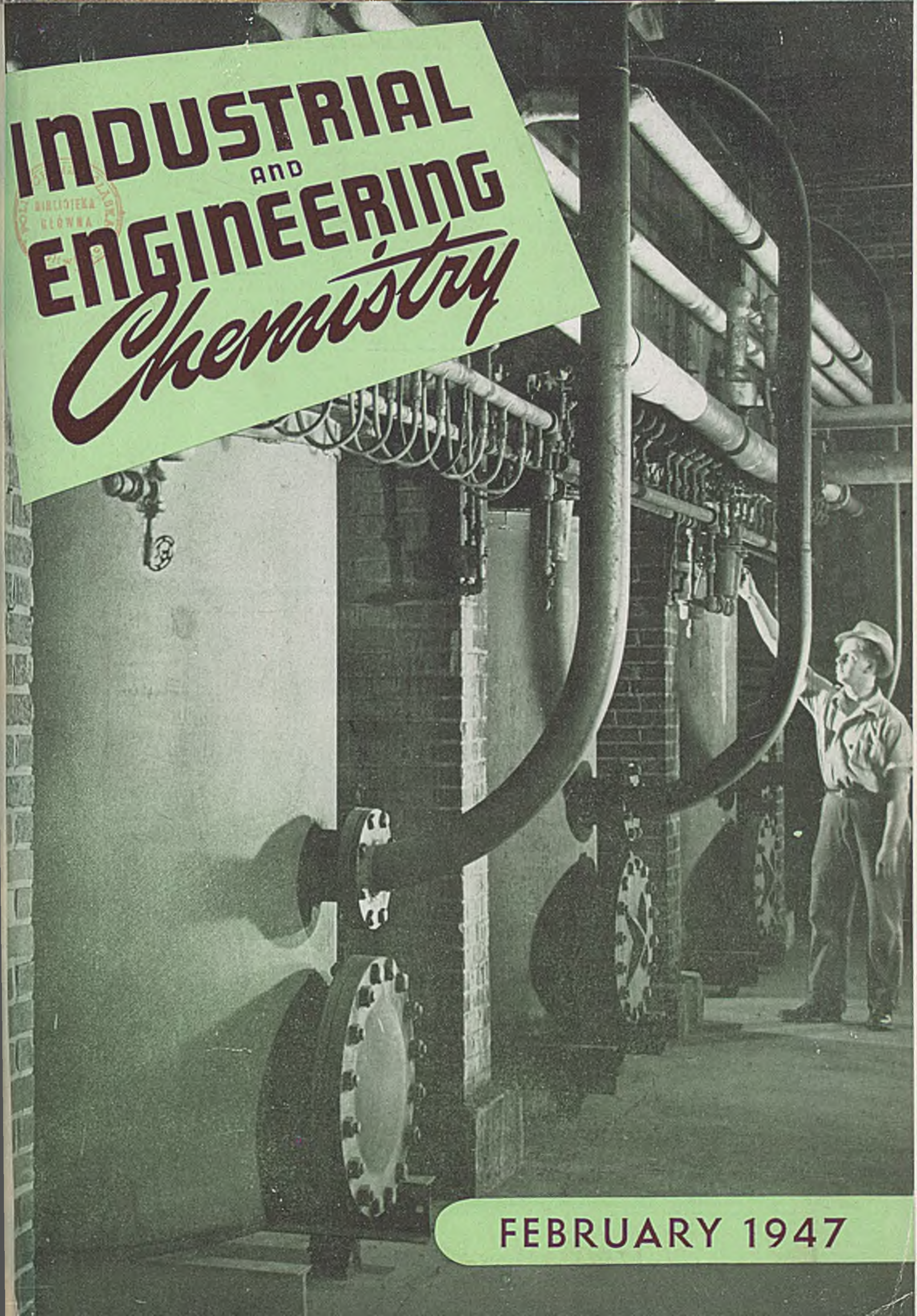
INDUSTRIAL AND ENGINEERING Chemistry



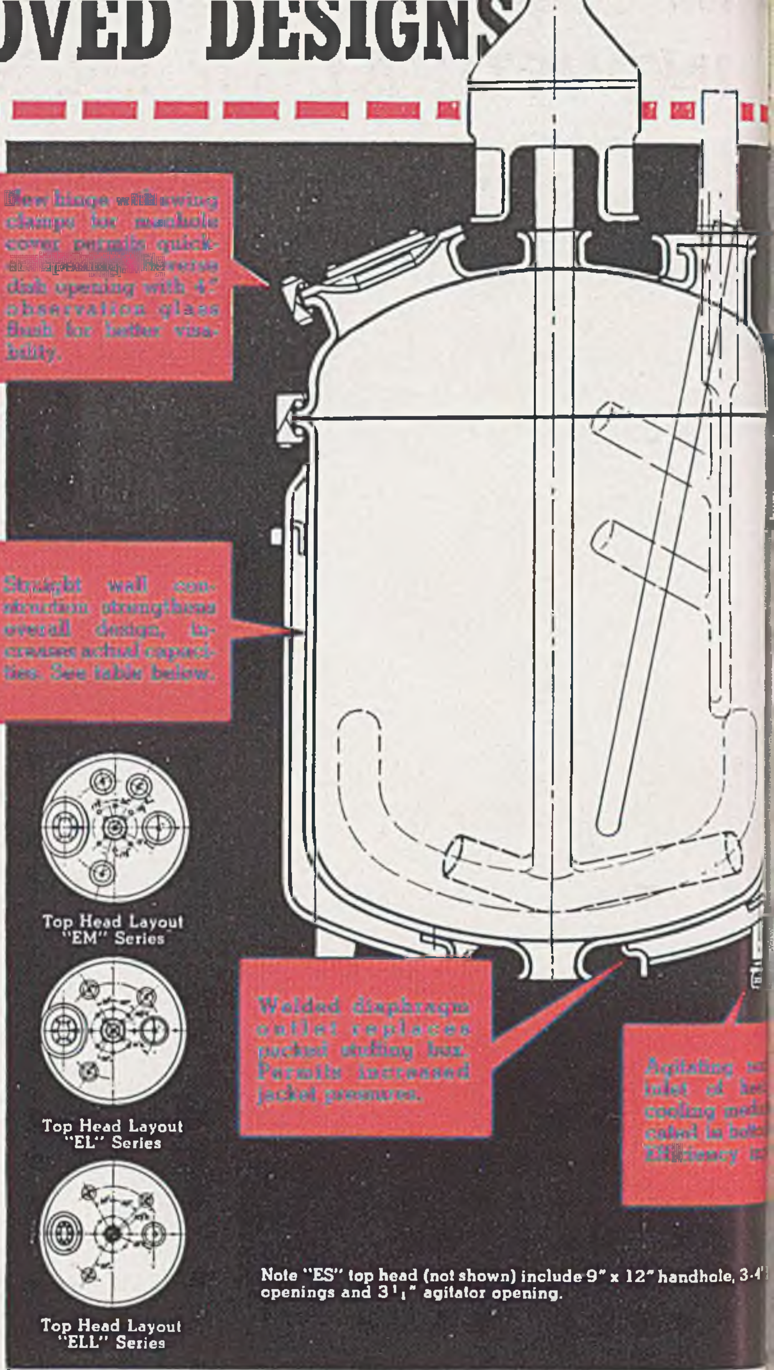
FEBRUARY 1947

Announcing IMPROVED DESIGNS

FOR PFAUDLER "E" SERIES Glass-Lined Steel REACTORS . . . Overall Construction Strengthened, Jacket Pressures Increased

SINCE 1927, Pfaudler's standard clamped-top, highly acid-resisting, glass-lined steel reactors have been specified wherever contact with metal proved undesirable. Processes involving hydrochloric acid at elevated temperatures and pressures are among the important applications as Pfaudler glass is resistant to all acids, except HF. Throughout this period, capacities have been increased and design improvements made to do each job better.

In line with this policy, Pfaudler announces further improvements, effective immediately. All "E" Series units will be built with straight rather than tapered side wall construction. This permits an increase in jacket pressure ratings from 75 to 90 psi, sufficient for the majority of "E" Series applications. (Higher pressures obtainable with special designs.) See drawing for other highlights. All details will be covered in new catalog which will be available later. However, these changes apply on "E" Series orders now outstanding, except where operating conditions require special construction.



New hinge with swing clamps for manhole cover permits quick- [illegible] opening. Reverse dish opening with 4" observation glass flush for better visibility.

Straight wall construction strengthens overall design, increases actual capacities. See table below.

Welded diaphragm outlet replaces packed stuffing box. Permits increased jacket pressures.

Agitating
inlet of he
cooling med
cated in bott
Efficiency i

Top Head Layout "EM" Series

Top Head Layout "EL" Series

Top Head Layout "ELL" Series

Note "ES" top head (not shown) include 9" x 12" handhole, 3-4"
openings and 3½" agitator opening.

How Capacities Have Been Increased

Series	*Rated Cap.*	*Actual Cap. Old Design*	*Actual C New Des*
"ES"	50 gals. 75 gals. 100 gals.	56 gals. 81 gals. 107 gals.	56 gal 83 gal 110 gal
"EM"	150 gals. 200 gals.	165 gals. 203 gals.	180 ga 225 ga
"EL"	200 gals. 300 gals.	207 gals. 304 gals.	236 ga 345 ga
"ELL"	500 gals. 750 gals.	514 gals. 783 gals.	565 ga 850 ga

Pfaudler

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ENGINEERS AND FABRICATORS OF CORROSION RESISTANT PROCESS EQUIPMEN

INDUSTRIAL and ENGINEERING *Chemistry*

FEBRUARY
1947

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ISSUED FEBRUARY 12, 1947
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Consecutive Number 3

Mother liquor tanks used in production of *p*-dichlorobenzene are shown on this issue's cover. Photo courtesy Dow Chemical Company.

