H. Gage to treasurer, and Per K. Frolich to director of research and development.

¶ July 2. Hooker Electrochemical Co. plans $8,000,000 chlorine products expansion program to be completed in 1949, E. R. Bartlett, president, says.∼∼Representative Gavin asks immediate halt of oil shipments to Russia, and exports of steel and pipe, in order that American petroleum industry can prepare itself "to meet any and all emergencies."∼∼To expand German export program, British Military Government officials propose temporary production of vanadium, one of 14 categories barred from German industrial potential by Potsdam Agreement. ∼∼Monsanto Chemical Co. announces appointment of R. M. Hitchens as research director of company's organic chemicals division.

¶ July 3. GE issues release by Atomic Energy Commission announcing program for installations of chemical processing plants to improve plutonium manufacture at atomic energy plant near Richland, Wash., world's second atomic city[1].

¶ July 4. Department of Commerce announces end of allocations for streptomycin; revocation does not affect export licensing controls administered by Office of International Trade[1].

¶ July 5. USAEC takes steps to create Division of Medical Research to intensify operations in beneficial use of atomic energy, and parallel Commission's divisions of Research, Engineering, Production, and Military Application, as result of recommendations made by its Medical Board of Review[2].

¶ July 6. Tennessee Corp., through subsidiary, Tennessee Copper Co., leases 180,000-ton-per-year sulfuric acid plant in Calacoosa, Ala., from Ordnance Department; record jump in superphosphate production expected.∼∼Carbide & Carbon Chemicals Corp. begins production of vinyl ethers at South Charleston, W. Va., plant[3].∼∼S. B. Penick & Co., manufacturers of botanical drugs and fine chemicals, establishes 5 research grants at Universities of Illinois, Wisconsin, California, Harvard and Scripps Metabolic Clinic; extends another at University of Michigan[4].

¶ July 7. UNAEC Working Committee gives tentative approval to Soviet proposal that international control plan provide for "destruction" of existing weapons when it becomes effective, instead of "disposal," as mentioned in Baruch plan.∼∼A.C.S. establishes committee of 11 leading chemists and chemical engineers to study methods for improving chemical education in our schools and colleges, W. Albert Noyes, Jr., President, announces. Group includes: Wm. G. Young, S. E. Q. Ashley, H. E. Bent, H. C. Brown, H. M. Crawford, J. S. Crout, J. B. Culbertson, S. B. Foster, H. F. Lewis, A. F. McGuinn, and R. C. Roberts.

¶ July 8. American plan of work for UN Commission on Conventional Armaments, previously adopted in preference to Russian plan by Commission, approved by Security Council, 9 to 0, Russia and Poland abstaining.∼∼Undersecretary of Commerce Foster opposes "drastically curtailing" American oil exports to Russia on grounds shipments are part of normal supply, and oil shipped during last 6 months would be consumed in U. S. in $3^{1}/_{2}$ hours.∼∼War Assets Administration announces sale of 100-octane gasoline refinery, Houston, Tex., to wartime lessee, Eastern States Petroleum Co., for $2,000,000.

¶ July 9. Frederick H. Osborn, deputy U. S. representative, urges UNAEC Controls Committee to limit atomic research by countries capable of producing significant quantities of nuclear fuel, foresees nuclear-fuel race as alternative.∼∼War Department announces 6 leading American scientists will depart July 15 to aid in evaluating plans for democratization of scientific research in Japan. Group consists of: Roger Adams, Merrill K. Bennett, Wm. D. Coolidge, Wm. V. Houston, Wm. J. Robbins, and Royal W. Sorenson[5].

¶ July 10. A.C.S. names Harold C. Urey as its representative for UNESCO, W. Albert Noyes, Jr., President, reports[6].∼∼National Vitamin Foundation, Inc., votes 4 grants-in-aid amounting to $32,000 for vitamin studies, R. S. Goodhart, scientific director, states[7].∼∼University of Chicago plans $10,000,000 construction program for basic scientific research in nucleonics, first building to be completed in spring, W. C. Hunnecke, vice president, says. ∼∼W. S. Richardson, president B. F. Goodrich Co., announces company will relinquish on Oct. 1 operation of 45,000-ton capacity Borger, Tex., American-made rubber plant it built for Government in 1942, to new operator, U. S. Rubber Co.[8]

¶ July 11. University of California's giant new cyclotron frees possible 30 nuclear particles in single bombardment, 10 or 15 previously unknown, as compared with 2 or 3 blasted from atomic nuclei by former smashers, Berkeley physicists tell American Physical Society meeting[9].

¶ July 12. Canadian Reconstruction Minister Howe says 20 parties are searching for radioactive materials in Northwest Territories; finds to be controlled by government.∼∼University of Chicago breaks ground for construction of $1,250,000 "Ion Accelerator" building intended to house latest atom-smashing de-

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[1] *Chem. Eng. News*, 25, 2092 (July 21, 1947).
[2] *Ibid.*, 2086 (July 21, 1947).
[3] *Ibid.*, 2164 (July 28, 1947).
[4] *Ibid.*, 2309 (Aug. 11, 1947).
[5] *Ibid.*, 2065 (July 21, 1947).
[6] *Ibid.*, 1993 (July 14, 1947).
[7] *Ibid.*, 2221 (Aug. 4, 1947).
[8] *Ibid.*, 2214 (Aug. 4, 1947).
[9] *Ibid.*, 2144 (July 28, 1947).

vices.∼∼Princeton University scientists release 325-foot chain of helium-filled balloons in attempt to transport 17 lb. of electronic equipment to 20-mile height; results will enable calculation of frequency of nuclear explosions caused by cosmic rays passing through ionization chamber.∼∼*Honolulu Advertiser* reports building of world's first airfield expressly for atomic warfare near Fairbanks, Alaska, the "most strategic spot on earth."

¶ July 13. Navy awards Texas Co. $6,325,000 contract to provide 8,000,000 gal. lubricating oil during fiscal year, R. L. Saunders announces.

¶ July 14. Netherlands Indies Government Trade Commissioner reports Indies have sufficient quantities of quinine salts on hand to increase shipments to U. S. by 50% during next 9 months.∼∼Explosion wrecks monochlorobenzene plant of Solvay Process Co. at Syracuse, N. Y.

¶ July 15. General Aniline & Film Corp. embarks on $15,000,000 plant expansion program at Rensselaer and Binghamton, N. Y., and Grasselli, N. J., to augment production of dyestuffs and photo chemicals, Jack Frye, chairman board of directors, announces.∼∼Hercules Powder Co. renews $10,000 fellowship grant at University of Delaware's entomology department, G. L. Schuster, director agricultural experiment station, reports.

¶ July 16. USAEC announces atomic city of Los Alamos, N. Mex., will be modernized in 3-year construction program calling for houses, schools, and church; Capt. Carroll L. Tyler appointed director of laboratory, where multi-million dollar improvement program is under way.∼∼House passes bill to create 24-member National Science Foundation to supervise scientific activities for Government and to promote work in field of "pure science[10]."∼∼Senate passes and sends to House bill authorizing $100,000,000 annual Federal loan to states to combat water pollution[10].∼∼E. M. Ford, president Wyandotte Chemicals Corp., announces tentative completion dates for 6 new chemical plants comprising $25,000,000 expansion program, as follows: glycol, September 1947; synthetic detergent, November 1947; chlorine, January 1948; light ash, March 1948; power plant addition, December 1947; and dense ash, June 1948.

¶ July 17. Office of Materials Distribution announces amendment of order covering cinchona bark, quinine, and quinidine, authorizing allocation control only over supplies of bark and drugs held in, acquired from, or made from government-owned stocks. ∼∼Cities Service Co. and Continental Oil Co. form Citcon Corp.; plan construction of $30,000,000 plant on 162-acre tract in Lake Charles, La., designed to be largest in U. S. for manufacture of solvent refined lubricating oils.

¶ July 18. Two new natural antibacterial substances, lateritin and licheniformin, show promise as agents for combating tuberculosis germs—one believed adjunct to streptomycin, H. R. V. Arnstein, A. H. Cook, T. H. Farmer, and M. S. Lacey of Imperial College of Science and Technology, London, and R. K. Callow, National Institute for Medical Research, London, tell XIth International Congress of Pure and Applied Chemistry meeting in London.∼∼Securities & Exchange Commission approves loan to United Natural Gas Co., Oil City, Pa., for construction of 71-mile pipeline to connect with "Big Inch" line.

¶ July 19. Karl Folkers, director organic and biochemical research, Merck & Co., Rahway, N. J., tells International Congress of Pure and Applied Chemistry conference of new findings in chemical architecture of streptomycin, first step toward duplicating nature's product by synthetic means.∼∼U. S. Public Health Service designates University of Illinois as sole facility in country for manufacture of bacillus of Calmette and Guerin, vaccine hoped to extinguish threat of tuberculosis in U. S. in from 20 to 40 years; wholesale processing will be started in new tuberculosis research hospital to cost $360,000.

¶ July 20. Monsanto Chemical Co. will operate new atomic energy laboratory under construction at Miamisburg, Ohio, by Atomic Energy Commission, and will engage in investigation of basic chemical problems in field of atomic energy.∼∼Standard Oil Co. (Ind.) in letter to employees and dealers, denies shipping single gallon of oil products to Russia, but states that all oil exports are made with full knowledge of U. S. Government.

¶ July 22. Congress sends to White House bill to create National Science Foundation, successor to wartime Office of Scientific Research and Development and expanding its function to cover all fields of science with emphasis on basic research. Bill provides for selection by foundation of director; carries no funds for operation[11].∼∼House votes 175 to 78 for continuation of premium price plan for copper, lead, and zinc for 2 additional years, and adds manganese to list.∼∼Canada reimposes oil export regulations in move to cooperate with U. S.

¶ July 23. USAEC informs Congress in semiannual report it is "establishing proving grounds in Pacific for routine experiments and tests of atomic weapons."∼∼American Legion proposes "fully effective" UN by trimming veto, granting Security Council new powers to control atomic and other weapons, and creating world police force.∼∼Mary Lura Sherrill, head, Chemistry Department, Mt. Holyoke College, will receive Francis P. Garvan Medal of A.C.S. honoring women in chemistry, W. Albert Noyes, Jr., President, announces.

¶ July 26. Fourth International Congress for Microbiology, attended by 1000 world leaders in bacteriology, unanimously adopts resolution "condeming in strongest possible terms all forms of bacteriological warfare." Selman A. Waksman, Rutgers University, receives Emil Christian Hansen Gold Medal and prize of 5000 kroner for work in using soil bacteria to combat diseases in men and animals.

¶ July 27. Chemical Corps plans disposal of 153,000 tons surplus chemical war materials including over 1000 tons chlorinated paraffin and about 2500 tons Impregnite.∼∼Construction operations on $10,800,000 modernization program begin at A. E. Staley Manufacturing Co.

¶ July 28. Department of Agriculture orders end of industrial sugar rationing; plan replaced by sugar inventory controls.∼∼USAEC announces construction of atomic pile and associated facilities for atomic research to be created at Brookhaven National Laboratory on 3700-acre site, formerly Camp Upton, L. I., will begin next month for completion in 1948.

¶ July 29. Alden H. Emery, Secretary, announces recent establishment of second A.C.S. Local Section outside U. S., in Puerto Rico; Hawaiian Section was chartered in 1922.∼∼Socony-Vacuum Oil Co. opens miniature lubricating oil refinery at Paulsboro, N. J., only one of kind in existence, to manufacture lubricants for experimental purposes.∼∼Bureau of Mines searches U. S. lignite fields for source of fine waxes formerly imported from area in Germany now occupied by Russia.

¶ July 30. Justice Department officials study Swedish Government Commission Report on alleged international oil cartel involving 3 U. S. firms and 3 foreign companies to determine to what extent activities violate U. S. antitrust laws.∼∼First quarter U. S. chemical exports indicate 1947 annual total will exceed $700,000,000, rise of $200,000,000 over that reached in 1946, and 4 times greater than prewar exports.∼∼Imperial Chemical Industries, Britain's largest chemical manufacturer, cuts soda ash production 30% due to coal shortage; action will seriously affect chemical and allied industries.∼∼Du Pont establishes service school in petroleum chemicals as first step in enlarged petroleum program.∼∼Sheffield Steel Corp. starts peacetime operations of Texas blast furnaces leased from WAA for 18 months, R. L. Gray, president, announces.

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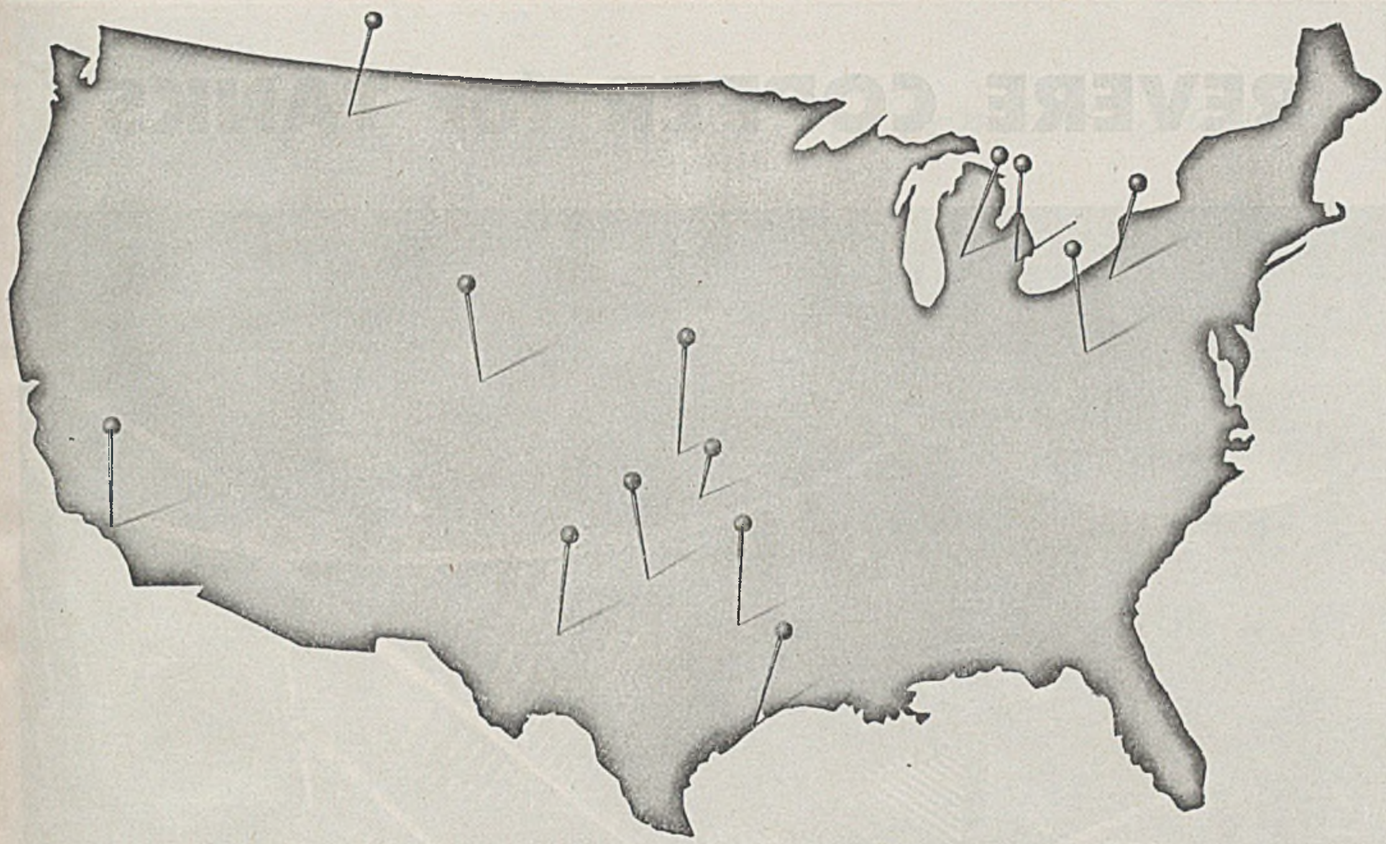
[10] *Ibid.*, 2127 (July 28, 1947).

[11] *Ibid.*, 2191 (Aug. 4, 1947).