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PROPERTIES OF SOME STANDARD GRADES OF CELITE MINERAL FILLERS

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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
Super Floss	White	Maximum 0.5% on 325 mesh	2-4 microns	Max. 1%	150	120	9	28	2.30

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

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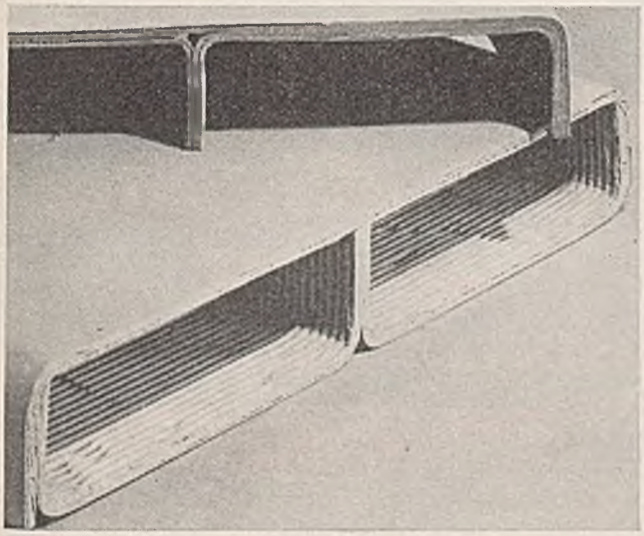
INDUSTRIAL and ENGINEERING CHEMISTRY....

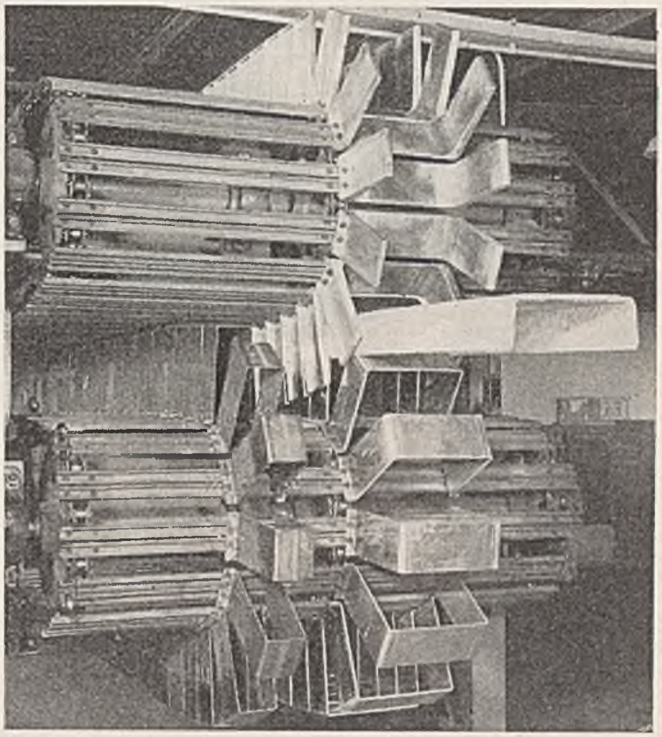
Reports ON THE CHEMICAL WORLD TODAY

NEW WRINKLE

Impregnation of paper and paperboard is not a new idea. A structural channel unit of corrugated boxboard is, and the idea materializes into a potent reality when the material is impregnated with sulfur. It all started from a business of manufacturing advertising displays from paper, starch, wood flour, rosin, and water. Came the war and Old King Cole, Inc., of Canton, Ohio, turned to converting these materials into mandrels for use in manufacturing self-sealing, bulletproof gas tanks. From there the road led to corrugated board and the idea of a disposable pallet. The Institute of Paper Chemistry had experimented with boxboard impregnated with sulfur in building a small house. When Laminite Products, Inc., a child of Old King Cole, developed a channel shape out of laminated single-face corrugated cardboard, it was found that the cardboard had surprising strength after being impregnated with sulfur. A disposable pallet became a reality.

Starting with ordinary corrugated chipboard, a product used extensively in the packaging industry, they cut and laminated the sheets into three plies, used sodium silicate as an adhesive, and formed the laminated board into channels by the application of light pressure, with the grain of the corrugations running around the U. Alternate wide and narrow channels, 14 and 5 inches wide with 4-inch legs, were joined with sodium silicate, and a two-ply cover was added to make pallets ranging up to 68 × 30 or 54 × 54 inches.


Assembled Unit


Channel-Making Machine

Dipping frames carrying the pallets were sent into a continuous tank 100 feet long, holding 175,000 pounds of sulfur, and impregnation took place at the rate of sixty frames per hour. The finished pallet was capable of supporting a dynamic load of 3500 pounds and a static load three times as great. These figures may be further improved when better paper can be obtained for use in the construction.

The success of the pallets led to the manufacture of channel boxes, 6 × 6 inches and of any desired length, for the shipping of aluminum tubing and trimming. Branching out along an entirely different line, the company experimented with tree guards made from the laminated sheets. Wax-dipped to overcome the disadvantages of wet weather, these guards have excellent spring and snap characteristics.

The sulfur-impregnating process was, however, not without its difficulties. Finding a dye stable in molten sulfur at 145° C. was one; evaporation of water from the boxboard and resultant bubbling of steam through the sulfur bath was another. Most important was the fact that the finished product was not fireproof and,

(*Continued on page 8 A*)

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

Do You Move Material that is Free-Flowing, Crushed, Granular, Ground, or Pulverized...?

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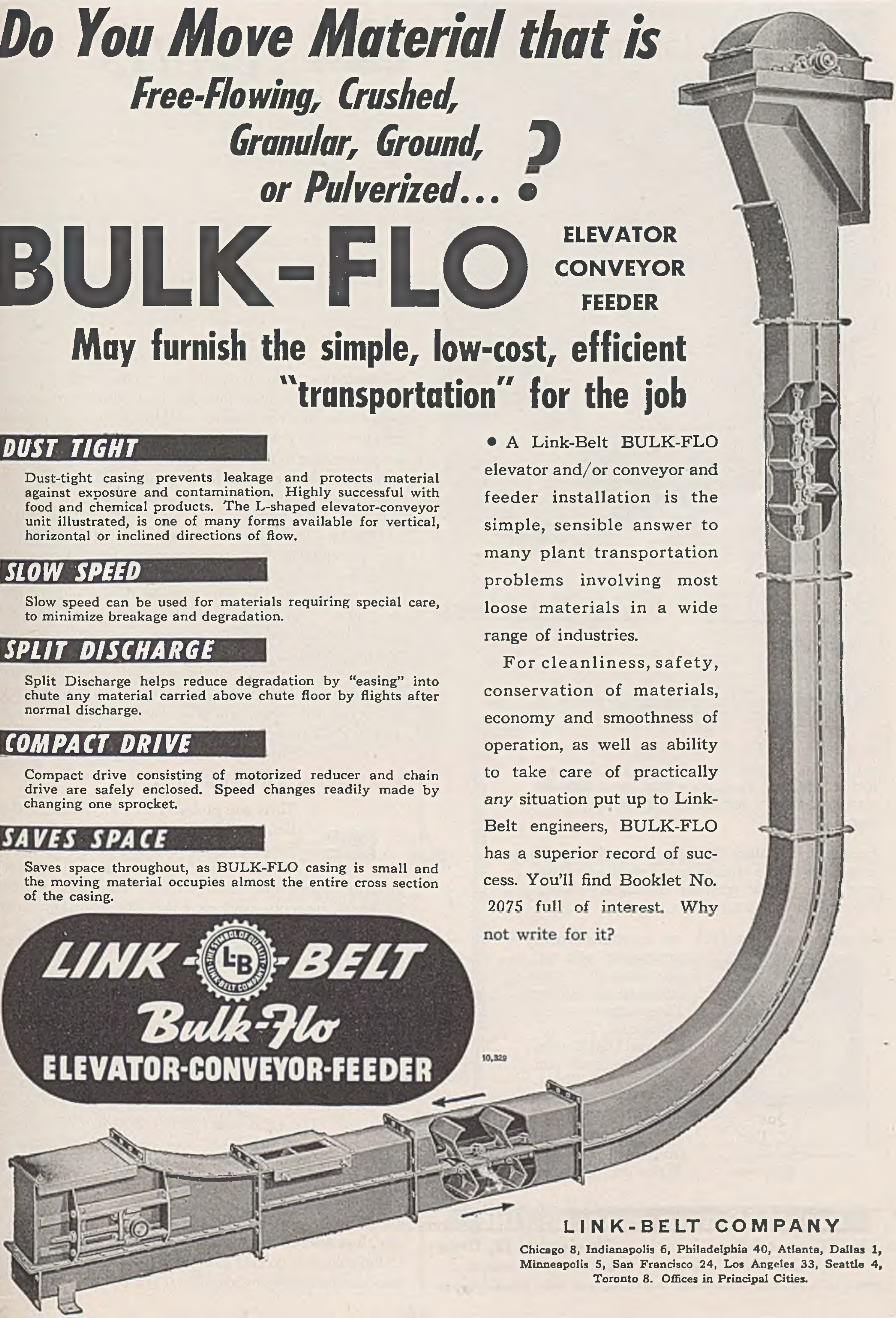

DUST TIGHT

Dust-tight casing prevents leakage and protects material against exposure and contamination. Highly successful with food and chemical products. The L-shaped elevator-conveyor unit illustrated, is one of many forms available for vertical, horizontal or inclined directions of flow.

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Slow speed can be used for materials requiring special care, to minimize breakage and degradation.

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Split Discharge helps reduce degradation by "easing" into chute any material carried above chute floor by flights after normal discharge.

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SAVES SPACE

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● A Link-Belt BULK-FLO elevator and/or conveyor and feeder installation is the simple, sensible answer to many plant transportation problems involving most loose materials in a wide range of industries.

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I&EC *reports*

if ignited, produced poisonous fumes of sulfur dioxide. This became the major stumbling block in the way of the subsequent idea of application in an integrated housing construction system.

Considerable development work has been done in cooperation with the H. K. Ferguson Company, which has been granted the rights to exploit this unit in the building and construction fields; a machine for the continuous molding of panels built along the same lines as the pallet has been put into successful operation. It was found that dipping the impregnated panels in a fire-resistant paint increased the fire resistivity to a slow-burning category. Experiments with certain types of phenolic resins and the so-called unsaturated polyester-type resins have not only reduced the fire hazard but have also improved the structural characteristics and increased the water resistance. Although such impregnations are more costly than that with sulfur, it is believed that when the proper type of paper is available, material can be produced which will have many applications in the building field.

These panels offer promise in the field of reinforced concrete design and may have considerable use in flooring, walls, and roof decks. Laboratory tests indicate that the panels compare favorably in insulating properties with any structural board now in use. Panels may possibly be provided with a variety of finishes, including plywood, metal foil, and plastic and paper sheet coating. Development work along these lines is being carried out by a number of companies in cooperation with Ferguson. The popularity of the laminated product has been sufficiently substantial so that the principal headache now experienced by the manufacturers is no longer technical but consists in procurement of an adequate supply of the good quality kraft paper needed in the construction. W.H.S.

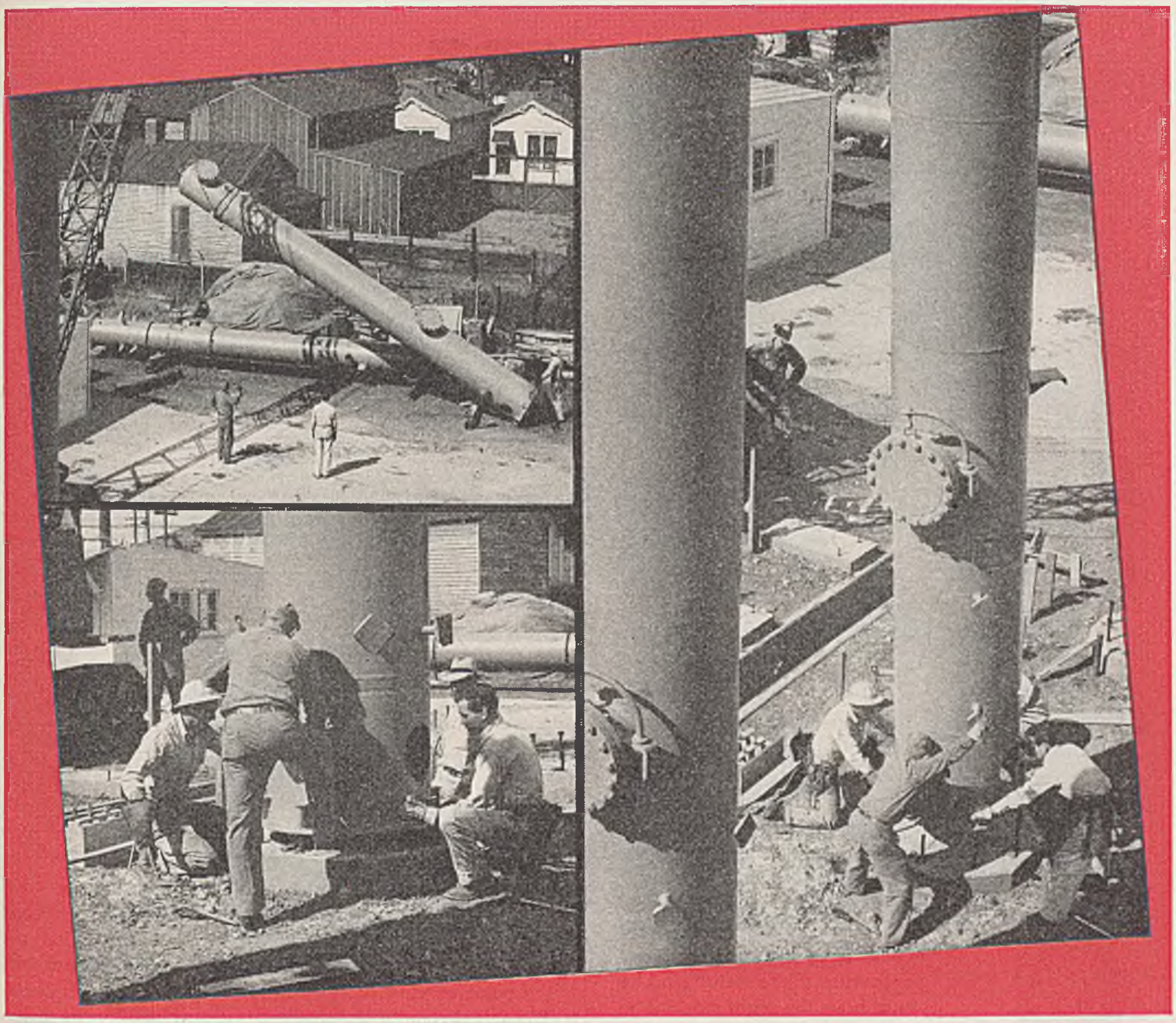
COLORFUL THOUGHTS

There are probably as many different definitions and descriptions of "color" as there are hues in a rainbow. The artist, dyer, physicist, chemist, psychologist, and salesperson each prefers to employ his own unique vocabulary to express his sensations or observations of that elusive quality. Joseph Addison's remark made in 1712 that "colors speak all languages" might aptly be twisted to "color is spoken of in all languages".

An interesting attempt to integrate all of these approaches to the subject was made by I. H. Godlove of the General Aniline and Film Corporation in a paper "Relation of Color Perception to Chemical Structure", presented before a recent meeting of his company at Shawnee-on-the-Delaware, Pa.

Unfortunately, Godlove pointed out, there are almost no complete works covering the entire field of color and chemical structure. The great mass of research on this subject by chemists and physicists has been concerned primarily with the relation of absorption spectra to chemical structure and only indirectly to color perception. This has been due in no small part to the belief that absorption spectra measurements are more precise than visual observations. People of antiquity, however, tended to believe what their eyes "told" them, and so color was defined in terms which today are used to define color perception or sensation.

(Continued on page 10 A)



Girdler construction crew sets up tower for HYGIRTOL *plant, which produces hydrogen of higher purity more economically than any other method.*

Girdler builds the gas processing plants Girdler designs

BECAUSE Girdler builds the gas processing plants Girdler designs, you can be sure of several important things:

A complete service, from one responsible source, that includes everything from start to finish of the job. Plant design that is thoroughly practical for construction. Construction in strict accordance with plant design. Plant tests and initial operation upon completion of construction—Girdler follows through until the plant is in full operation and you know all about how to use it.

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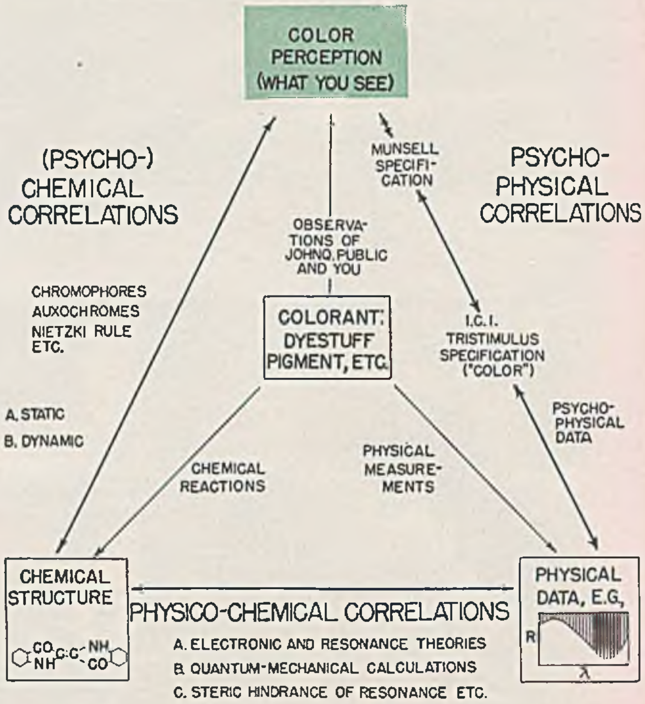
DESIGNERS, ENGINEERS AND CONSTRUCTORS OF GAS PROCESSING PLANTS

I&EC *reports*

A possible means of tying up the different approaches to the subject of color into a self-consistent philosophy was presented by Godlove in the following schematic diagram:

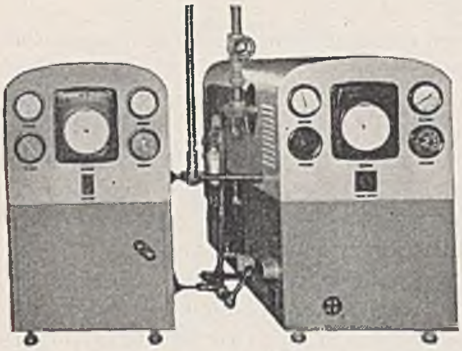


The colorant, a dye or pigment, is symbolized by the box in the center of the triangle. The effect an individual receives by observing this material results in color perception, the quality which, in the last analysis, is the most important from the point of view of the manufacturer of consumer items. The actual color of the colorant is determined by the molecular construction of the material; the construction is achieved by the controlled chemical reactions used in the dyestuff industry, represented by the line connecting the colorant box to the "chemical corner" of the triangle. In like manner the use of physical methods to measure the absorption spectra and other characteristics of the colorant material is shown schematically as the line joining the color box to the "physical corner" of the triangle.