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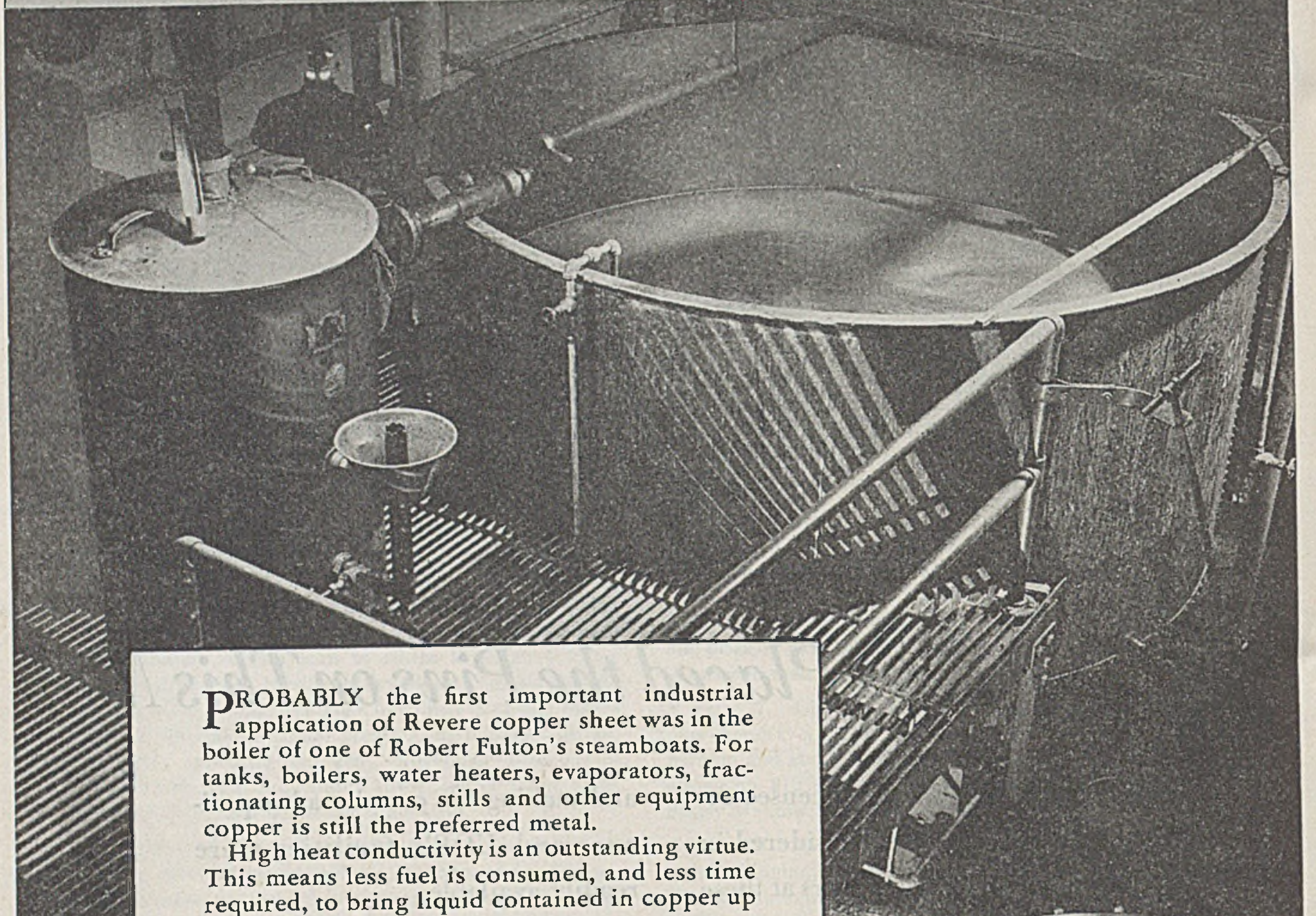

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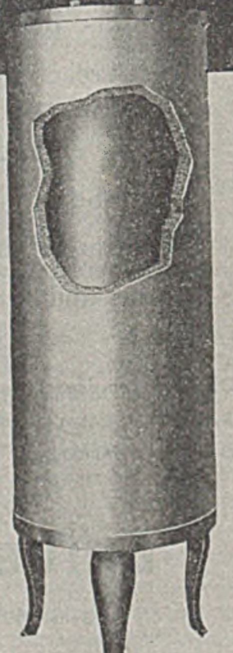

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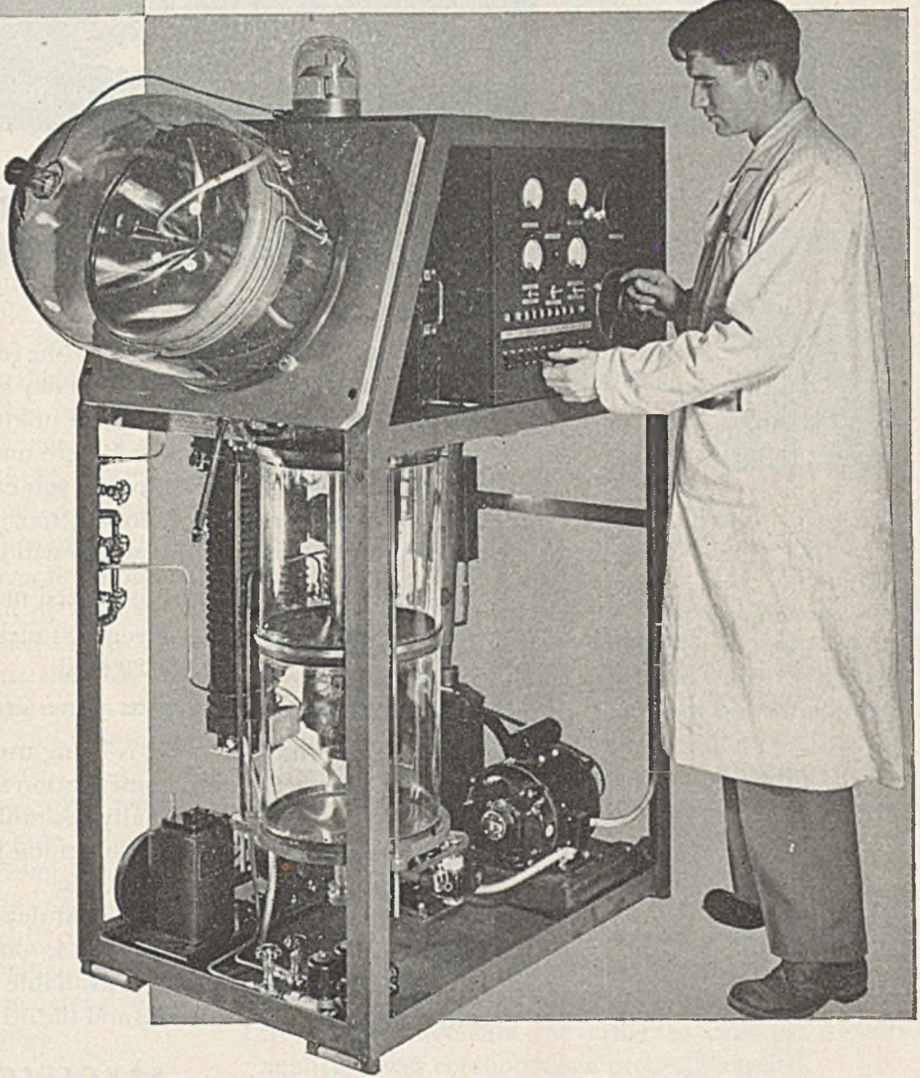

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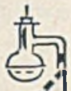

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Equipment and Design

Economies in fabrication can be attained by proper evaluation and comparison of riveting, casting, and welding.

by Charles Owen Brown

Recently we devoted two columns to a brief description of welding fundamentals, touching only the essentials of this magical method of fabricating metals. Our editor has suggested that the chapter will be complete only when some comparison is drawn between riveting, casting, and welding as means of creating structures and equipment. A simple, clear comparison of these three types of construction is not easy to draft, and we found it difficult to assemble the appraisal we desired. Surprisingly, several equipment manufacturers were very noncommittal and would place no definite values on any of the three types. The usual answer was a hedging statement that the type of construction depended upon a great many factors. Others believed that riveting, casting, and welding are too divergent in character to be compared.

An exception to these uniformly negative verdicts was generously given the writer by an able, resourceful consulting metallurgist, William Barker Brooks of Pittsburgh. From a rich experience in metals, alloys, and welding problems, Brooks quickly made some general observations and developed some definite fields for the three types. We have drawn extensively on his theories for a discussion of this subject.

Comparisons

Casting metals and fabrications by riveting are not becoming obsolete because each has merits no competent engineer can ignore. Like the blacksmith's art, riveting especially is not expanding to account for so large a share of new manufacturing as is welding. Riveting is no match for such a versatile tool as welding and is further penalized by a sharp increase in labor costs. A clear comparison, however, is very difficult to make, as a few examples will demonstrate.

Welding is often used on castings and to augment riveted work, and the combination in each case is better in quality and lower in cost than the use of either procedure alone. Large bed plates for electrical machinery, main frames for locomotives, and stern frame halves for ships have been cast in sections and then welded together to give a better product of lower cost. Crank shaft forgings for ten-cylinder Diesel engines are not only heavy but long and awkward billets of steel. They are costly to handle during machining, and only one bearing can be machined at one time. But by welding twenty small single-throw forgings together at the neutral center point of each bearing, a superior crank shaft results in a much shorter time, since several machine stations can work on the twenty small forgings at one time and complete all the rough machine work. Fluid metal can be poured so as to flow into the intricate corners of some very complicated shapes, but if the physics of heat flow, shrinkage, and solidification are not properly provided for, an imperfect casting will result which must be discarded. If such a casting is divided into two or three simple pieces easily cast, these can be welded into a better finished job with no rejects. Few castings are really sound homogenous solids like rolled or forged steel. A welding repair is often necessary to save the casting.

Evaluations

The examples given define the first principle in a comparison of welding with other types of construction: Riveting, casting, and welding are not strictly competitive—each augments the other to produce a better quality, lower cost job when properly applied.

Many classes of work can be made wholly by riveting, casting, or welding, but under certain conditions these types of construction change places. Take, as an example, fabrication of a 10 × 10 inch box-type support bracket. A blacksmith would cut a 10 × 20 inch piece of steel plate and bend it at the center to a right angle. Two triangular pieces of steel with two edges bent to a right angle are then riveted to the outer edges of the larger angle to form a triangular box support bracket. The welder would cut a piece 10 inches wide from a 10 × 10 inch 90°-angle beam, then two right triangular plates from a steel sheet, which are welded to the cut edges of the angle beam and form a box support bracket. Both of these brackets can be welded to a steel tank, but if they are to support a cast-iron structure, each must be riveted to the cast iron, and this would change the preferred type of fabrication. A bracket of this size and type can be cast easily from steel, but if only a few are wanted it would be cheaper to make them by gas cutting the material and welding the parts. If 2500 are

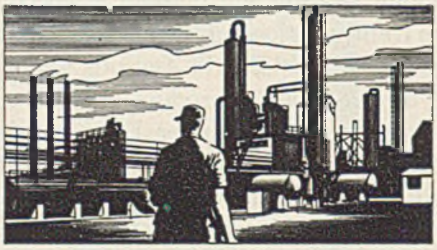
(Continued on page 82 A)

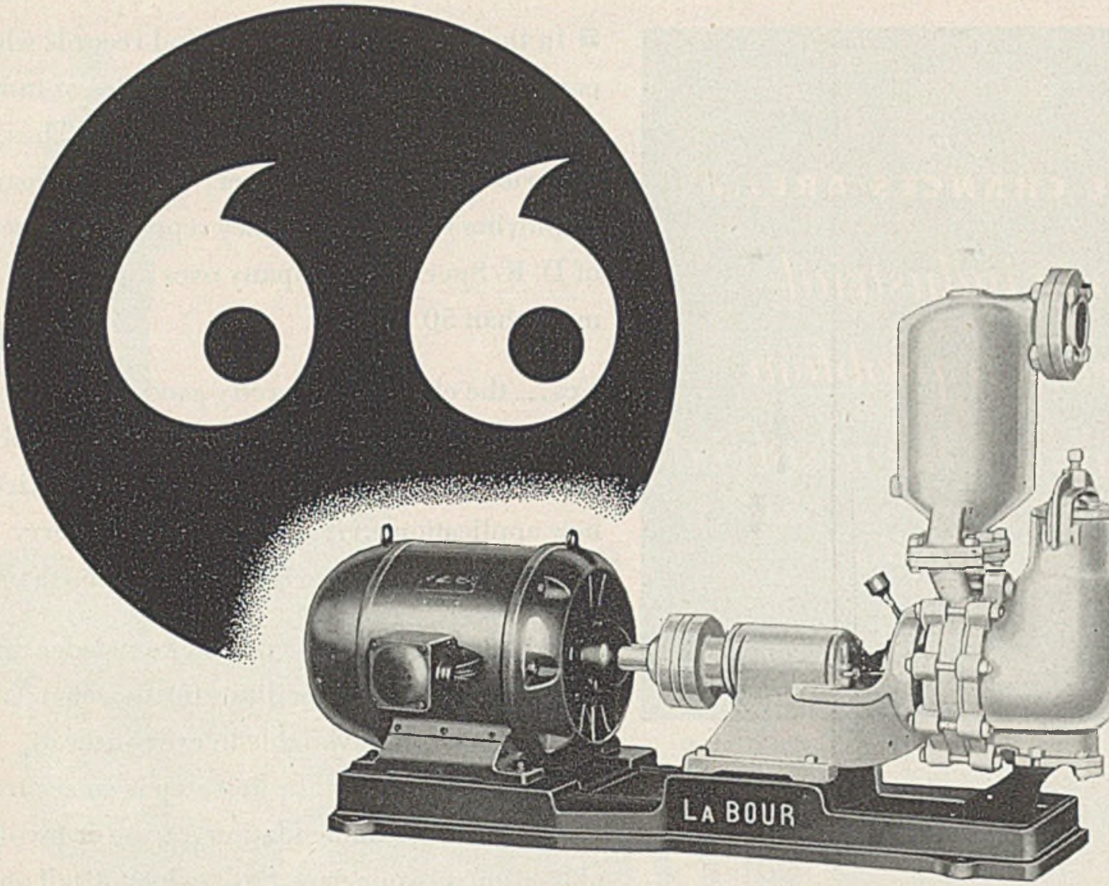
Equipment and Design

wanted, casting would prove to be more economical. The second principle in the comparison of construction types is: Outside or indirect conditions may completely reverse the preferred type of construction.

In the given example both welded and cast brackets can be made of nearly equal weight and strength. The riveted bracket is much heavier. There is necessarily a great deal of dead weight in all riveted work—overlapping seams, punchings from rivet holes and rivet heads. There is also a lesser but appreciable waste of metals in castings. Cast steel has a slightly lower design stress than does worked steel, and certain sections of castings must be made thicker than the actual load requires. In certain places—tall buildings, ships, and airplanes—this excess weight is a direct penalty. Around chemical plants all riveted work is objectional, not because of excess weight but because of corrosion. Rivet holes are points of stress concentration, and liquids and salts have a way of accumulating between faying edges and under caulking beads. Protective painting is less costly and far more effective on solid metal. Fusion welding eliminates these objectionable points. The third principle in this comparison of construction types is: Under certain conditions one special factor is of extraordinary importance and dictates the type of construction regardless of the other factors.

That rare commodity, creative thinking, is highly essential in all welded work. In riveted work the craftsman closely executes the work as laid out directly on the material by an engineeer, who follows the designs of several other engineers. In production work machine gages and jigs often aid in accuracy. Castings are made from patterns or actual models produced by the pattern maker from carefully engineered designs. Several people have an opportunity to create and perfect the final article. But the final perfection of all welded work is to some extent the sole contribution of the welder. An efficient, sound design must start with an intelligent understanding of the advantages and limits of welding. Welds can approach monolithic character and very light weight for the load carried, but flexibility decreases and care must be taken to avoid notch effects and sections of concentrated strain. These considerations define the fourth principle of this comparison: Welds must not ape the designs and contours of riveted or cast equipment. Weld designs should be functional and able to fill the highest qualifications.

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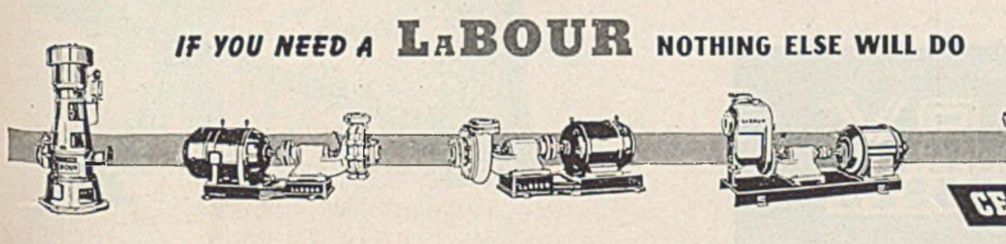