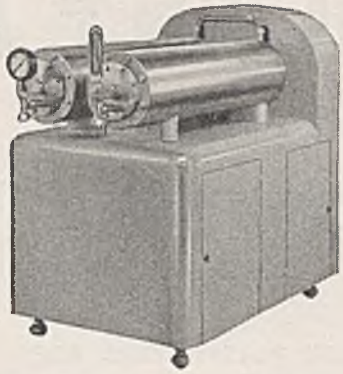
The perimeter of the triangle shows a possible correlation of many of the approaches to the theory of color. For instance, color perception can be integrated with chemical structure by traveling directly along the left leg of the triangle or indirectly by traversing the right leg and the base. The first journey would take one through predominantly static conceptions, such as theories of chromophores, auxochromes, salt-forming color-intensifying groups, Nietzki's rule, Schutz's series, etc., and also through the dynamic chemical interpretations of color phenomena, such as tautomerism, oscillation of benzenoid and quinonoid linkages, isorropesis, etc.

The indirect route of correlating color perception with chemical structure starts with the Munsell notation system on the psychophysical leg. This system of color classification, which is almost entirely psychological in approach, is most commonly employed in the art fields and embraces some nine hundred different colors.

(Continued on page 12 A)

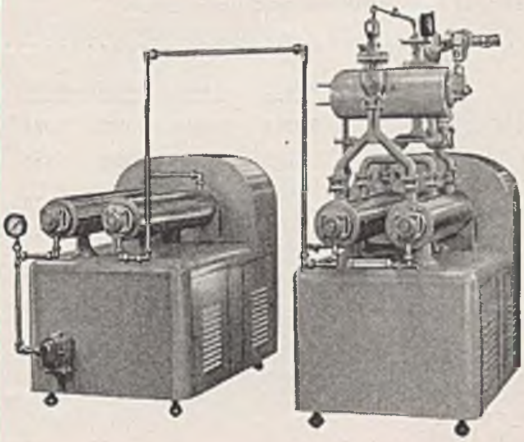


LUBRICATING GREASE



OR SHAVING CREAM

OR PARAFFIN WAX



OR INDUSTRIAL STARCH

i&ec reports

The Munsell notations define a color in terms of three dimensions—namely, hue, chroma, and value. Hue is the actual perceived quality of the color (blue, red, blue-green, etc.), chroma is the saturation measurement of the given hue, and value represents the actual "grayness" of the color under consideration. Thus, a pale yellow would be closer on a comparative value basis to a light gray or grayish white than it would be to a very dark red or brown.

Sooner or later in any attempt to integrate all of the different approaches, the philosopher is faced with the need for furnishing a step in which the instrumental measurements are made to overlap or coincide with an individual's evaluation of the color. It was here that the work of McAdam and the subsequent conversions of his data by Nickerson were of inestimable value in filling the gap. McAdam used the faculties of a standard and (he hoped) normal observer to match successive spectrum lights of varying wave length with a mixture of three primary lights of the International Commission on Illumination. His data from these tristimulus specification studies, as they were called, were converted into Munsell terminology by the culminant work of Nickerson, and the troublesome gap was bridged.

This section of the right leg is connected with its junction to the base diagrammatically by the notation "psychophysical data", which is known today as the "1931 I.C.I. Standard Observer and Coordinate System for Colorimetry".

From this point on, the indirect method of correlating color perception with chemical structure consists entirely of instrumental and theoretical considerations, to the exclusion of individual human evaluation. The junction of the right leg and the base is represented as the accumulation of physical data, restricted to the consideration of absorption, transmission, and reflection spectra only.

The base of the triangle is shown schematically as the connection between the observed physical data and the chemical structure of the colorant. This correlation includes, as subsections, (*A*) electronic and resonance theories, (*B*) quantum-mechanical calculations of the absorption spectra, and (*C*) steric hindrance effects, concerned with the inhibition of complete resonance by the lack of coplanarity of two rings in the structure of any other geometrical effects. Godlove points out that *A* is probably more truly typified as a consideration of the resonance between various electronic structures, the "true" chemical structure being a hybrid of these.

R.L.D.

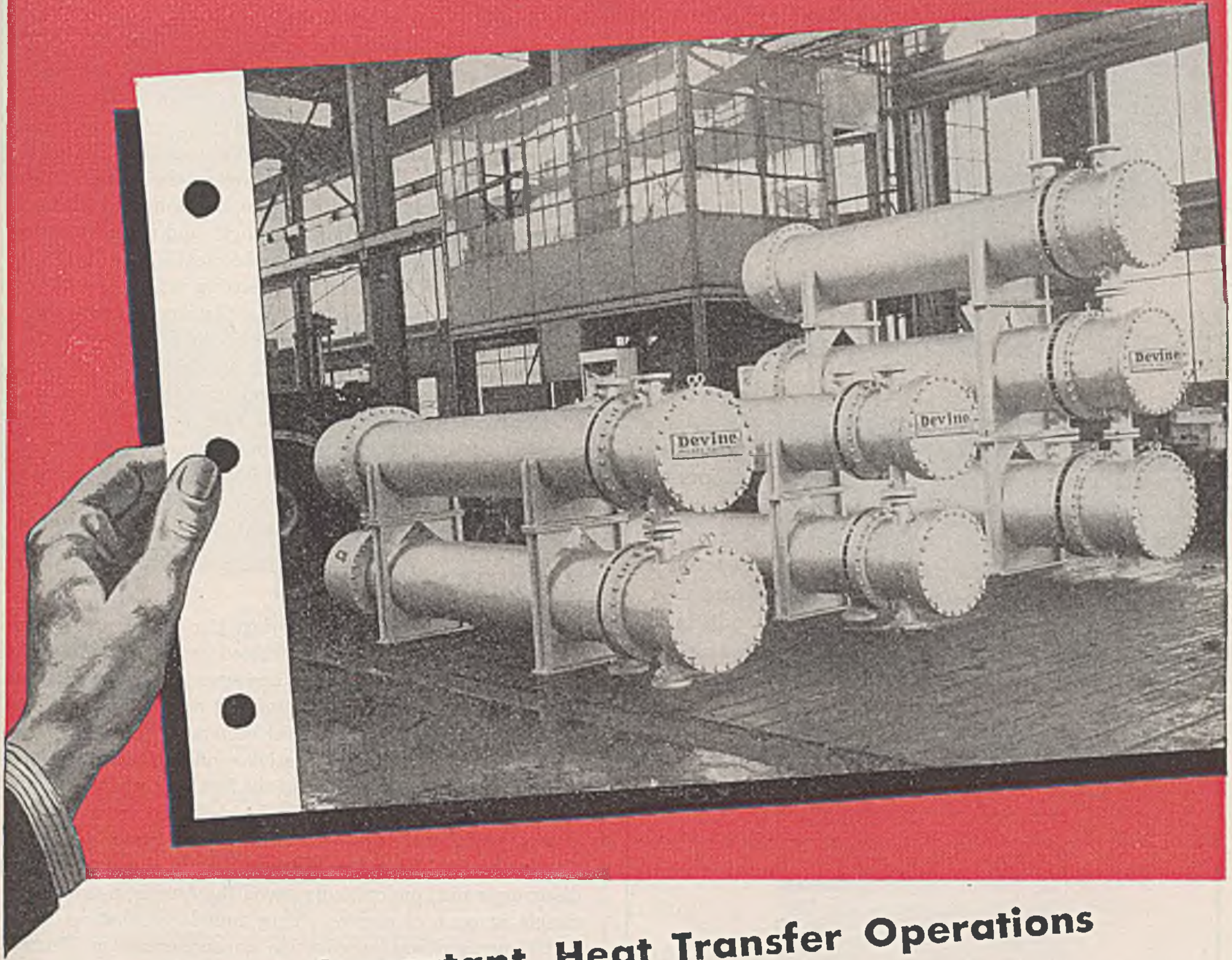
PORE PLASTICS

In spite of the fact that the age of plastics is now considered a *fait accompli*, there is occasionally a new application ingenious enough to cause our ears to prick up. Such is the fairly recent solution to the problem of sanding-up of producing wells, considered by authorities in the work-over branch of the petroleum industry to be one of the most important developments of the last five years.

Sanding-up is the movement of sand into a well bore or casing in sufficient volume to halt or seriously reduce the flow of oil, water, or gas, and occurs principally in unconsolidated sand formations. Plastics have been a panacea in a number of oil-field

(*Continued on page 14 A*)

Devine
HEAT EXCHANGERS



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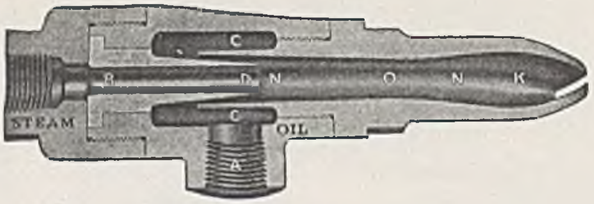

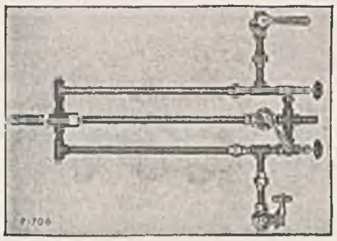

I&EC reports

plugging problems, but sand consolidation had a severe requirement for its solution: the plastic used could not form an impervious seal. It had to be capable of bonding the individual sand grains in place without materially reducing the effective permeability of the formation.

At the recent Galveston meeting of the Petroleum Division, American Institute of Mining and Metallurgical Engineers, A. C. Polk, Jr., of Dowell, Inc., told of a thermosetting plastic material which proved successful in 80% of the cases tried. Introduced into the well in the liquid state, it penetrated the sand at low pressure, and solidified with adequate compressive and tensile strength and inherent permeability. Basically of the phenol-formaldehyde type, the plastic is so modified as to adapt setting rate to specific and varying bottom-hole temperatures. "Inherent" permeability is brought about by shrinkage and by the presence of certain chemical compounds which permit the formation, on application of a differential pressure across the plastic (either as existing normally at the bottom hole or applied through portable surface pumps), of a porous and permeable set. The result is a formation in which the individual sand grains are bonded together, retaining 85 to 90% of the original permeability of the formation. W.H.S.

MATCHLESS ECONOMY

In these days when our solons are so outspokenly preoccupied with trimming the national budget and saving the "peepul" from "crippling taxation", it has become quite the fashion to discuss governmental economy. However, even back during the days of the active conflict, there were some groups who did not lose sight of the fact that what "we owed to ourselves" would eventually be deducted from our pay checks. Within the first year of the United States' participation in the war, Chemical Warfare Service chemists made a discovery which undoubtedly saved the American taxpayer a sizable amount of money. They found out that barite at $10.00 per ton was as effective an accelerator in Thermit bombs as was the $195.00-a-ton barium nitrate conventionally used. In fact it was a little better. Furthermore, it operated with secondary 92% pure, granular aluminum instead of the more expensive 98% pure grained aluminum used with the nitrate, and did not require sulfur and castor oil binders. All in all, it was a considerable simplification.

The older standard incendiary mixture known as Therm-8 had the following composition: iron oxide scale, 59.2%; barium nitrate, 15.0%; granular aluminum (92%), 20.8%; grained aluminum (98%), 3.8%; sulfur, 0.9%, and castor oil, 0.3%. The new barite mixture had only three components: iron oxide scale, 59.2%; granular aluminum (92%), 25.3%; and barite, 15.5%.

The best results were obtained when sufficient aluminum was used to react with all of the barium sulfate present in the barite, assuming the impurities to be inert. Varying the ferrous oxide content in the iron scale from 22 to 7.1% had no apparent effect on the behavior of the bomb. It was found that bombs containing aluminum from different sources had different rates of combustion. This variation was attributed to differences in apparent density. (*Continued on page 16 A*)

From Tennessee and Iowa TWO PLANTS NOW SUPPLYING *Furfural*

HERE'S good news for users and prospective users of furfural and its derivatives. On November 1, 1946, The Quaker Oats Company purchased the furfural manufacturing plant at Memphis, Tenn., formerly owned by the government. This plant, operated for the government during the war by The Q. O. Chemical Company, a wholly owned subsidiary of The Quaker Oats Company, supplied all the furfural requirements for the government's vast synthetic rubber program. Now, this same personnel continues under the new ownership to run this plant, government needs being supplied from here as before.

TWO SOURCES FOR INDUSTRIAL USERS

Excess capacity from the Memphis plant, the largest furfural producer in the world, as well as the entire facilities at the Cedar Rapids plant, are now available to industrial users of furfural and its derivatives. With these two sources, widely separated geographically, users of furfural are further assured of an uninterrupted flow of furfural in ample volume to meet their needs.

FURFURAL'S VERSATILITY WARRANTS YOUR INVESTIGATION

This versatile aldehyde, the cheapest pure aldehyde available today, is rapidly growing in importance in a wide variety of applications. If you are not entirely familiar with its current uses and reactions, we suggest you write on your letterhead for literature we have available.

The Quaker Oats Company CHEMICALS DEPT.

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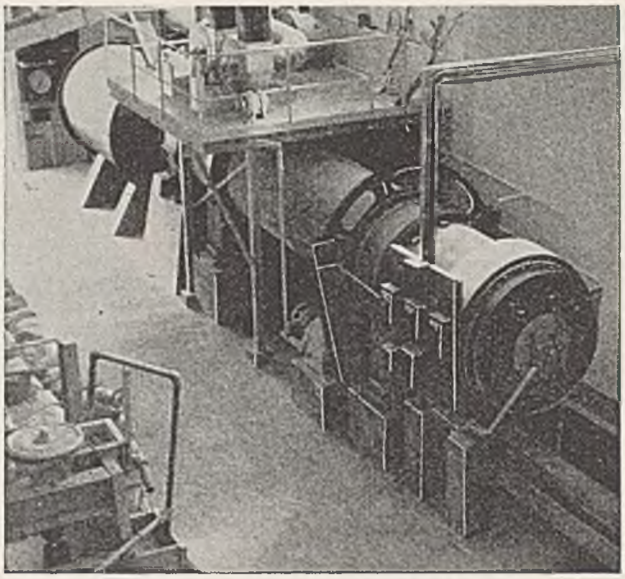
FURFURAL • FURFURYL ALCOHOL • FUROIC ACID • TETRAHYDROFURFURYL ALCOHOL



I&EC *reports*

Although the heat of reaction of the barite bomb (800 calories per gram) is almost 20% less than that of the Therm-8 type (960 calories per gram), military effectiveness tests indicate that the simpler type will do more damage. When placed on a white pine board, 12 × 20 × 2.5 inches, and ignited, the barite bomb penetrated the board more than twice as fast as did its older rival. It also took a 10% edge in igniting a slat placed 1 foot to the side of the bombs and another 3 feet above. Except for the filling, the bombs used in the test were identical.

The barite mixture came out on top in the storage and handling tests also. It had the advantage of being unaffected by moisture, whereas barium nitrate is strongly hygroscopic. An added advantage is an ignition temperature well above 1000° C. compared to 700–760° C. for Therm-8. This makes it safer while in process.

Yes, all this and cheaper too. M.L.K.

PAINTBRUSH PLASTICS

An absorbing example of wartime ingenuity in plastics application is reported by Chandra Kant in the September 7, 1946, issue of *The Chemical Age*, a British publication. Resin-impregnated-canvas jettison tanks for airplanes have been fabricated in the field through a method developed by India's Council of Scientific and Industrial Research.

A sewed canvas bag, of 75-gallon capacity and the usual torpedo shape, is made from a single thickness of canvas complete with two internal perforated baffles that also serve as reinforcements. The bag is rolled up and sent to the point of use accompanied by 20 pounds of a resin powder of the following composition: dewaxed lemon shellac 44%, portland cement 44%, casein 4.5%, sodium carbonate 4.4%, urea 2.2%, and borax 0.9%.

To make the tanks, the powder is mixed with 4.5 gallons of water and placed in the bag, which is pumped up to an air pressure of 2 pounds per square inch. The inflated tank is rolled around to coat all inside portions thoroughly, and the resin that oozes through the cloth is spread on the outside. Some hours later the plastic has set enough to permit the tank to be used. A concentrated load of 80 pounds could be withstood easily by a finished tank.

Most processes for production of laminated plastics containers require large presses. This adaptation was developed to avoid the requirement of heavy machinery and permit its use in India's "cottage industry". A 4-gallon gasoline "blitz can" was another product made by essentially the same method. It consisted of two resin-impregnated canvas layers which were stiffened with bamboo strips and to which the resin could be applied with a paintbrush. D.O.M.

CUT HEAT EXCHANGER REPLACEMENT COSTS WITH

"KARBATE"

BRAND

HEAT EXCHANGERS—THEY LAST *Indefinitely*

● "Karbate" Heat Exchangers will help you end the expense and delay of constantly replacing corroded heat exchangers!

"Karbate" Heat Exchangers are chemically inert. They are free from corrosion scale formation. Thus, they will stay on the job indefinitely—saving substantial replacement costs over the years.

"Karbate" Heat Exchangers have other stand-out features: A remarkably high rate of heat transfer • Extreme heat shock resistance • Light weight • Strong, sturdy — able to take rough treatment • Can be made in a variety of sizes and types from the simple plate to the large tube-bundle types.

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"KARBATE" MATERIAL UNAFFECTED BY

Hydrochloric . . . sulphuric . . . lactic . . . acetic . . . hydrofluoric acids . . . and by special caustic vapors . . . and other corrosive liquids and gases.

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Unit of Union Carbide and Carbon Corporation
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These characteristics give you some idea of why so many firms have replaced ordinary mineral oils or oils of other origin with Sonneborn purified petroleum hydrocarbon oils (white mineral oils). The complete list of properties is an extremely long one, and the range of industrial applications is virtually unlimited.

For latest information on Sonneborn Hydrocarbon Oils and help on your problem, send coupon or write, specifying use intended.