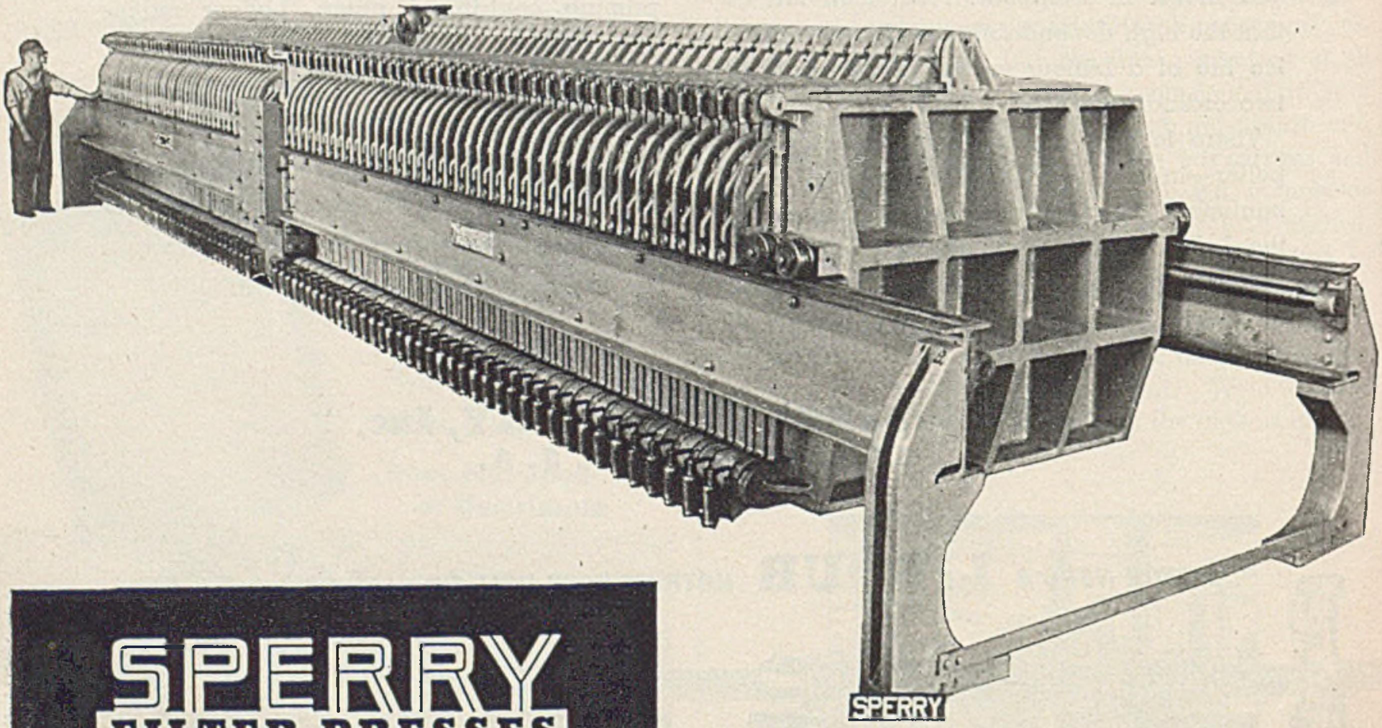
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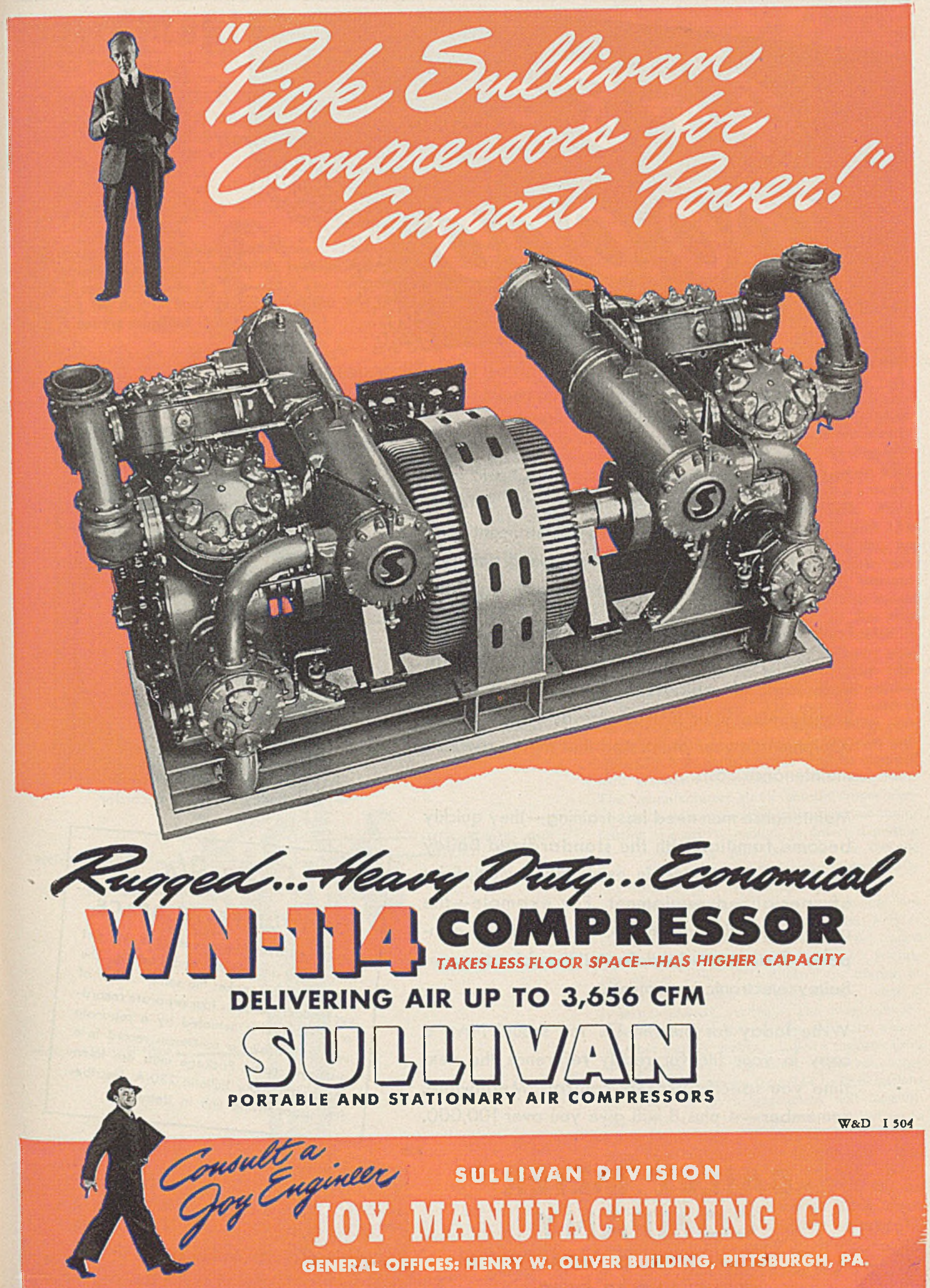

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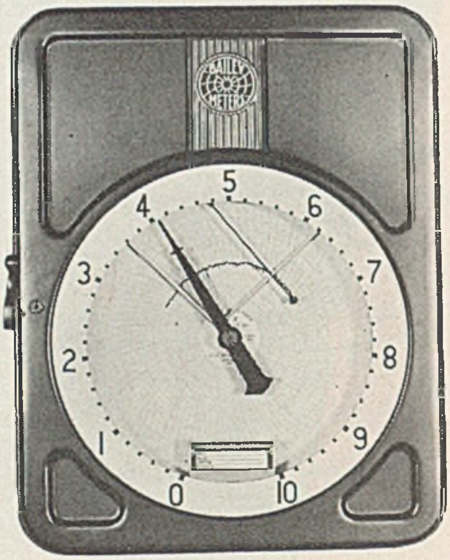

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Instrumentation

A variable area type of flowmeter and a thermocouple vacuum gage are discussed this month with respect to new applications, combinations, and protective devices.

by Ralph H. Munch

Perhaps the most widely used type of flowmeter is the variable head type in which the pressure drop across an orifice is used to indicate the flow rate. The fundamental law governing the flow of fluid through an orifice may be written in the following simplified form:

$$Q = KA\sqrt{h}$$

where Q = volume of fluid flowing per unit time
K = constant for a given type of orifice and fluid
h = pressure drop across the orifice

This equation states that if the orifice area is constant, the flow varies as the square root of the pressure differential. Thus in a variable head flowmeter, the scale is nonlinear, being compressed at the low end and open at the high end. Because of the inconvenience of this type of scale, many instrument manufacturers are now producing flowmeters of the variable area type, in which the orifice area is varied to produce a constant pressure drop. The equation shows that if pressure drop h is constant, the flow rate is directly proportional to orifice area A; meters operating on this principle have a linear scale. The most familiar instruments of this type are rotameters.

Flowmeter

The Bailey Meter Company, 1050 Ivanhoe Road, Cleveland 10, Ohio, has just placed on the market a new electronically operated flowmeter of the variable area type. As Figure 1 shows, the meter body carries a cylindrical port sleeve with rectangular ports cut in it. Sliding in the port sleeve is a metering plug which is pulled downward by a spring or weight. Fluid enters from the left, passes up through the port sleeve, and forces the metering plug up until a sufficient port area is opened to permit passage of the fluid under the constant pressure drop fixed by the calibrating spring or weight. With this arrangement the flow rate is proportional to the orifice area, which is proportional to the height of the metering plug in the port sleeve. An impedance-bridge telemetering system is used to indicate the position of the metering plug. The receiving unit of the impedance bridge is a standard Bailey electronic indicator or recorder with its scale calibrated in flow units. Either may be supplied with standard pneumatic control equipment. The manufacturers state that the impedance-bridge telemetering system with electronic amplification is sensitive enough to detect a motion of the metering plug as small as 0.00005 inch. The receiver can be located at practically any distance from the transmitter.

As was mentioned, these instruments are available in both spring-loaded and weight-loaded types. The spring-loaded type causes a pressure drop of approximately 10 pounds per square inch. It is suitable for marine or mobile use because it will operate even if it is not exactly vertical. The weight-loaded type, which must be installed with the weight chamber exactly vertical, causes a pressure drop of 2 pounds per square inch. The two types cover full scale ranges from 144 to 3840 gallons per hour. A given instrument will measure flows over a 50-to-1 range and be sensitive to 0.25% of full scale. The manufacturers recommend these instruments for difficult jobs; they are especially suitable for use with viscous fluids, and vibration will not impair the accuracy of the measuring system. These instruments are described in Bailey bulletins 231 and 233.

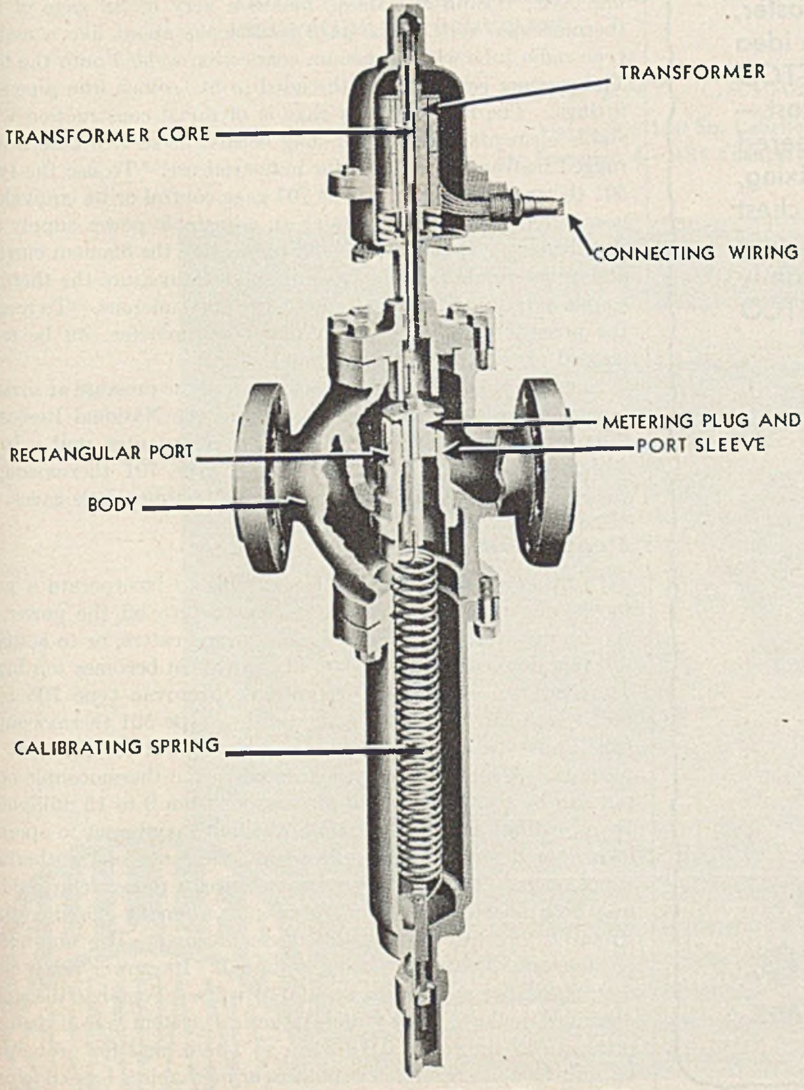
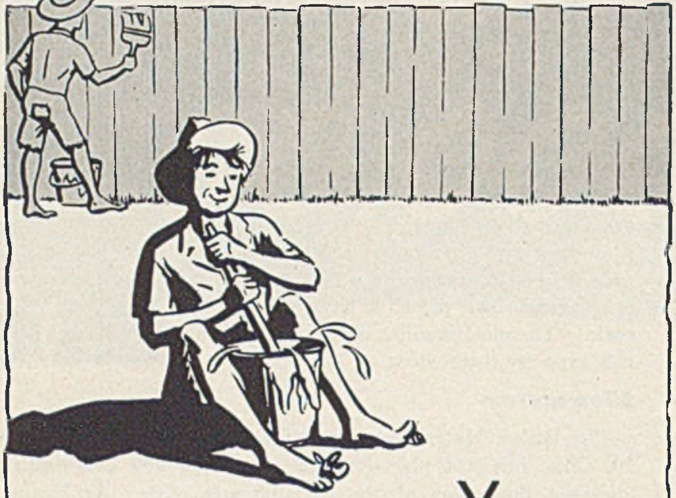
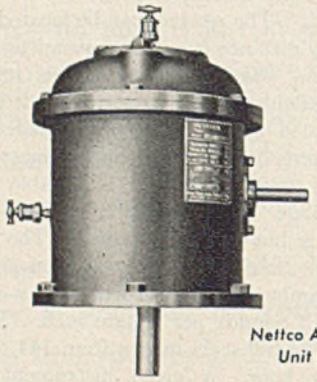


Figure 1. Bailey Area Meter Transmitter

(*Continued on page 88A*)





Instrumentation

New uses

It is interesting to note that the area type of flowmeter represents a new application for the standard Bailey electronic recorder. The original application was to resistance thermometry. The oxygen recorder and the combustibles recorder followed. Then thermocouple temperature recorders and differential pressure instruments were announced. Applications have also been made to speed and position measurement, and smoke density and gas analyses. All of these applications are made possible by primary elements which convert the variables named into resistance changes or voltages which a standard instrument can measure. This group is a nice example of a highly integrated group of instruments which makes maximum use of a minimum number of standard parts. Planning of this type should prove beneficial to both manufacturers and users of instruments.

High vacuum gage

We have previously mentioned various instruments for measuring low pressures. Among them was the Pirani gage, the operation of which depends on the fact that the thermal losses from a heated filament vary rapidly with pressure in the range below 1 or 2 mm. In the case of the Pirani gage the temperature of the filament is determined by measuring its resistance. The thermocouple gage depends on the same principle as the Pirani, but uses a small thermocouple welded to the filament to measure filament temperature. The National Research Corporation, 100 Brookline Ave., Boston 15, Mass., makes a very useful gage of the thermocouple type. The gage itself looks about like a metal-type radio tube with a vacuum connection welded onto the top. The vacuum connection is threaded to fit $^{1}/_{8}$-inch iron pipe size fittings. The fact that this gage is of metal construction with stable elements designed for long consistent service makes it a rugged instrument suitable for industrial use. To use the type 501 thermocouple gage, a type 701 gage control or its equivalent is required. This unit contains an adjustable power supply for the filament. It has an ammeter to measure the filament current and a meter calibrated in pressure units to measure the thermocouple output. The range is from 1 to 1000 microns. To record the pressure, a standard recording potentiometer can be used instead of the thermocouple meter.

In many cases, it is desirable to measure the pressure at several points in the system. For this purpose the National Research Corporation supplies type 702 five-point adapter unit. It is designed for use in conjunction with type 701 thermocouple gage control unit and up to five type 501 thermocouple gages.

Protection

In many types of work it is desirable to incorporate a protective device into a vacuum system to turn off the power to certain apparatus, such as diffusion pump heaters, or to actuate warning devices if the pressure in the system becomes too high. The National Research Corporation's Protovac type 705 is a unit which can be used together with a type 501 thermocouple gage and type 701 thermocouple gage control for this sort of purpose. A sensitive relay connected to the thermocouple output can be set to operate at any output from 0 to 15 millivolts. By adjusting the relay, therefore, the unit may be set to operate at any predetermined pressure within the range of the thermocouple gage. The sensitive relay energizes a power relay, which may be connected to a normally open or normally closed control circuit to operate any type of device desired. The unit must be manually reset after being actuated. Its power relay contacts are rated at 10 amperes at 110 volts. Together the units described make a very simple practical system for measuring pressures in the range 0.001 mm. to 1 mm. and for protecting vacuum systems from power failures or mechanical breakdowns.