PHYSICAL CHARACTERISTICS*

Specific Gravity: 0.775 to 0.895 @ 60°F.
Saybolt Viscosity: 30 to 345 @ 100°F.
Distillation Range: 370 to 800°F.
Flash Point: 170 to 420°F.
Fire Point: 190 to 480°F.
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Aniline Point: 175 to 230°F.
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Dielectric Strength: Above 29 K.V.
Sligh Oxidation Number: 0.0 to 0.9
Copper Stability Test: Not less than 20
Molecular Weight: 175 to 400
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(*These characteristics represent the entire range of Sonneborn Hydrocarbon Oils — not any one oil.)

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U.S.I. CHEMICAL NEWS

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

Sulfanilamide Activated By Urea and Urethan

Sulfanilamide in quantities insufficient to inhibit growth of bacteria becomes bacteriostatic when mixed with urethan or urea, according to a paper published recently. In addition, the author states, urethan increases the solubility of sulfanilamide at least two times and of sulfathiazole at least three times. The report also indicates that urethan improves the action of penicillin, particularly in the treatment of mixed infection of wounds.

Increases Soap Lather

To improve the lathering of soap, a method has been devised which consists of treating the soap with nitric oxide prior to the salting out process. The soap afterward was said to give a thicker and finer lather than without this treatment.

THE MONTH IN TEXTILES

A flameproof, mothproof, and non-shrinking wool is said to have been developed . . . Limited commercial production of nylon staple fiber — a material claimed to have outstanding properties of strength, abrasion resistance, and dimensional stability — is announced . . . A method for lubricating fibers at a stage prior to spinning is patented . . . Congress will be asked to enact a law forbidding interstate transport of highly flammable textiles, according to a reputable source . . . A waterproof and stainless fabric is marketed which is said to need no special stitching . . . A report on synthetic fiber developments in Germany is made available . . . The British announce a new organization to undertake research into the growing and breeding of cotton . . . A device is produced which accurately determines the amount of moisture in wool . . . A new finishing agent for cotton and rayon fabric, described as a water-soluble gum finish of low viscosity and good stability, is manufactured . . . A new dry-cleaning fluid is placed on the market.

New NF VIII Available

The new, completely revised and enlarged National Formulary has just been issued. It is said to represent the culmination of four years of planning and work by the Committee on National Formulary, the staff of the American Pharmaceutical Association Laboratory and hundreds of collaborators.

Ups Starch Solubility

The solubility of starch in aqueous solutions is said to be increased by a process patented recently. The process consists primarily in treating the starch with a soluble inorganic chlorite under prescribed conditions of heat and pressure.

New Shampoo Stabilizer

The turbidity tendency of shampoo compositions can be decreased notably by the use of ~~a~~ stabilizing agent, described as an anion-active salt of a monoalkyl sulfate, according

1946 Advances in Drug Field Used Many U.S.I. Chemicals

Intermediates, Solvents, and Other Chemicals Supplied for Amino Acid Therapy, and Treatment of Leukemia, Malaria and Ophthalmia

The cascade of "wonder-drugs," fed by seven years of intensive war-time research, swelled last year as new pharmaceuticals hit the market and as "top-secret" labels were removed from many war-time developments. During the year, U.S.I. continued to supply the pharmaceutical industry with many chemicals, intermediates, and solvents. Among its major contributions was a new low-cost method for synthesizing the up-to-then rare and expensively-priced methionine, a vital amino acid for which wide use is foreseen in human foods, animal feeds, and the treatment of various diseases.

Also introduced last year were new therapies for periodic ophthalmia and leukemia, the dreaded "cancer of the blood," in which riboflavin and urethan respectively played prominent parts. Government scientists disclosed the development of a new synthetic drug, "SN 7618," which is said to be superior to both atebrin and quinine in the treatment of malaria. Familiar pharmaceutical stand-bys, such as ethyl acetate, ethanol, acetone, and butanol, gained new stature by their applications in the manufacture and processing of vitamins, hormones, barbiturates, "sulfa" and other drugs.

Low-Cost Methionine

Practically unobtainable before 1946, methionine is now available to pharmaceutical manufacturers for much-needed applications, thanks to the new U.S.I. manufacturing process which slashes costs about 97 per cent. Anticipated uses for this compound, which is one of the ten amino acids necessary for the growth and repair of animal tissue, include the treatment of shock, burns, exposure, as well as poisoning from a wide range of compounds. It is reported that protein hydro-

(Continued on next page)

New Scale Simplifies Solution Preparations

To simplify the preparation of solutions in which the weight of water must be figured, a new scale has been developed which is claimed to save considerable time for pharmacists and chemists because unit weights replace tedious mathematical calculations. The new scale is graduated into units, called "yagles." Each "yagle" is equal to one per cent of the weight of a fluid dram of water (454.6 grams).

Hormone Combats Ulcers

A group of American scientists have announced the isolation of a new hormone which is claimed to have brought relief to 40 of 58 patients suffering from peptic ulcers. The hormone, known as enterogastrone, is said to be derived from the mucous lining of the upper intestinal tract of pigs.

Mildew Resistance Tests

A summary of the tests used to determine the mildew and rot resistance of textiles and the effectiveness of textile fungicides have recently been published. Complete laboratory details of the more important tests are given.

In 1846, William Morton made the first public demonstration of the use of ether as an anesthetic.

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

Pharmaceutical Advances in 1946

(Continued from page one)

lysates fortified with methionine have been employed with outstanding success in the treatment of peptic ulcers and starvation cases.

Hope for Leukemia Victims

To the many victims of leukemia, for which no cure has yet been found, new hope came last year as British scientists announced a definite palliative effect in many cases when urethan treatments were used. The results were reported to be similar to those obtained from X-ray therapy which has been employed for some time to give temporary relief and to prolong life in chronic forms of the disease. Urethan therapy, it was noted, dropped the total white blood count to normal limits and raised the hemoglobin level.

New Antimalarial

After four years of extensive research the U. S. Government's Board for the Coordination of Malarial Studies finally came up with a new antimalarial, "SN 7618," which, it is claimed, relieves malaria three times faster than atebrin or quinine, and with fewer ill effects. An important intermediate in the manufacture of this drug, is noval ketone (5-diethylamino-2-pentanone), a product of U.S.I.

Wider Use for Old Stand-bys

Familiar chemicals continued to play important roles in the pharmaceutical industry in 1946. A stir was created when it was announced that ethanol was found effective in the treatment of rats' cancer, but the greatest pharmaceutical manufacturing use for this compound was still found in the processing of vitamins, hormones, and plant extracts. Other solvents, such as amyl alcohol, amyl acetate, butanol, and acetone entered into the same type of processing. Riboflavin extracts were suggested as a cure for periodic ophthalmia, "moon blindness," a disease common to horses. Diethyl carbonate and diethyl oxalate were used in the preparation of barbiturates; ethyl acetoacetate in the manufacture of antimalarials, leucine, antipyrine, and Vitamin B_1; and ethyl acetate in the processing of "sulfa" drugs, such as sulfadiazine.

25,000 ATTEND FIRST AUTOMOTIVE INDUSTRIES SHOW SINCE PEARL HARBOR

More than 450 exhibitors displayed products ranging from seat covers to hydraulic springs at the Automotive Service Industries show held recently at Atlantic City under the joint sponsorship of the MEMA and the MEWA. The show attracted about 25,000 visitors. Shown here at the U.S.I. booth, left to right are: J. F. Creamer, Horton, Gallo, Creamer Co., W. J. Fried, U.S.I., J. T. Fleming, Horton, Gallo, Creamer Co., W. W. Newell, U.S.I., A. E. Tongue, U.S.I., H. L. Snyder, Jr., U.S.I., T. M. Bennett, U.S.I., J. Blessing, Harrisburg Auto Parts Co., and E. B. Mower, George W. Myers Co.

TECHNICAL DEVELOPMENTS

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

A modified carnauba wax, having an alleged melting point of 178-180 degrees F, is recommended by the manufacturer for use in self-polishing floor waxes, and in the production of carbon paper and carbon inks. **(No. 159)**

USI

An easy method for testing tension in a strand of thread, yarn, or cord is said to be supplied by a new tensometer which measures tension directly in pounds. Clipped on a moving continuous cord, the instrument is reported to record fluctuations with a minimum of error. **(No. 160)**

USI

Quantitative test papers for determining concentrations of quaternary ammonium compounds are now on the market. Strength in parts per million is rapidly measured merely by dipping the papers in the solution, according to the manufacturer. **(No. 161)**

USI

A "fool-proof" liquid adhesive, stated to require no catalyst or special preparation for use, is described as a tough, flexible cement having a six-months' minimum package stability. The manufacturer states that the adhesive can be applied without thinning by brushing, roller coating, or dipping. **(No. 162)**

USI

An odorless lanolin, said to be applicable to the manufacture of cosmetics, is reported to have a new non-darkening pale color. **(No. 163)**

USI

A lighter-than-cork insulating material is described as a cellular rubber that will not absorb moisture and is fire-resistant, rot-resistant, and unaffected by acids, oil, vermin, and termites. Said to be a more efficient insulator than cork, it is specially recommended for refrigerator trucks. **(No. 164)**

USI

Four types of phenolic cements, designed primarily for acid-proof brick or tile in the construction of acid tanks, pulp digesters, acid towers, and floors, have been developed. Supplied as powders, the cements are reported to set in 4 to 6 hours at room temperature and to retain their physical properties over a wide temperature range. **(No. 165)**

USI

A new rubber accelerator, which is alleged to make tires more resistant to thread cracking and ply separation, has been announced. It is said to be especially beneficial in the processing of synthetic rubber. **(No. 166)**

USI

A new fungicide and spray adjuvant that will not wash off in rain or dew, according to the manufacturer, is described as an air-drying adhesive which can be used as a carrier for insecticides and other fungicides. The compound is mixed with water and can be used in all standard equipment, it is stated. **(No. 167)**

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

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

Ethanol (Ethyl Alcohol)
- Specially Denatured—all regular and anhydrous formulas
- Completely Denatured—all regular and anhydrous formulas
- Pure—190 proof, C.P. 96% Absolute
- *Super Pyro Anti-freeze
- *Solox proprietary Solvent

***ANSOLS**
- Ansol M
- Ansol PR

*Registered Trade Mark

ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Dibutyl Oxalate
- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

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

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

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

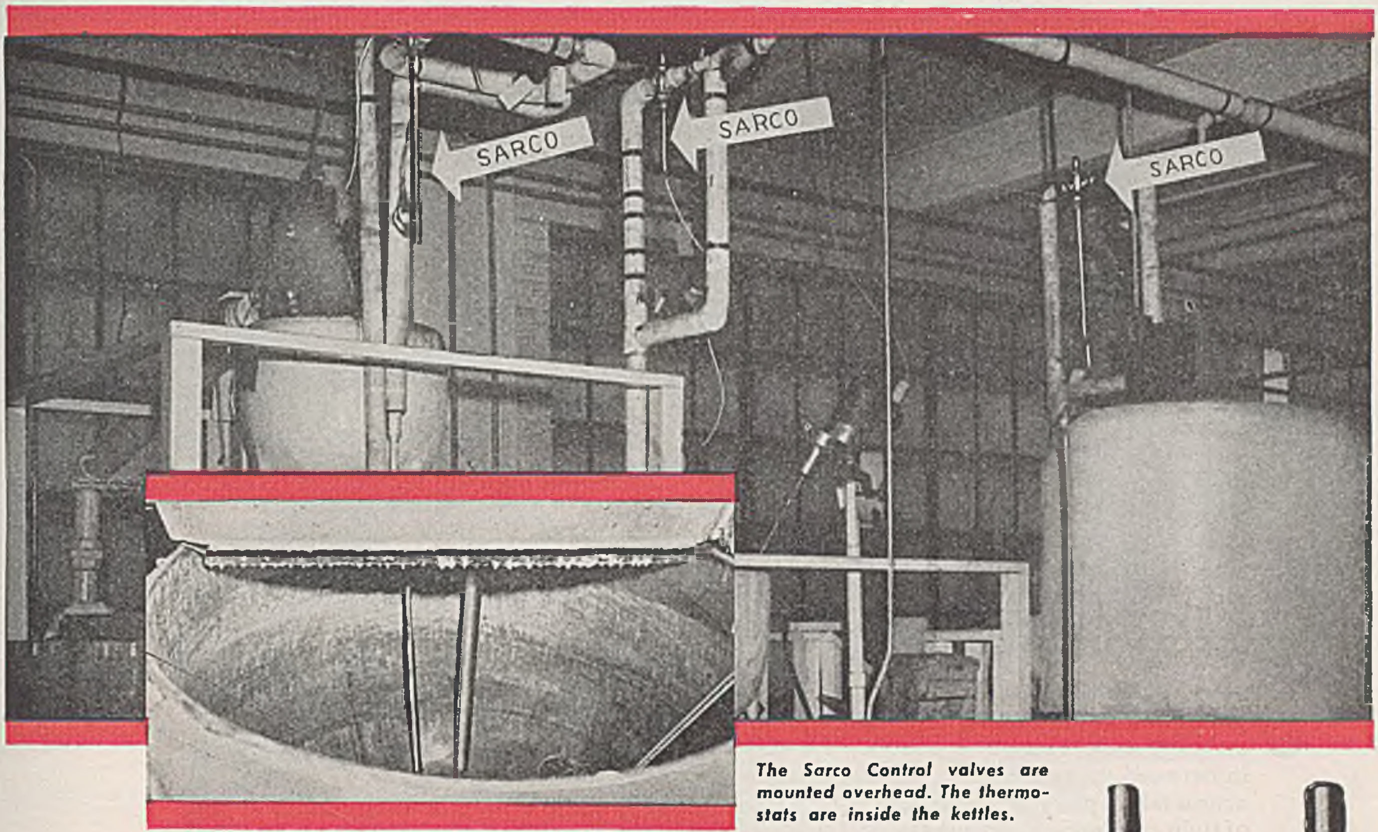
FEED CONCENTRATES
- Riboflavin Concentrates
- *Vacatone 40
- *Curbay B-G
- *Curbay Special Liquid

ACETONE
- Chemically Pure

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

OTHER PRODUCTS
- Collodions
- Ethylene Glycol
- Nitrocellulose Solutions
- Ethylene
- Urethan
- *dl*-Methionine

Printed in U.S.A.



The Sarco Control valves are mounted overhead. The thermostats are inside the kettles.

Buy Wheelco

because of the Electronic link between Measuring & Control Functions

1. The COILS carry an oscillating current generated by an electronic tube.
2. This is the TEMPERATURE SETTING POINTER on which the coils are mounted.
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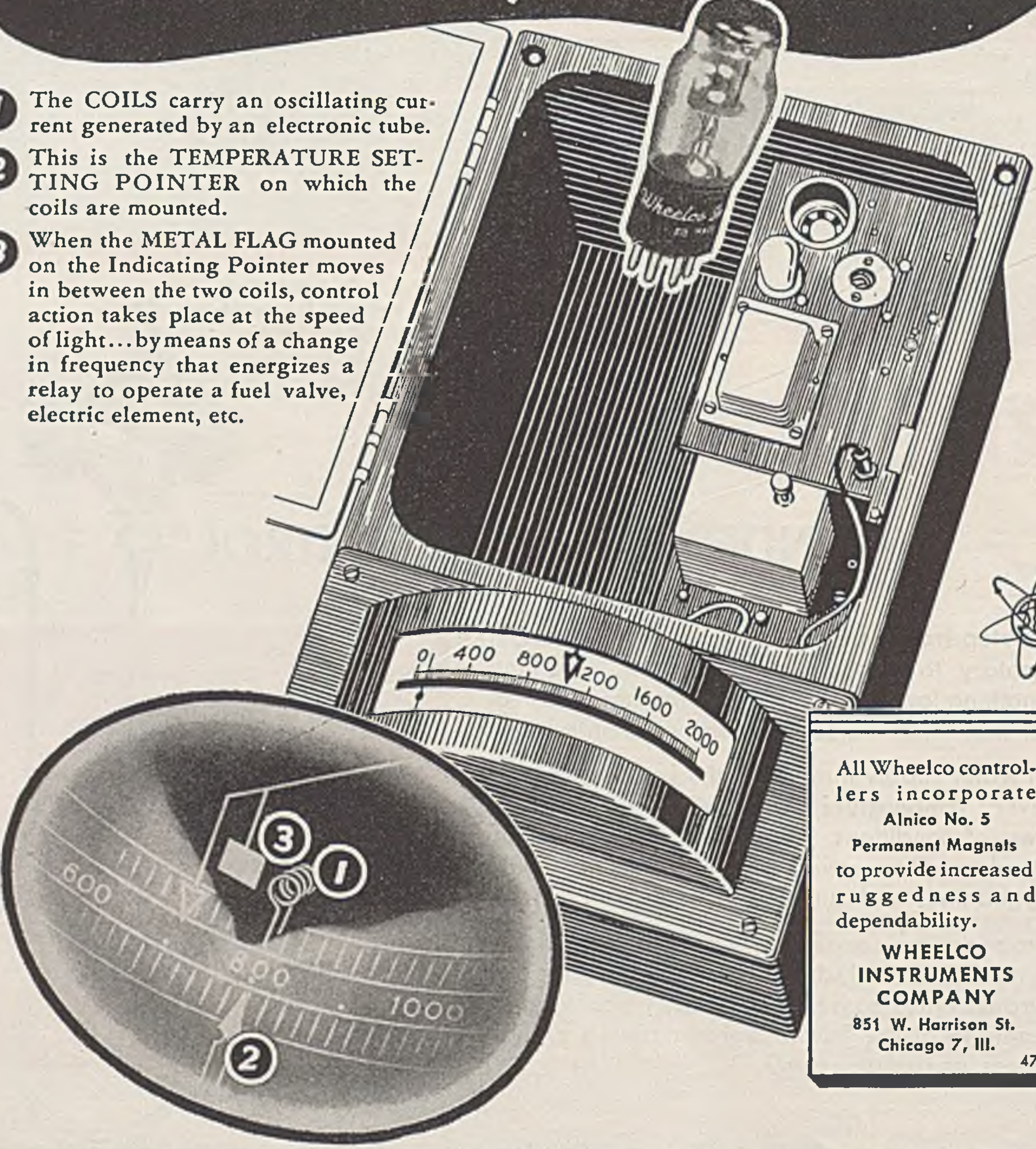

All Wheelco controllers incorporate **Alnico No. 5 Permanent Magnets** to provide increased ruggedness and dependability.