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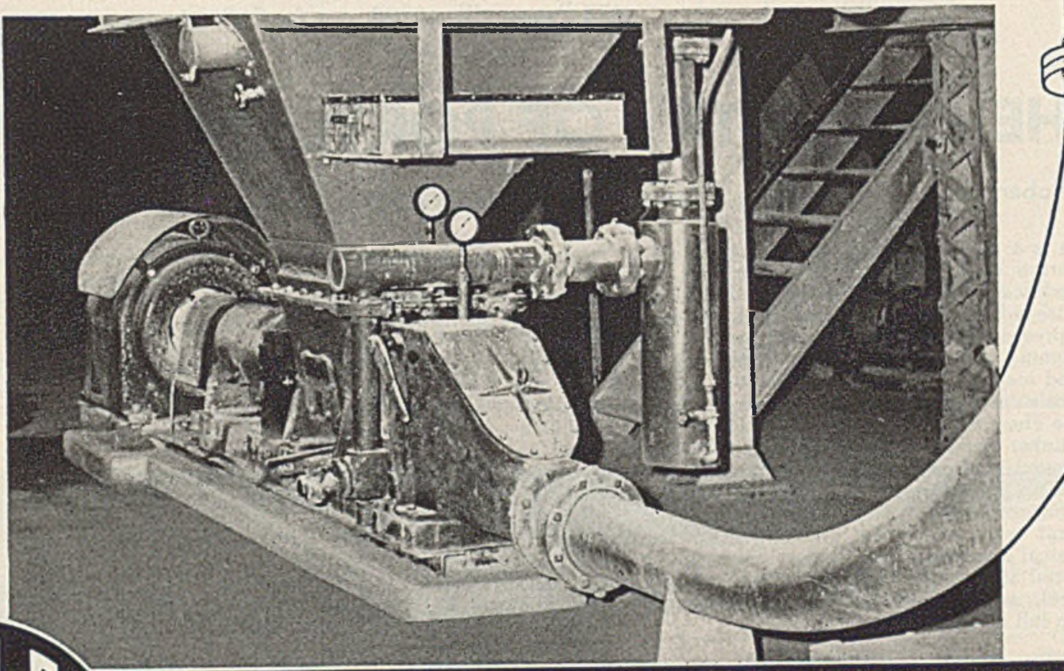

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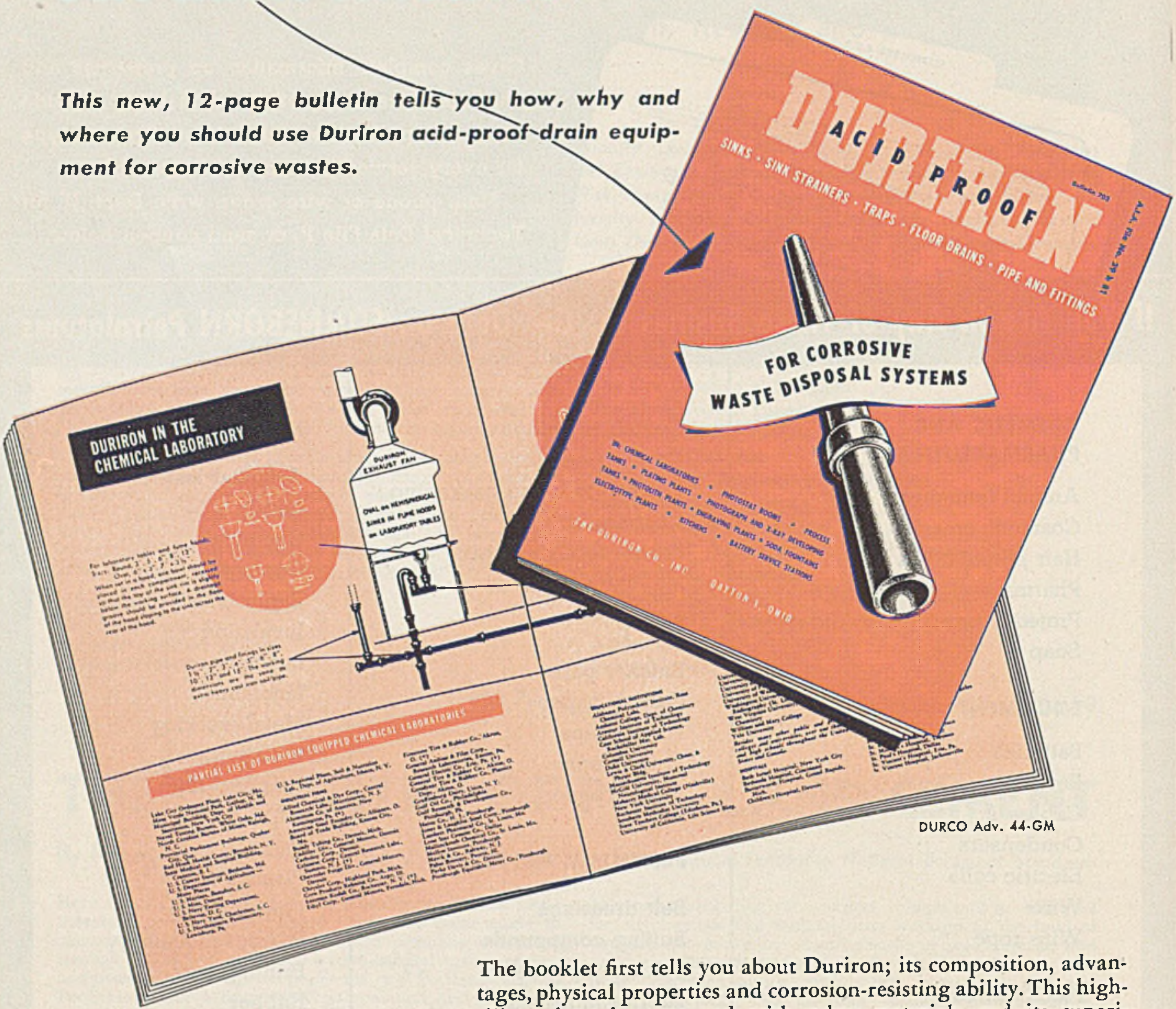

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Corrosion

Cathodic methods for protecting equipment from corrosion and new developments in materials are described.

by Mars G. Fontana

Cathodic protection methods are often used in industry for prolonging the life of equipment by reducing or almost completely eliminating the corrosion that would normally occur. Cathodic protection consists, briefly, of supplying an electric current, either external or by galvanic coupling, to a specific metal surface in such a manner that the usual electrochemical corrosion reactions are stifled or counteracted. The basic principles of galvanic corrosion are put to practical and beneficial use through cathodic protection. Galvanic or two-metal corrosion, its destructive effects, and methods for alleviating this form of corrosion were described in the July issue (page 85 A).

The methods of cathodic protection fall into two general classes: methods using sacrificial anodes and methods involving impressed currents or potentials. In the former, metals or alloys higher in the electromotive series than the metals or alloys to be protected are electrically connected or placed in contact with the equipment to be protected. In the second classification, a current is applied by means of an external source of power.

Sacrificial anodes

Sacrificial anodes are usually made of zinc, magnesium, and aluminum, or alloys of these metals, depending on the nature of the metal or alloy to be protected. The rate of corrosion on these anodes is accelerated, and the attack on the other metal in the couple is reduced, because of galvanic corrosion effects. The sacrificial anodes are designed so that they can be readily replaced, if necessary. In other words, parts to bear the brunt of the corrosion are purposely and extraneously attached or connected to the equipment or structures involved.

Galvanized steel, steel coated with zinc, is perhaps the most familiar material involving cathodic protection. The zinc is anodic and corrodes preferentially, and thus protects the steel. Bare spots on the steel surface, formed because of mechanical damage or corrosion of the coating, are protected by the surrounding areas of zinc.

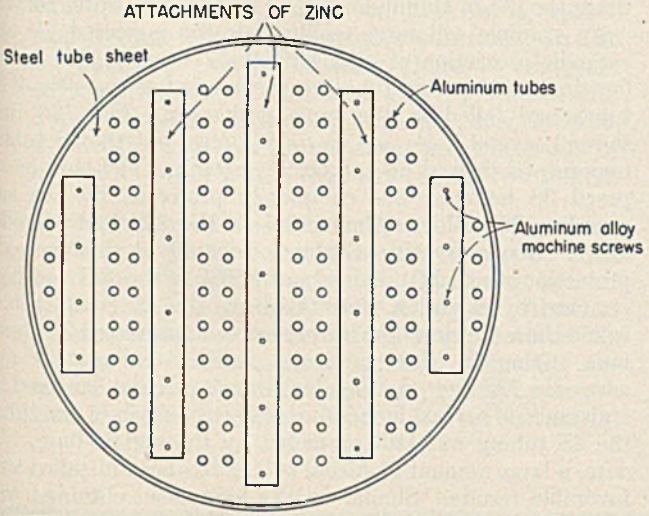

Figure 1. Cathodic Protection of Heat Exchanger

A more recent development is aluminized steel, which consists of steel coated with aluminum. This material was produced before the war, but normal development was retarded, largely because of the shortage of aluminum. Aluminized steel should now find many industrial applications.

Coatings of such metals as nickel and copper on steel would produce the reverse effects and accelerate the corrosion of exposed steel.

As far as chemical process equipment is concerned, perhaps the most widespread use of cathodic protection involves the protection of aluminum equipment by means of zinc strips. For example, zinc strips attached to the inside of an aluminum tank are used to protect the vessel from corrosion by the liquid handled. In some cases the attack by the process liquor is negligible, but the cooling water on the outside of the vessel is corrosive to the aluminum; consequently the strips are attached to the outside of the vessel. Aluminum-zinc couples should be checked in the water to be handled, because sometimes the galvanic effects are reversed in hot waters.

Quite often a third metal is used to minimize the galvanic effects between two other metals. Figure 1 (after R. B. Mears and R. H. Brown) shows an example of the use of zinc strips to protect aluminum tubes from galvanic corrosion because of contact with a steel tube sheet in a heat exchanger. Zinc anodes cannot, of course, be used in media which rapidly attack zinc—for example, dilute mineral acids.

Spacing and positioning of the zinc or anodic strips is important because, in general, the protection decreases as the distance from the anode is increased.

Household hot water tanks are protected by means of sacrificial anodes. Other examples include submarine hulls, tanker ballast tanks, and aircraft, particularly in marine service.

A large amount of money is saved annually because of cathodic protection of underground pipe lines, such as the Big Inch, for transporting gas and oil across large portions of the country. It might even be stated that this method for transporting fluids would not be economical in some sections of the country if cathodic protection methods were not utilized. Protection is mandatory, particularly in damp soil (marshes and stream crossings). Zinc, aluminum, and magnesium anodes are used for this purpose. In recent years the impressed-current methods have gained in favor in spite of higher installation costs.

Impressed current

When a metal corrodes in contact with an electrolyte, many anode and cathode areas are set up on the metal surface. Current leaves the anode which corrodes and enters the cathodic areas, which tend to be protected. If current from an external source is applied so that current is entering the metal over its entire area—or, in other words, if the local currents are neutralized or overcome—corrosion is minimized. This, briefly, is the principle of cathodic protection by means of impressed currents.

(Continued on page 94 A)

Corrosion

The direct current power source for the impressed current could be wind chargers, engine generator sets, or rectifiers of various types, depending upon the location of the equipment or the pipe line and other economic factors. The anodes could be made of metal or an inert material such as carbon. In the case of pipe lines, available scrap iron or steel is often buried near the pipe and used as the external anode. Many factors, such as conductivity of the soil, spacing and location of anodes, and current densities, have to be considered in these installations. Pipe-to-soil potentials must be carefully explored.

A pipe line is a simple structure from the geometric standpoint and therefore readily amenable to protection by impressed currents. Ordinary tanks are also easy to protect. For example, commercial units are available and quite commonly used on water storage tanks to eliminate interior painting and also contamination of the water. These installations usually require only a small amount of maintenance and care; but, because of this fact, the plant man sometimes neglects to give them any care at all, with the result that the effectiveness of the protection is decreased.

Complicated shapes and structures, such as are found in a distillation column, are difficult to protect because of the complex electrical arrangement required. In general, cathodic protection is not applicable where the metal or alloy involved would normally corrode at a rapid rate.

Alclad 3S

A recent development in connection with aluminum tubing should extend the use of this material in chemical plant process equipment. The comparatively new Alclad 3S consists of 3S aluminum tubing with an inner lining of 72S alloy, which is anodic to the 3S and accordingly protects the 3S tubing cathodically from corrosion. The 72S is an aluminum-zinc alloy. These tubes were first made by drawing a 3S tube over a 72S tube (no metallic bond between the two), but they are now made with a metallurgical bond (clad) between the 72S coating and the 3S aluminum core. The material at present is produced with the 72S cladding only on the inside of the tubes.

Aluminum possesses good heat transfer properties and shows good resistance to organic chemicals, waters, sulfur compounds, ammonia, concentrated nitric acid, hydrogen peroxide, boric acid, chromates, and other chemicals. As a result, aluminum tubing is widely used for condenser tubes. In some cases, however, aluminum is pitted by water. Laboratory tests and some service experience have shown that the presence of 72S in the Alclad 3S will increase four to ten times the life of aluminum tubing in corrosive water service.

An example will serve to illustrate the increased life and cathodic protection of tubing by the 72S material. In one location an Alclad 3S tube was removed after two sets of 3S tubes had failed in the same exchanger. The 72S liner showed several holes and corroded areas, but the 3S tubing underneath showed no appreciable attack. The bare or exposed 3S material was completely protected by the surrounding 72S alloy. About 10% of the 72S had corroded away. A conservative assumption would be that cathodic protection would be provided until 50% of the 72S had been removed by corrosion. On this basis the Alclad 3S tubing would show ten times the life of bare or unprotected 3S aluminum tubing in this particular service. In another case where the 72S liner (not bonded) was ripped and damaged for a distance of several inches during the rolling-in of the tubes, the 3S tubing was still protected by the anodic liner. To date, a large amount of Alclad tubing has been installed with favorable results. Similar results have been obtained with Alclad 3S sheet in other applications.

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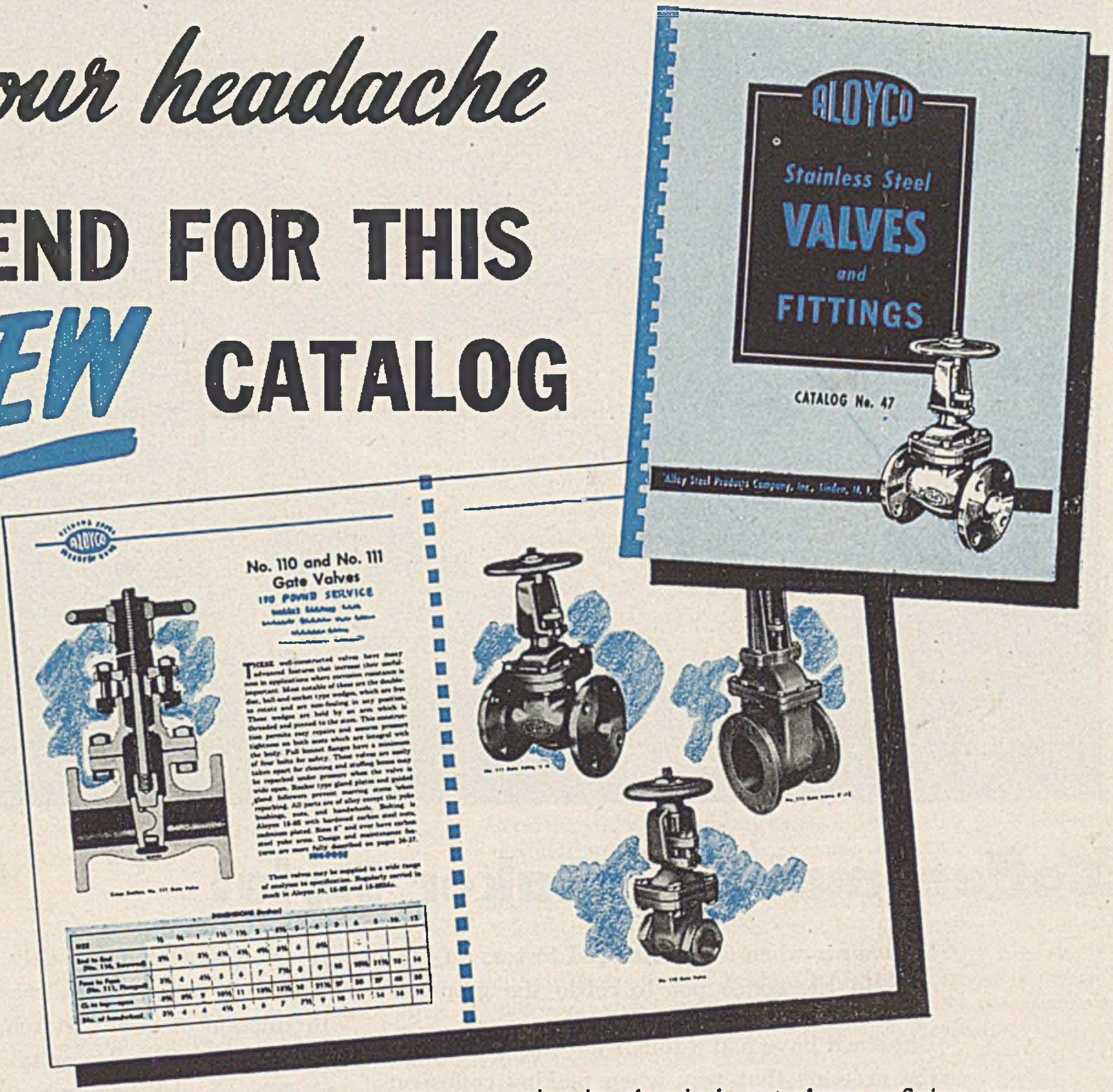

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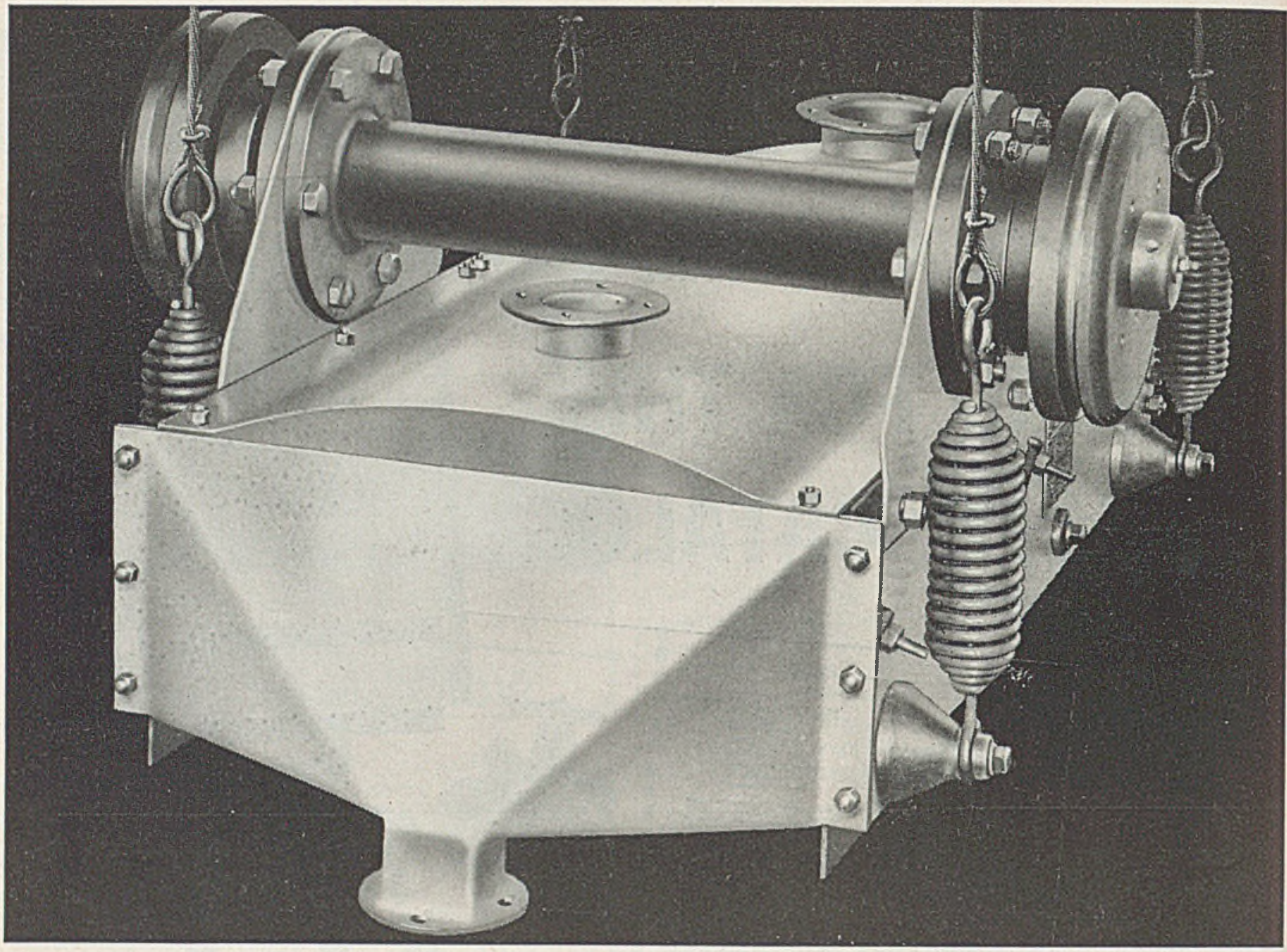

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Plant Management

The layout of small production runs requires an unusual amount of work from the production executive.

by Walter von Pechmann

A NUMBER of chemical products are now being manufactured which were developed during the war but were not available to the public until recently. Since they depend upon the public's approval and/or changes which have to be made, these products are often manufactured on a rather small scale. Unlike the case of large production runs, the cost of manufacture for these chemicals is high. Lack of experience in manufacturing methods and production control, and variations in product specifications are the main reasons for the high manufacturing cost. It would pay, however, to spend time on standardizing production procedures and to lay out the flow of production according to methods usually employed in the manufacture of large quantities. Proper planning and utilization of previous experience, combined with some ingenuity, will make it possible to produce chemical products at a reasonable cost, even if they are made on a comparatively small scale.

Small production setups are often planned to fit into existing surroundings, with the thought that no money should be spent for machinery and working equipment which might have to be discarded within a short time. This line of thinking does not take into consideration the fact that increased labor cost due to waste motion mostly outweighs the original saving, and that it is extremely difficult to make a product of consistently good quality with unsuitable equipment. Using machinery not entirely fit to manufacture a certain product has further disadvantages: If a machine is overloaded, its natural life is often reduced, and if only part of the machine's capacity is utilized, manufacturing costs increase unduly.

Accounting

The manufacture of products in small units requires accurate accounting, a good sales forecast, efficient production scheduling, and, above all, full utilization of labor and materials, if unit costs are to be kept within reasonable limits. Accounting figures should be based on true records of actual performance, and not derived by averaging the cost of large production runs and adding an arbitrary percentage to compensate for the higher costs involved in small production runs A job-cost system should be used for small scale runs in order to obtain actual costs. By no means should a standard cost system be employed, since the establishment of standards will have to be based on related experience which is often misleading. Production executives should be supplied at short and regular intervals with statistical information which will tell them if the changes they have made have increased or decreased the manufacturing cost. This is necessary because savings in one direction frequently increase the cost in another, and these increases often cannot be detected and seldom can be evaluated without the accountant's help.

It is difficult to foretell the sales volume of new products which are usually made in small quantities. Sales departments should, nevertheless, give production executives figures of anticipated sales. If any guessing has to be done in this respect, the sales department should do it.

On the basis of figures obtained from the sales department, the production executive will have to schedule his production. Top management sometimes does not realize that laying out production on small runs involves just as much, and sometimes even more, work for the production executive than setting up a big production. This is due to the fact that services usually available to him, such as assistance from the industrial engineering, accounting, and engineering departments, are often not at his disposal. These organizations are likely to be working on other more important projects, or they cannot render any assistance because the production executive himself often has no clear conception of the flow of work until many small difficulties have been ironed out. Top management, therefore, should give production executives sufficient time to set up the new production, and should not think that the organization of small scale production is a minor task which can be handled as a side line.

All department heads who are involved in production should discuss their problems together before they decide on the flow of production or the production setup in their departments. This is necessary in order to establish temporary standards and to eliminate duplications. For example, opinions frequently vary in regard to the type of material which should be used for equipment. It would make no sense if one department head insisted on the use of stainless steel or nickel tubing while another department head advocated ordinary steel piping. The grade of raw materials to be used should be decided by all department heads if no specifications are available. The extent of testing the product during its manufacture should be the same in all departments, and duplications should be avoided. Frequently products are retested simply because they enter a new department; but if no change has taken place since the last test has been made, the department receiving the material should accept the test results of the other department. In the event that a department head does not rely on a test made by another production department, all tests might be conducted in a centralized unit, such as a research laboratory if no production control laboratory is available. It is sometimes possible to transfer equipment from one department to another or to route the flow of production in such a manner that idle equipment in the plant can be used even if the product has to be moved from one department to another and back again. Insisting on a straight flow of production, and insisting that a product which has left a department should not be returned to it, often causes costly installations which could be avoided.

Planning

The flow of production in individual departments should be carefully planned. Although existing equipment might have to be used, there is no reason why it cannot be altered temporarily to suit the new production setup. Heights of tables, for example, can easily be changed, even if it should become necessary to install new legs when the temporary setup is completed. Furthermore, movable equipment allows a saving in floor space. Installing casters on tables, and setting storage containers and even vessels used for manufacturing onto trucks, should be considered. Sometimes it is possible to change equipment in such a way that it can be used for two purposes. Instead of blocking a production area with a table which is only occasionally used, the table top can be installed with hinges on the wall clearing the area usually occupied by the table, to make room for other equipment.

A production executive sometimes hesitates to manufacture various types of products in one

(Continued on page 98 A)

area, because he fears mixups and contamination of products due to improper use or improper cleaning of equipment by employees. Conditions of this type can often be overcome by using color schemes or certain types of containers which vary according to products. The writer once saw a rather interesting setup where every piece of equipment was marked with some particular color, to indicate the type of product for which it could be used; here operators did not seem to have any difficulty in selecting the proper equipment.

Almost exclusively, labor is a factor which increases the cost of products manufactured on a small scale. This is only natural because often one has to work with makeshift equipment and untrained personnel. Nevertheless, labor figures can usually be reduced considerably if the following steps are taken:

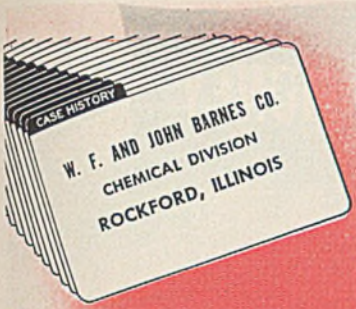
Production personnel should be made thoroughly familiar with the product to be manufactured. Their suggestions in making improvements should be welcomed. Workers should be cautioned against possible difficulties which might arise and should be warned that unauthorized changes will not be permitted. It would be good policy to call attention to obvious imperfect installations, and to explain why better equipment or methods cannot be used at that time; such an explanation will prevent submitted suggestions which cannot be put into practice and also will eliminate unjustified criticism which is always likely to be offered when workers are asked to participate in affairs of management.

In order to keep labor figures at a minimum, two things should be taken into consideration: unnecessary employment and labor wastage. Since time cycles on various operations are frequently unknown before production starts, the tendency exists to put one operator on each job, thinking that "things straighten themselves out" in time and that several jobs can be combined at a later date. Arrangements of this nature usually cause trouble. Intentionally or unintentionally, employees adjust the speed of their work according to the work assigned to them; attempts by management to eliminate waiting periods, or to increase the speed of work after an employee has gotten used to his job, are often resented. At the start of a production run it is better to assign more work to individuals than they can handle, because employees then have a goal to strive for. Furthermore, some operations can be simplified to a greater extent than was originally expected, and employees who cannot handle the job completely can be given assistance by other employees whose time is not fully utilized any more.

Start-and-stop waste should be reduced as much as possible. This means that everyone will have to be familiar with his duties before production starts. Management will have to see to it that all employees are supplied with the necessary tools, so that no time is wasted in hunting for wrenches, thermometers, etc. Sufficient spare equipment should be available to prevent interruptions which might affect the entire production.

Efficiency

Cleanup operations should be carefully planned. Labor costs are often above normal despite properly layed out productive operations because the time factor for cleaning has not been given sufficient consideration, and operators are allowed to determine the degree of cleanliness to be achieved and the time it takes to get equipment ready for the next batch. It is important to keep the working crew busy until quitting time. The fact that an operating cycle is completed half an hour before the end of the working day does not mean that everybody can take it easy. There are usually a number of tasks which can be performed for the following shift or for the next day's work. "Stop" labor wastage in the chemical industry constitutes a great percentage of unproductive time which can be eliminated without much effort.



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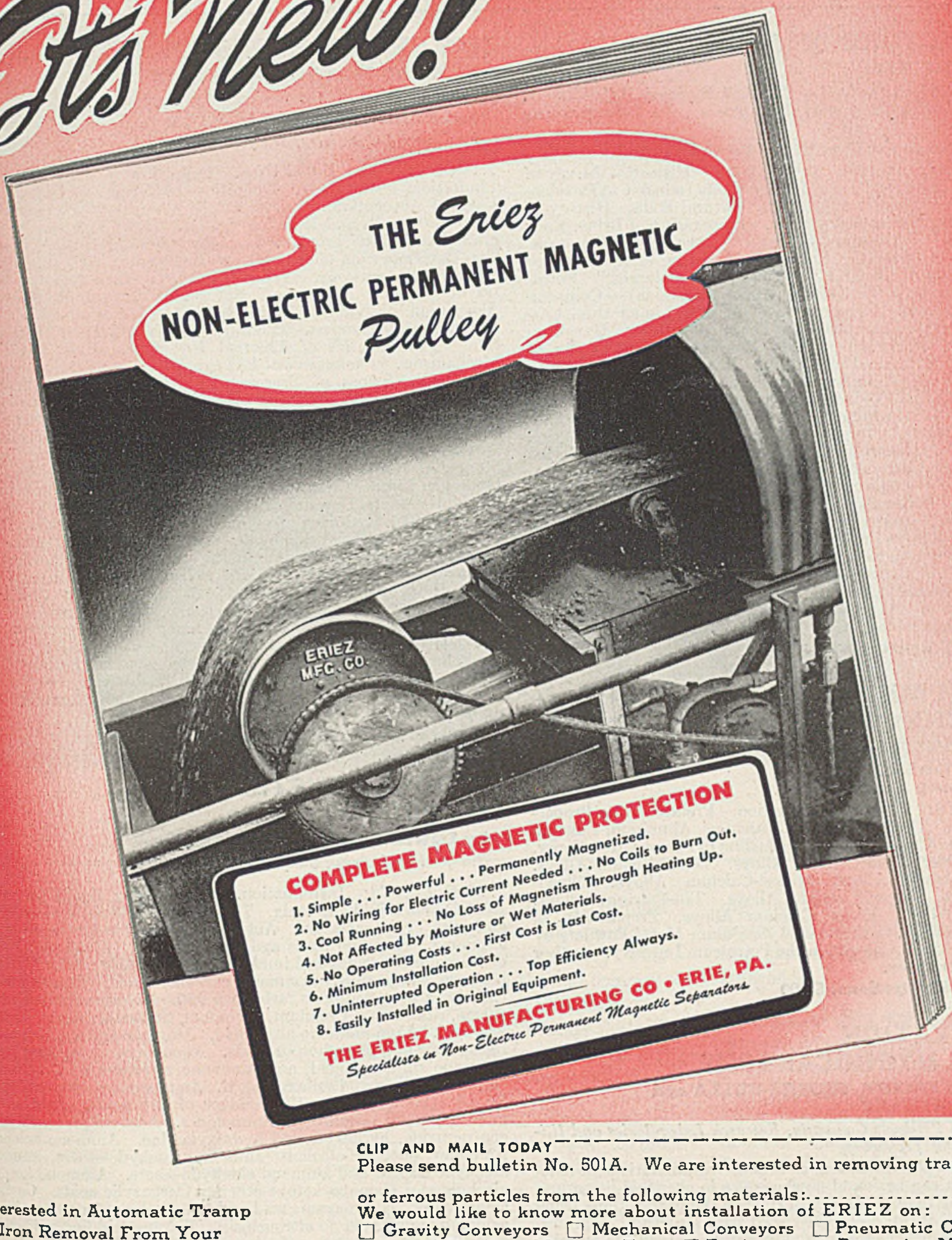

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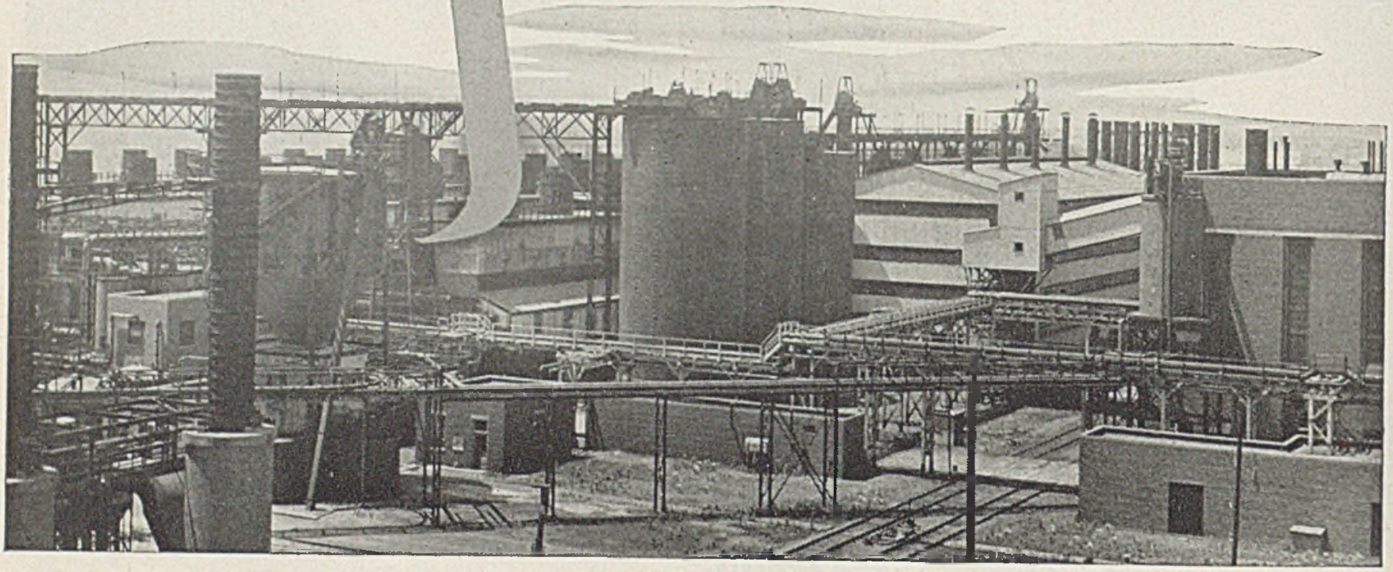

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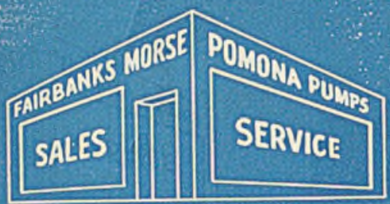

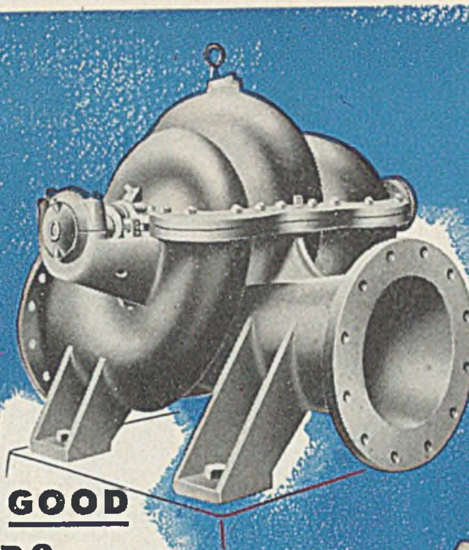

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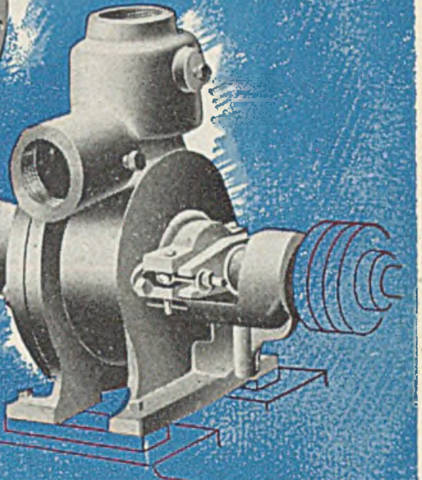

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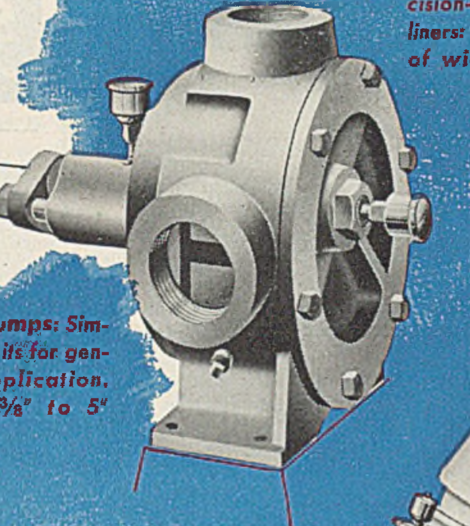

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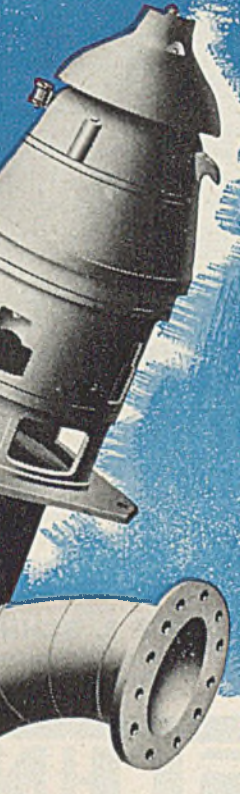

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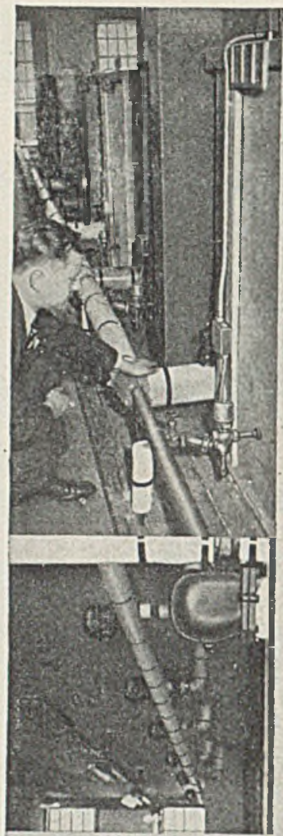

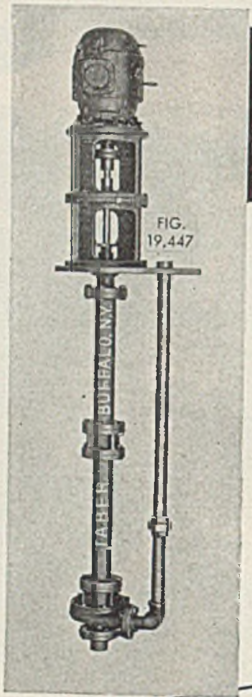
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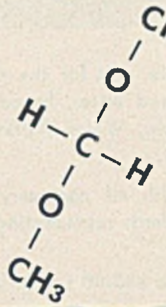

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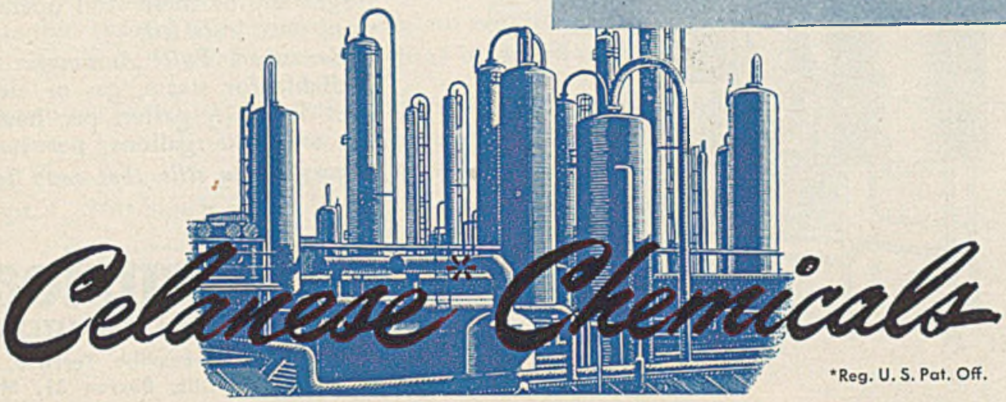

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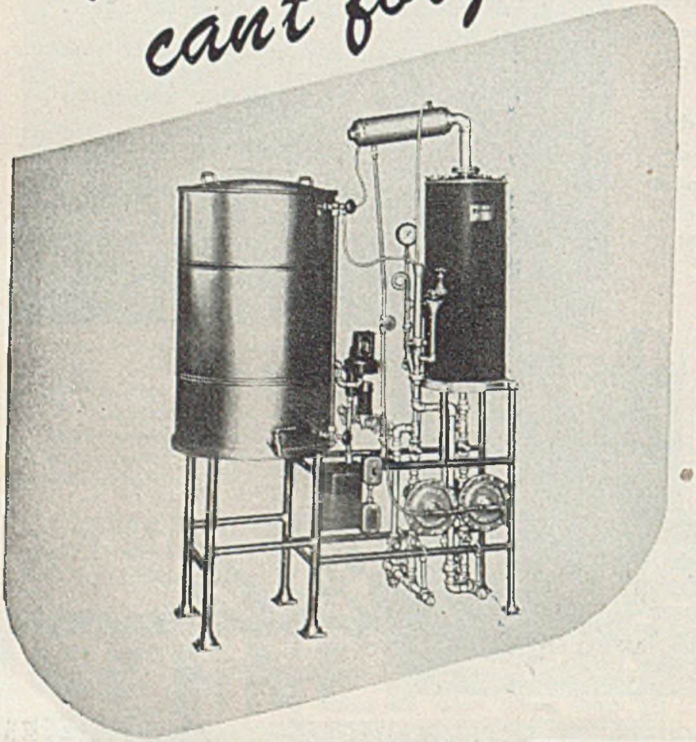

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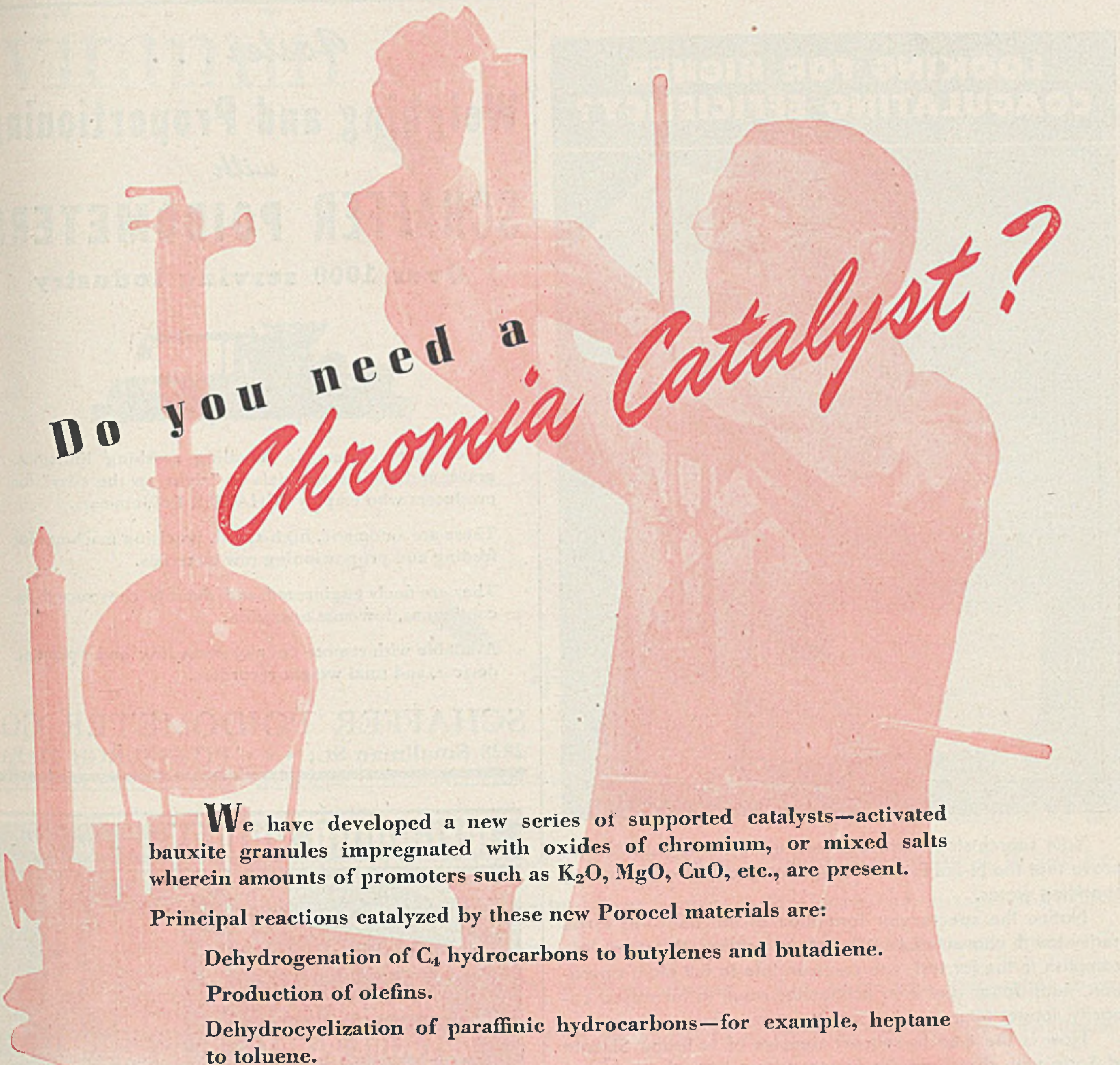

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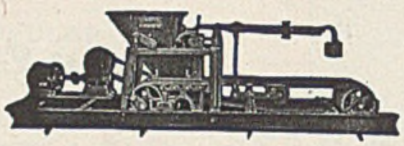

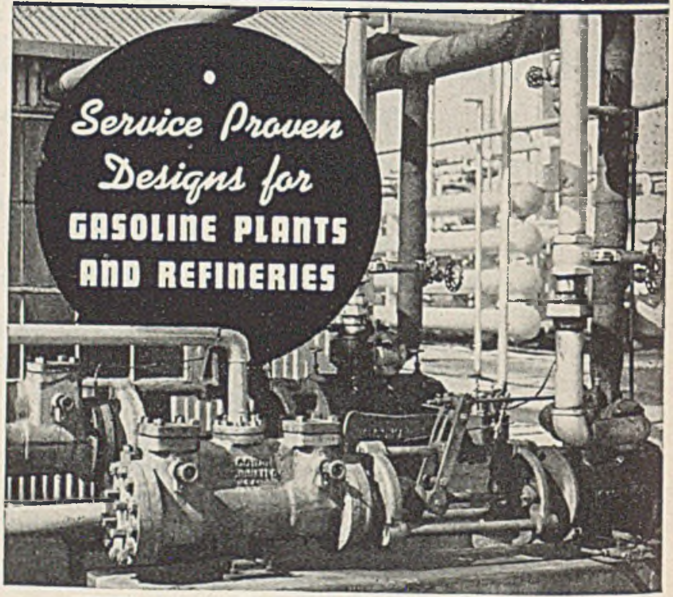
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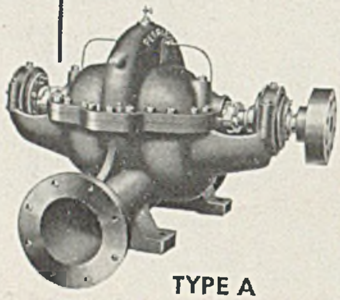

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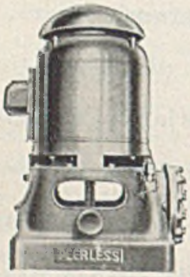

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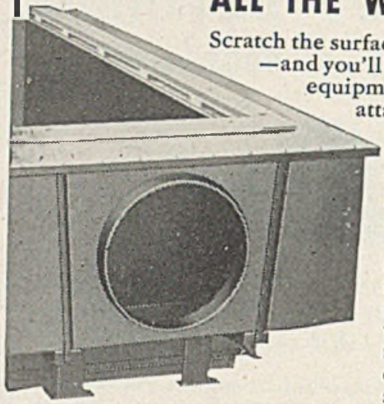

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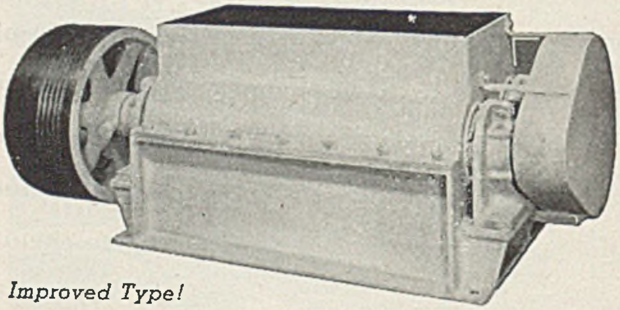

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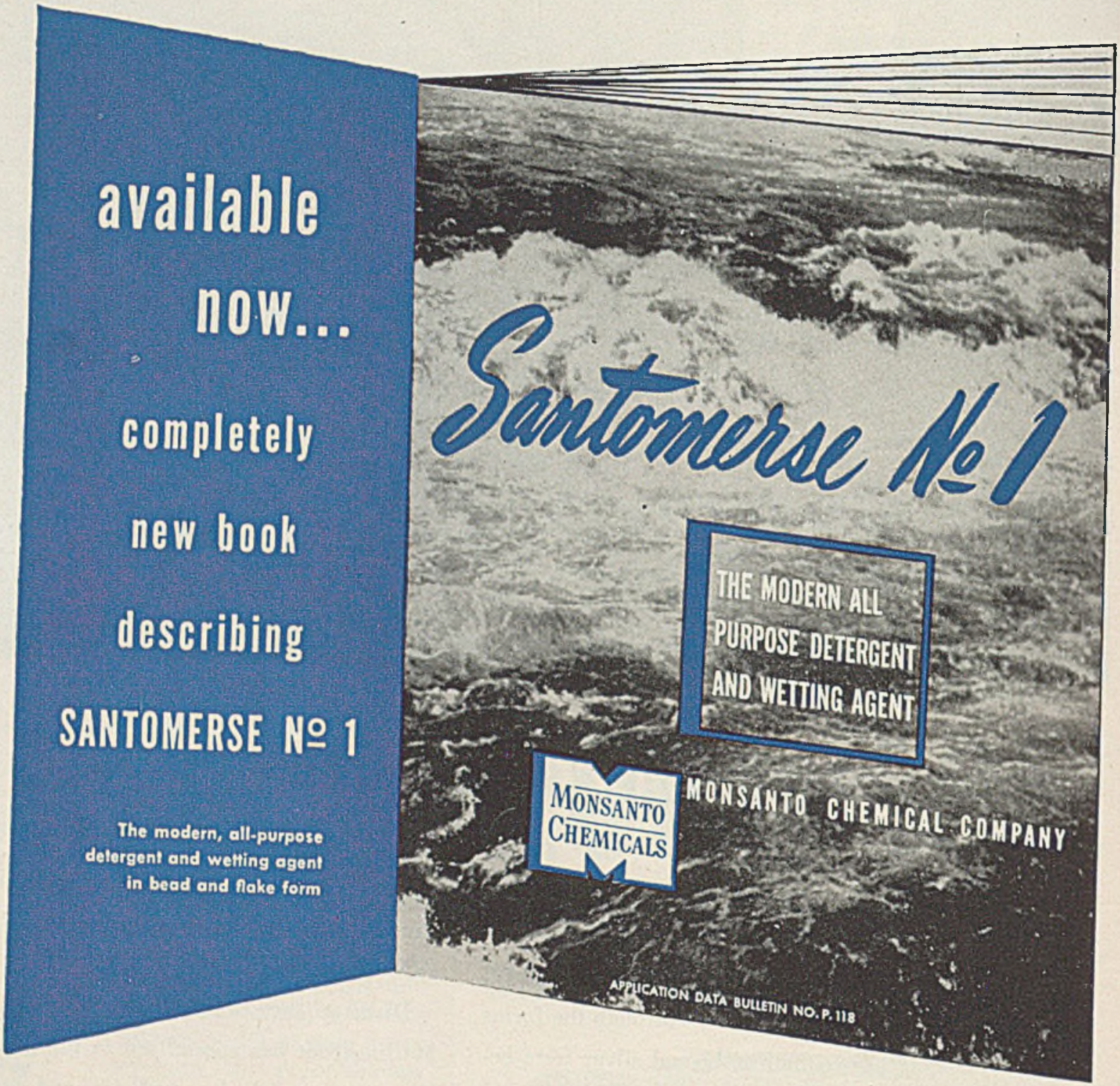

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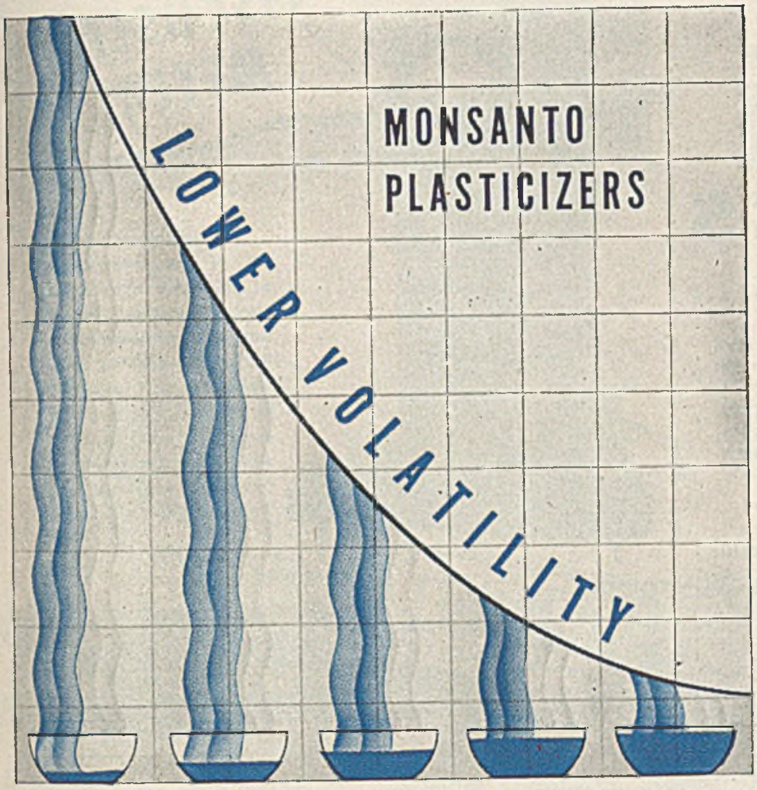
Santomerse No. 1 is an alkyl aryl sulfonate. It is manufactured in dry form of uniform quality, is free flowing and can be easily blended with other materials. It is readily soluble in cold or warm, soft or hard water.

Greatly expanded plant capacity will presently make Santomerse No. 1 available in increased quantities, in flake and spray-dried bead form. The bead form has low bulk density and is particularly suited to packaging for household use. The flake form has numerous commercial and industrial applications.

Send for your copy of this new Application Data Bulletin No. P-118. Also request copies for others in your organization who may be interested in getting complete data on this modern, all-purpose detergent and wetting agent. Contact the nearest Monsanto District Sales Office or write MONSANTO CHEMICAL COMPANY, Phosphate Division, 1705 South Second Street, St. Louis 4, Missouri.

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



Lower ranges of volatility are being established by a series of new Monsanto plasticizers, now well advanced in the process of development. Their greater permanence will add increased usefulness to many applications.

In addition, extensive field tests and laboratory findings indicate that these new Monsanto plasticizers will also provide high standards of compatibility, flexibility, fire retardance, heat and light stability, elasticity, abrasion resistance.

For the present, most of these Monsanto plasticizers are not commercially available, since their production depends largely on chemicals now in short supply. However, Monsanto research and field tests are being continued with emphasis on those new plasticizers that can be produced from raw materials most likely to be available soonest, in greatest quantities.

If you have any present or prospective plasticizer problems, Monsanto may be able to help you with application suggestions.

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Suggestions for formulating, and other valuable information and tabular data, are contained in Monsanto's book "Wood Preservation with Santophen 20 in Oil Solutions by Pressure Processes." Send for your copy.

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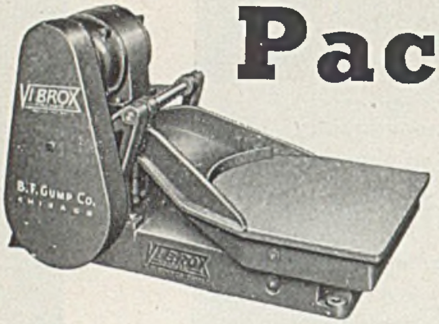

No. 41 Vibrox Barrel Packer—for packing 100 to 750 lbs. of materials into barrels, drums, kegs, or fibre containers.

The smooth, continuous, Vibrox — vibrating — rocking — motion quickly packs and settles dry, flaked, granular, or powdered materials so efficiently that smaller containers can usually be used for a given weight of material. Besides container savings, labor costs can be substantially reduced. The combination of these savings frequently pays the cost of a Vibrox Packer in 60 to 90 days.

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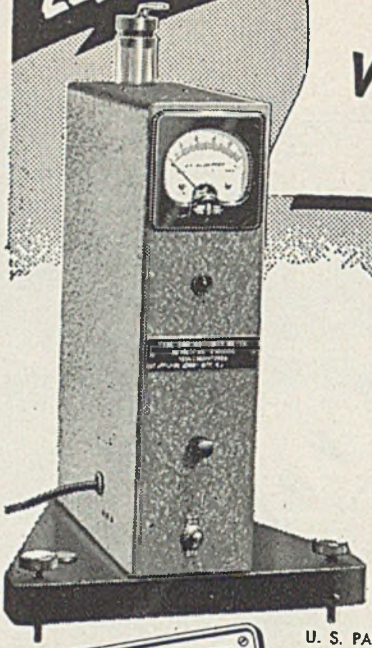

This instrument retains all of the advantages of the well established Hercules method without any of its disadvantages. Range extended to cover from 75 to 1,000,000 centipoises Constant temperature jacket built-in. Automatic timer can be furnished upon request. Write for bulletin No. 451.

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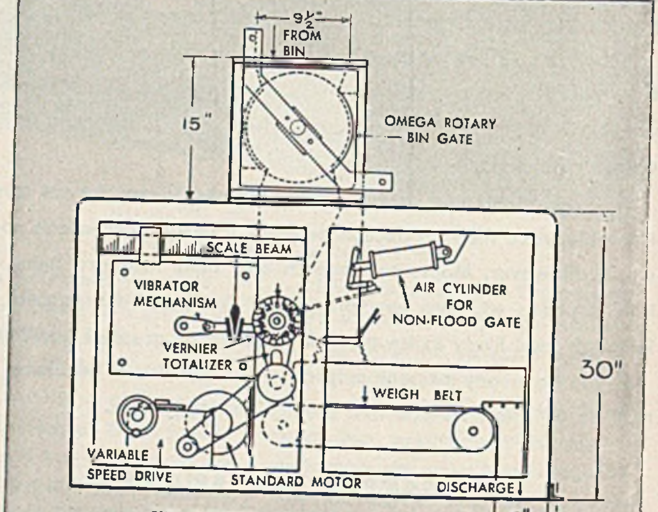

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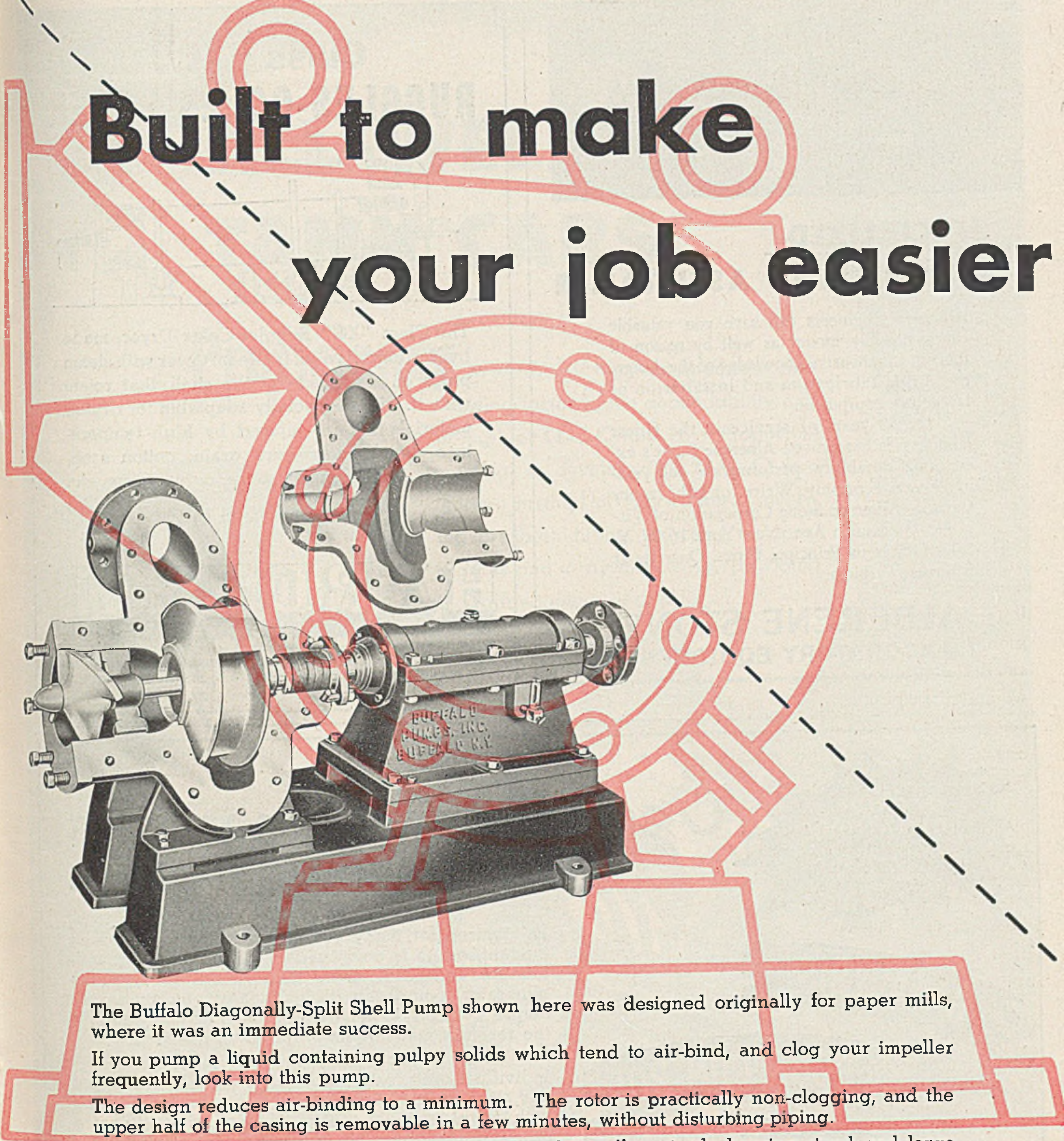

The Buffalo Diagonally-Split Shell Pump shown here was designed originally for paper mills, where it was an immediate success.

If you pump a liquid containing pulpy solids which tend to air-bind, and clog your impeller frequently, look into this pump.

The design reduces air-binding to a minimum. The rotor is practically non-clogging, and the upper half of the casing is removable in a few minutes, without disturbing piping.

All oversize construction — husky casing shaft and impeller, sturdy bearing stand and large bearings — all give you longer wear without repair.

Write for details about the Buffalo "DS" Pump.

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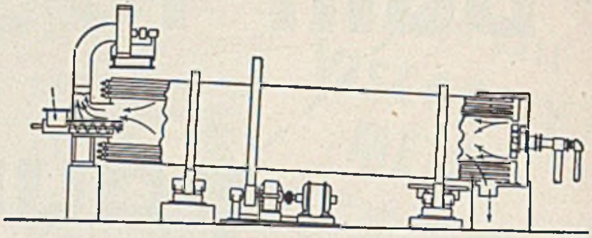

The Class "XC" Ruggles-Coles Dryer, made by Hardinge, is a rotary steam dryer with steam pipes on the inside of the shell that rotate with it. It is especially adaptable for drying materials that are injured by high temperature—such as brewers' grain, cotton seed, starch feed, tobacco stems, corn germs, etc.

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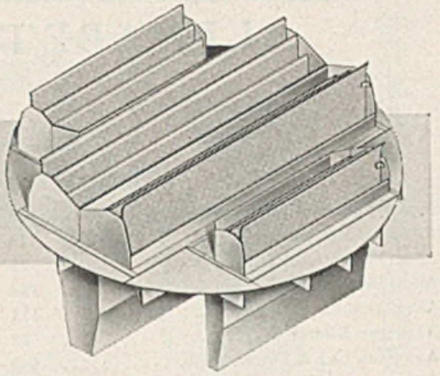
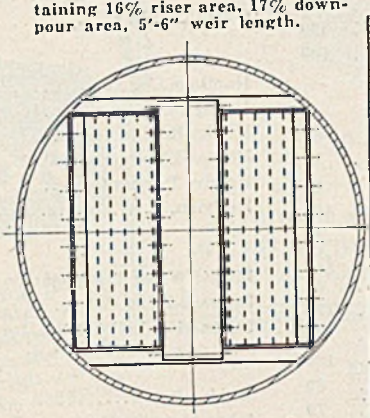
30% to 50% Greater Capacities with the KOCH KASKADE FRACTIONATING TRAY

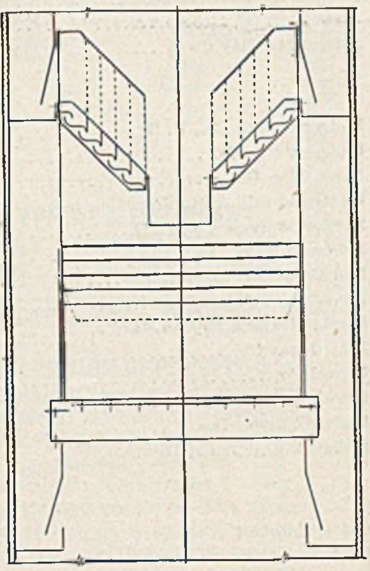


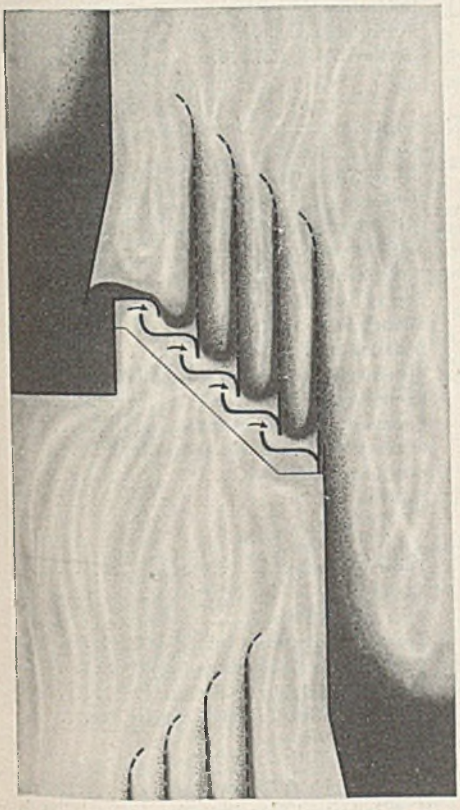
Complete assembly view of 6-foot Kaskade tray.

Fifty per cent greater capacities with 20% fewer trays — that's the result of plant tests comparing the new Koch Kaskade fractionating tray with standard bubble trays performing the same jobs of fractionation or stripping. In existing towers, Kaskade trays have replaced conventional bubble trays which were considerably overloaded — and in every case the Kaskade trays have done a better job of fractionation than the standard bubble tray.



4'-0" diameter Kaskade tray containing 16% riser area, 17% downpour area, 5'-6" weir length.





In this new Koch Kaskade tray, the liquid enters through a downpour from the tray above and is fed into one of parallel vapor streams entering from the tray below. The resulting mixture is hurled against a solid plate to which is attached a perforated plate. The velocity of the mixtures creates considerable centrifugal force, which forces all the liquid and much of the vapor through the perforations. The liquid separates from the vapor on the other side of the baffle in a vigorous bubbling action, and flows down the baffle to feed into the next trough where the operation is repeated. Due to the stair-step arrangement of troughs, large quantities of liquid can be handled with no build-up from one trough to the next.

Koch Kaskade fractionating trays are adaptable to any size column — easily installed or removed — suitable for fabrication from any type alloys — comparable in cost to conventional trays.

Koch Kaskade trays have been used successfully in crude distillation cracking plant towers, absorbers, extremely close cut naphtha fractionation, recovery and stabilization units, and in other varied services for several years.

We will gladly send you our illustrated brochure No. 101 on the Koch Kaskade fractionating tray. Write us today.

U. S. PATENT
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Merz plants in every case are designed to meet the special requirements of the material to be treated. They allow for working at a predetermined temperature, and are therefore particularly suitable for selective extraction of two or more solutes from one raw material. Unknown matter is previously tested in the laboratories to find out the best method of treatment. Merz plants can be arranged to work in series, providing greater capacity with maximum economy. In many cases, existing plants can be modernized and adapted to the Merz System.

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SIX ADVANTAGES* OF MERZ PROCESS AS APPLIED TO EXTRACTION OF VEGETABLE OIL (*illustrated in diagram*)

1. Never more than 1% of oil remains in the residues as against losses of up to 10% by the pressing process.
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4. Oils recovered are of pure natural color and cleaner than those obtained by pressing. They can easily be converted into first-class edible oils.
5. Merz plants are simple in design and operation. Their maintenance costs and capital outlay are much less than that of presses.
6. Merz plants permit the individual treatment of all kinds of oils, seeds and residues at a definite temperature and allow the use of all kinds of solvents, whether inflammable or non-inflammable, and either hot, cold, or in vapor form.

* *Equally important advantages exist in other applications of the Merz process. Write for complete details regarding Merz plants and their advantages for your own material.*

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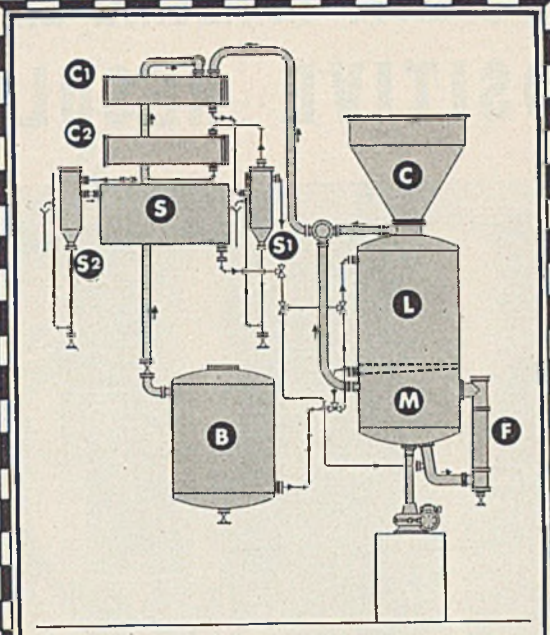

LAYOUT OF A TYPICAL MERZ PLANT FOR THE RECOVERY OF VEGETABLE OILS
Illustrating just one application for Solvent Extraction

DESCRIPTION OF PROCESS: Crushed seed is charged into Extractor **L** from Hopper **C**; solvent from Tank **S**, and weak solution from the preceding charge stored in Miscella Tank **B** are fed into the Extractor **L** where it quickly dissolves the oil. This solution passes through a specially designed filter bottom to Chamber **M**, separated from Extractor **L** by an intermediate division bottom, and connected with Calandria Heater **F**. Circulating rapidly, the evaporation of the solvent commences at once. While the concentrated solution passes back to **M**, and is there mixed with fresh solution coming from **L**, the solvent vapors rise to the Condensers **C-1**, and **C-2**. There the solvent is recovered according to requirement, either hot (Water Separator **S-1**), or cold (Water Separator **S-2**), and returned to Extractor **L** until a test indicates that practically no oil remains in the seed. The weak solution in **L** is then usually collected in **B** and used again in the following charge. Any solvent remaining in the seed residues, as well as in the oil, is driven off by live steam, accelerated by the use of suitably designed mechanical stirring gear, which also aids in discharging the residue.

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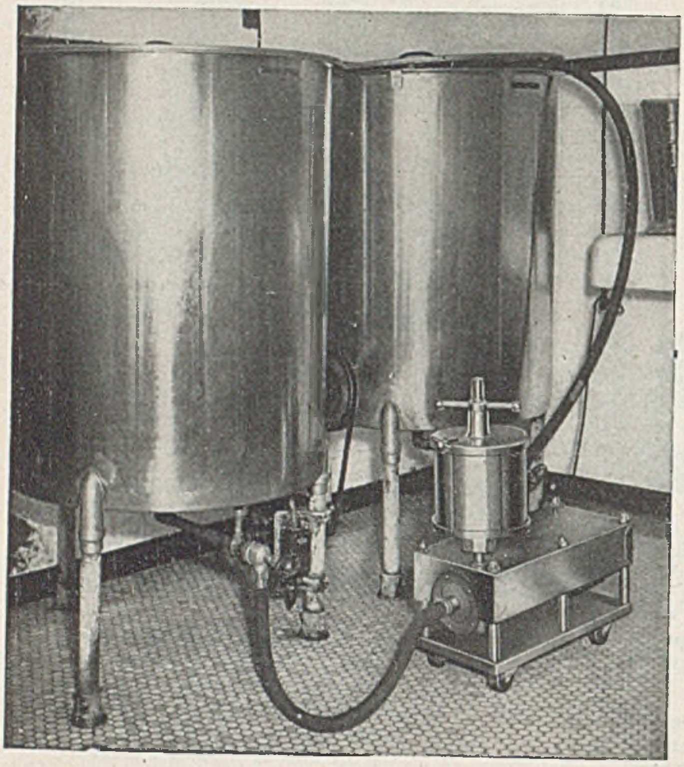


Sidelights and TRENDS

August 1947. The value of all goods exported from this country in 1946 was nearly double the value of imports into the United States; this amounts to a record peacetime excess of exports of $4,800,000. (Chamber of Commerce pamphlet, "Foreign Trade of the United States," Feb. 1947)

■ Curtailment of an entire year's shipments of oil to Russia would supply this country with only enough oil to make up a two-day deficit between current domestic production and demand. Shipments to Russia in the past six months totaled 730,000 barrels; crude oil output in this country, averaging over 5,000,000 barrels daily, is 700,000 barrels a day under demand. (*United States News*, p. 4, July 18, 1947, and *Oil and Gas Journal*, p. 137, July 1947)

■ Japan's consumption of chemical insecticides has become concentrated in calcium arsenate. From a prewar average of 983 metric tons, use of this chemical grew to 1595 tons in 1946; lead arsenate, derris, and nicotine sulfate were 28, 30, and 2.1% of prewar consumption, respectively. (*Oil, Paint and Drug Reporter*, p. 43, July 14, 1947)

■ In two years the production of the new synthetic antimalarial, paludrine (N_1-*p*-chlorophenyl-N_5-isopropylguanidine acetate), has increased from nothing to a rate of 100 tons a year. In preliminary investigations acute attacks of benign and malignant tertian malaria have been controlled by this agent in all cases without serious side effects. (*Chemical Trade Journal*, p. 614, June 1947, and *Chemical Abstracts*, p. 4433, Aug. 1946)

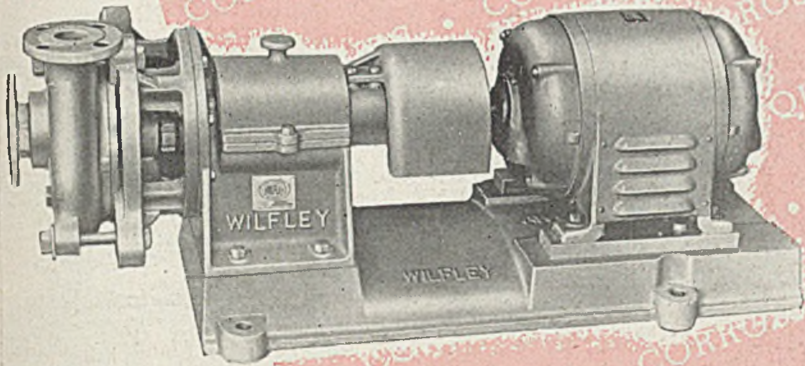
■ A new glass, Neodex, has been developed for lamp workers to replace didynium glass. Neodex, which can be molded, absorbs sodium light, and provides protection against infrared radiation and visible glare. Its greenish-blue neutral color does not obscure the visibility of the hot glass. (*Industrial Chemist and Chemical Manufacturer*, p. 388, June 1947)

■ Exports of medicines and sanitation supplies from the United States to seventeen Latin American countries totaled over 61 million dollars in 1946, compared to 7 million in 1937. The Latin Americans have become familiar with our products as a result of health programs instituted with the cooperation of our Government. (*World Report*, p. 1, July 22, 1947)

■ Production of chemicals in Canada increased from a prewar figure of 122 million dollars to 356 million in 1946. Exports advanced 350% and imports 75% between 1939 and 1945; the value of imports from the United States was close to $4 million dollars in 1946. (*Chemical Age*, p. 806, June 1947)

■ Gum rosin production will rise an estimated 15–20% in the present crop season, with a corresponding increase in gum turpentine. The output of wood rosin and steam-distilled turpentine is expected to increase by 25–30%. (*Domestic Commerce*, p. 69, June 1947)

■ Cotton consumption in this country for the season starting August 1, 1947, is estimated at 8.5 million bales, compared to an average prewar (1934–38) consumption of 6.5 million. Prewar exports were around 5 million, whereas this season's United States exports are expected to amount to only 2–3 million bales. World stocks have been reduced about 10 million bales in the last two years and are now estimated at only 27.5 million. (*Business Week*, p. 31, July 5, 1947)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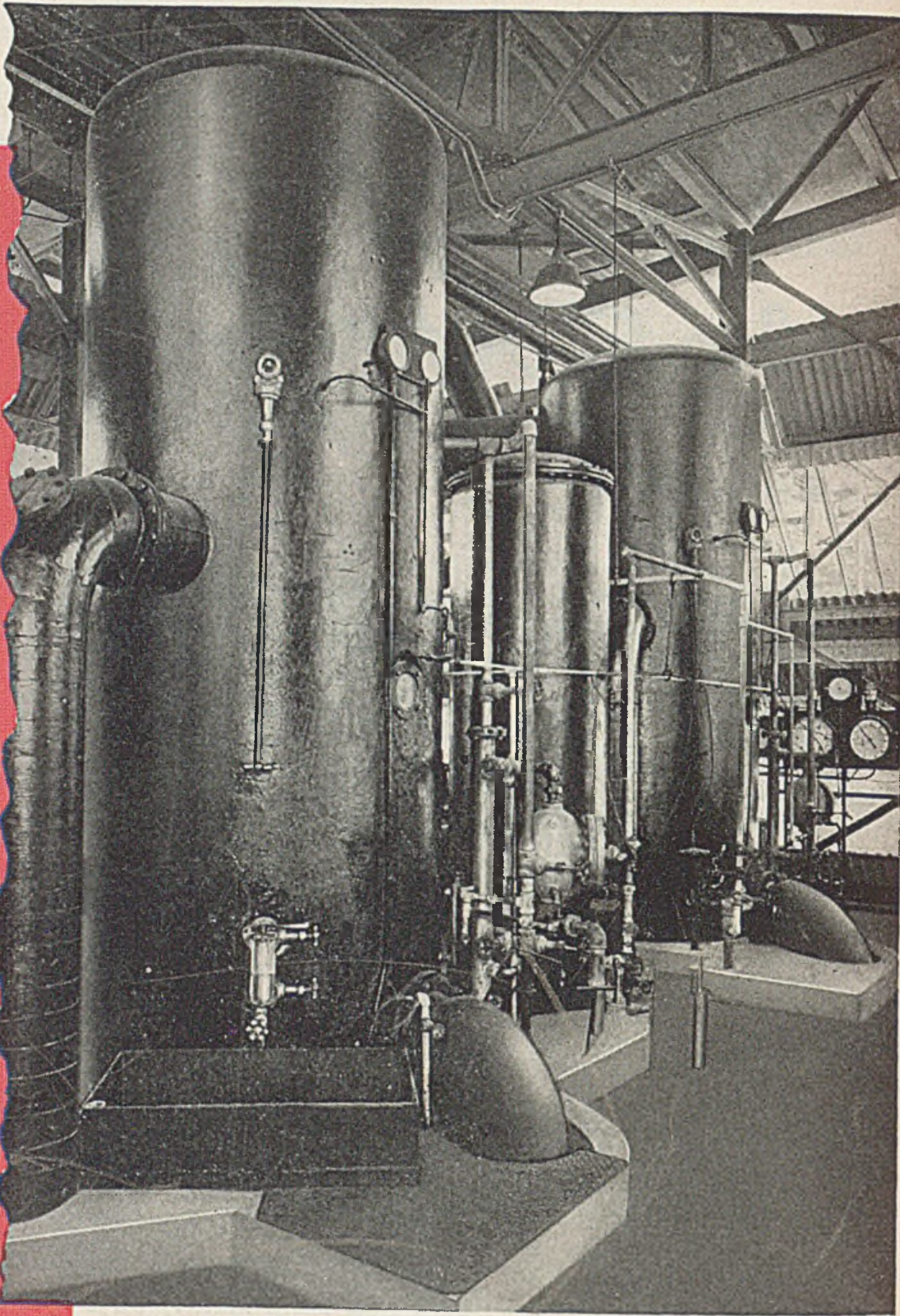

Substantial savings, that help build profits, result from the virtually complete recovery of solids obtainable with Buflovak Evaporators, recovery recorded as high as 99.9 plus %!

A high recovery of solids is always obtainable with all materials, ranging from delicate heat-sensitive products to corrosive crystal-forming liquids. The prevention of entrainment also contributes largely to the outstanding performance of Buflovak Multiple Effect Evaporators, by avoiding the coating on the outside of the tubes in the final effects.

Buflovak Evaporators have high rate of evaporation, simplified automatic control of operation, and advanced construction throughout.

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LOW HEAD CIRCULATORS

A NEW TOOL *for Engineers from the Engineering Laboratories of* MIXING EQUIPMENT CO., INC.

Making Possible the Use of Standard Agitators as Low Head Circulators

The use of propeller agitators for the controlled circulation of liquids is an accepted procedure. However, considerable difficulty due to inaccurate and incomplete information concerning performance characteristics has always existed in applying such devices. Because of the continued demand for such devices, Mixing Equipment Company has made the essential performance tests, correlating accurately the rate of flow in gallons per minute for various heads up to and including twelve inch. Since these data are entirely dependable, it will be possible to use Lightnin Mixers and Mixco Agitators as LOW HEAD CIRCULATORS with entire confidence when job requirements can be stated in gallons per minute at a definite head.

INFORMATION NECESSARY TO APPLY

It will be seen that it is essential that the head be accurately specified and that the gallons per minute required be clearly stated, together with physical characteristics of liquid handled. Otherwise, the selection of the proper circulator is indeterminate. The Company assumes no responsibility for computing or estimating heads or gallons per minute for any given operation. Full responsibility will be assumed for selecting the proper circulator to meet customer's requirements.

An excerpt from engineering tables on file in our Engineering Dept. is shown so that sensitivity of flow in relation to head can be observed. Shown are capacities and heads for a 20″ dia. propeller, operating at standard speed of 420 R.P.M.

Head (Inches)	1″	2″	4″	6″	8″	10″	12″
Gallons per Min.	6040	5170	4840	4300	3840	3440	3080

LIMITATIONS

No claim is made for the circulators to take the place of pumps. It will be noted that a twelve-inch head is all that can be economically achieved. Efficiency and performance curves or tables are not issued. The data presented applies solely to the agitators standard with Mixing Equipment Company and wide variations will be noted if other impellers with different pitch-ratio, blade area and shape of blade are used. In each case the propeller must be surrounded with a shroud ring or design performance will not be achieved. This shroud ring must provide proper clearance which will be specified by us for each application.

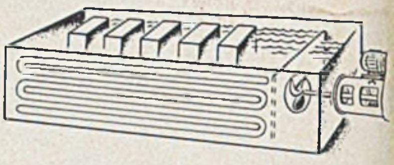
Unlike standard applications for mixers and agitators, data at present is limited to water-like materials, no data having been developed for viscous conditions.

Since horse power is affected by both head and specific gravity, the selection of mixer model and motor is made after selection of impeller size.

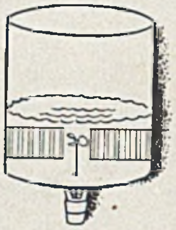
TURBINE APPLICATIONS

While it is in general more simple to apply a propeller as a low head circulator, it is also possible to so apply radial impellers of proper design to achieve the same results. Slightly higher heads up to 18″ may be obtained with radial impellers. These will not be offered, however, except where limitations of shaft length or horse power requirements favor that choice.

SUGGESTED USES AND POSSIBILITIES



BRINE CIRCULATOR. The use of a propelle for brine circulation in ice making is a com mon application. Here the user from experi ence specifies the gallons per minute ordinaril at low heads from one to six inches, the resul being faster heat exchange from ammoni coil to brine and from brine to the ice cans

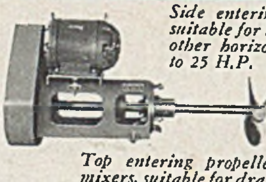


APPLICATIONS IN CALANDRIAS permit achievement of design performance by controlled velocity through the tubes. This offers the most exact method of predicting heat transfer performance in a closed vessel.

A SIDE ARM CIR CULATOR permi continuous addition of chemicals withou short circuiting, o permits circulatio for heat exchang purposes where th vessel has crowde coil conditions o unconventional heat ing elements, such a gas-fired tubes, close ly packed tube bun dles, etc.

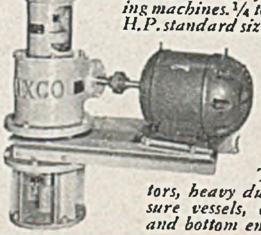
OTHER APPLICATIONS which suggest themselves include the use of the device in a draft tube, in a horizontal cylindrical tank to achieve a desired distribution of circulation, or in a vertical draft tube in a conventional vessel so as to produce a predicted velocity in the remaining part of the vessel as for heat exchange with coils or jackets.

The EQUIPMENT



Side entering propeller mixe suitable for brine circulators an other horizontal applications. to 25 H.P.

Top entering propeller mixers, suitable for draft tube, side arm circulator and dyeing machines. ¼ to 3 H.P. standard sizes.



Turbine Type Agit tors, heavy duty, for open or pre sure vessels, calandrias etc. T and bottom entering. 1 to 50 H.

Process-Adapted-Agitation

MIXING EQUIPMENT CO., INC.
1062 Garson Ave., Rochester 9, N. Y.
Please send me the literature checked:
☐ B-66 and B-76 Side Entering Mixers
☐ B-68 and 68B Permanently Mounted Mixers for Pressure Vessels and Open Tanks
☐ B-75—Portable Mixers (*Electric and Air Driven*)
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet
Name____________________
Title____________________

OP-ENTERING LIGHTNIN MIXCO

MIXING EQUIPMENT CO., INC.