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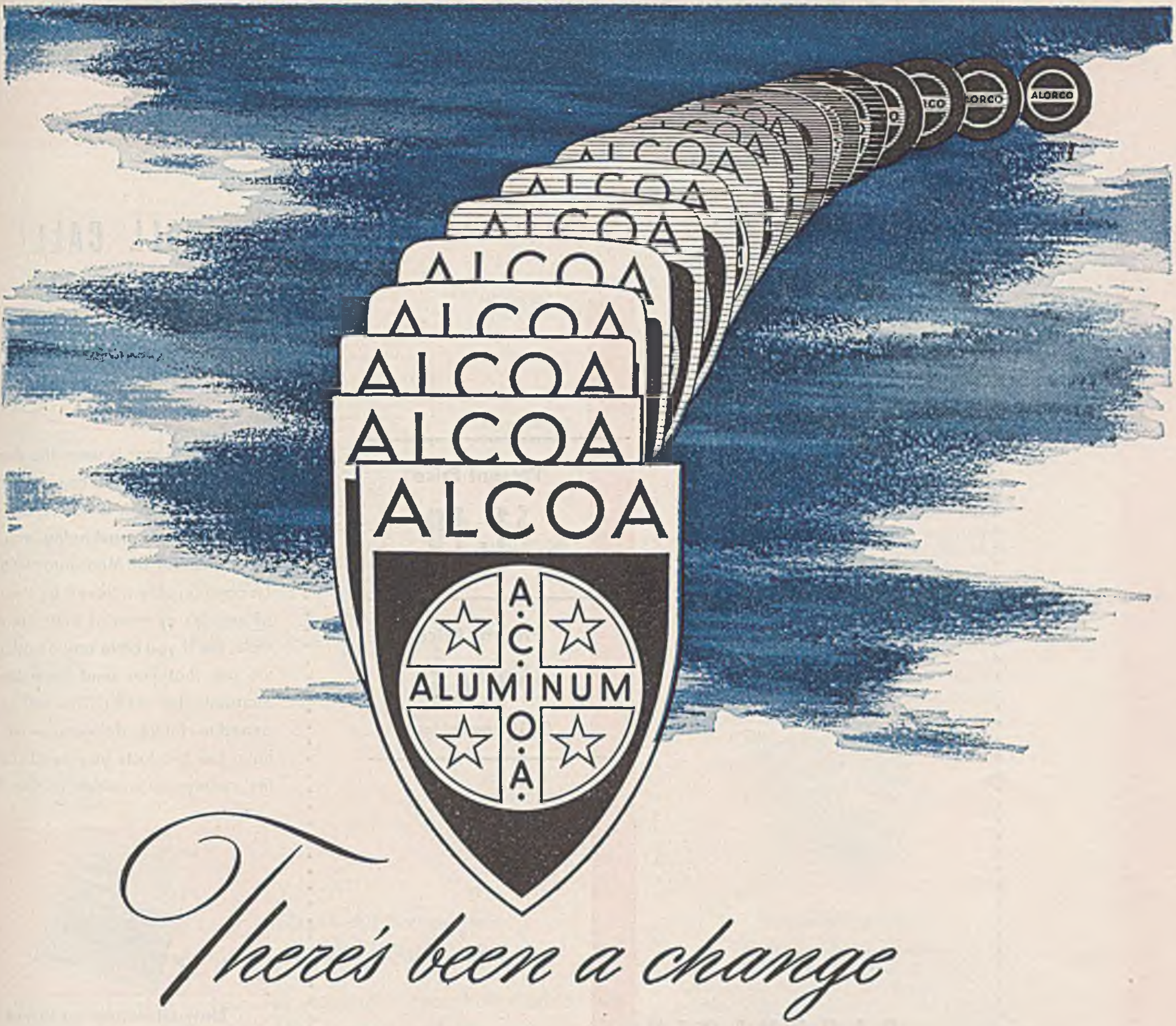
Speed · Simplicity · Serviceability



The same top quality Aluminas and Fluorides—produced by the Aluminum Ore Company, and for years sold under the "Alorco" brand name and trade-mark—now carry the ALCOA trade-mark. They will be marketed exclusively by the Chemicals Division of Aluminum Company of America.

Just as the ALCOA shield has long been the symbol for the best in aluminum—so now look to it for the best in aluminas and fluorides.

ALCOA ALUMINAS are versatile chemicals. They are used as hard-biting abrasives . . . as high temperature refractories . . . as catalyst carriers . . . for drying gases and liquids . . . and employed in dozens of other ways. More likely than not, the spark plug "porcelains" in your car are made of *Alcoa Alumina.*

ALCOA FLUORIDES are used in many ways . . . for laundry compounds . . . for preserving wood . . . and as *Alcoa Cryolite Insecticide* to protect both farm and orchard crops. Let us tell you how these Alcoa products can serve you. Call your nearest Alcoa sales office, or write ALUMINUM COMPANY OF AMERICA, CHEMICALS DIVISION, 1911 Gulf Bldg., Pittsburgh 19, Pennsylvania.

ALCOA *Aluminas and Fluorides*

FORMERLY SOLD UNDER THE TRADE NAME "ALORCO"

FOR YOUR INFORMATION

NO PRICE INCREASE

Present Price

$1.40

Prewar Price

$1.45

(in 100-pound lots)

SACCHARIN . . . Although production costs have advanced considerably during the war period, no increase in the price of Saccharin has been scheduled. In fact, Monsanto's present pound price, in 100-pound lots, is lower than its prewar price—$1.40 compared to $1.45. Price of single 5-pound cans remains $1.65 a pound, unchanged since before the war.

While capacity was materially increased during the preceding 5 years, unsettled labor conditions curtailed production during the past 6 months. However, with production now resumed, it is expected that Monsanto will be able to meet all normal requirements on a current basis in the early part of 1947. Also, it is anticipated that appreciable gains will be made on the present backlog of demand.

MONSANTO CHEMICAL COMPANY, Organic Chemicals Division, 1700 South Second Street, St. Louis 4, Missouri.

ROLL CALL!

Although the war is over, the shortage of drums isn't—due of course to a basic shortage of steel. In many cases this poses an acute packaging and shipping problem at Monsanto which can be considerably relieved by the return of empties as soon as they are available. So, if you have any empties may we ask that you send them back to Monsanto for credit. This will greatly expedite future deliveries—we may have the products you need, but not the containers in which to ship them.

New Literature on Wood Preservation with Santophen 20*

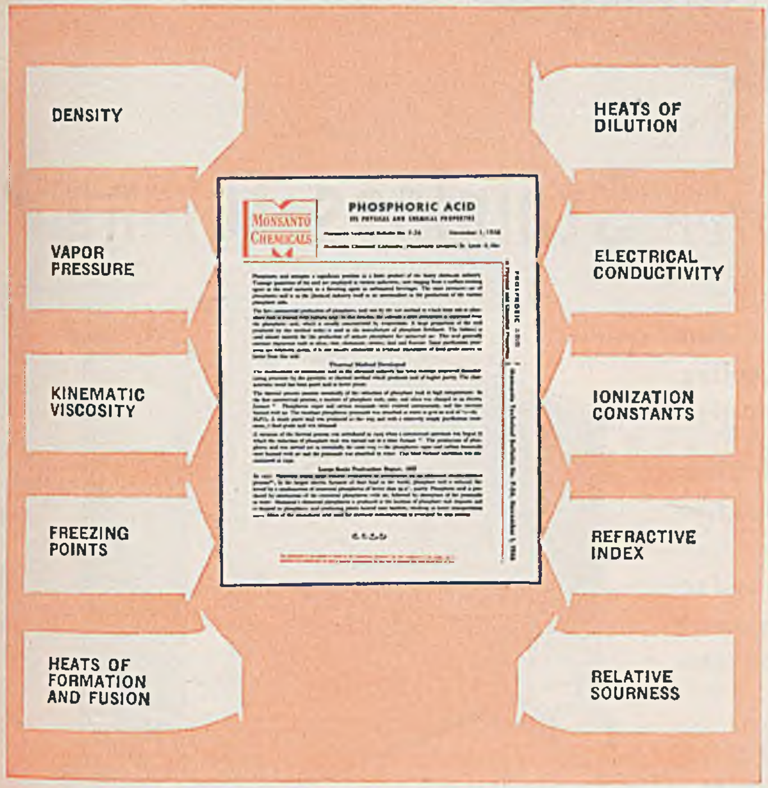
(Monsanto's Pentachlorophenol, Technical)

Recently published, this 16-page booklet forms a valuable text on wood preservation with Santophen 20* in oil solutions by pressure process. It is liberally illustrated and contains numerous tables and reference data concerning the characteristics of this recognized wood preservative. Send for your copy.

Expanded Production of Synthetic Detergents

Monsanto recently announced a $3,000,000 plant expansion program for the manufacture of synthetic detergents. Construction is already under way and it is anticipated that the new plant will be ready for operation in the latter part of 1947.

News of Monsanto Chemicals and Plastics for the Process Industries...February, 1947



In 12 Handy Tables — All Available Physical Data on PHOSPHORIC ACID

Through many years of research Monsanto's Phosphate Division has attempted to catalog and correlate all available physical and chemical data on phosphoric acid—and here the results have been distilled into twelve handy reference tables and four pages of explanatory notes.

From the tabulations in this fact-packed bulletin, graphs of the desired size and range can be prepared. Data are included on acids of a wide range of strength up to the strong phosphoric acids wherever available.

Write on your business letterhead for your copy of this helpful Technical Bulletin No. P-26 on Phosphoric Acid—a product recognized as one of the most versatile and widely useful tools of the chemical industry.

Address MONSANTO CHEMICAL COMPANY, Phosphate Division,
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District Offices: New York, Chicago, Boston, Detroit, Cleveland, Cincinnati, Charlotte, Birmingham, Los Angeles, San Francisco, Seattle. In Canada, Monsanto Ltd., Montreal, Toronto, Vancouver.

Does this mean anything to you?

No, this isn't another picture of the moon! The "rugged terrain" you see is simply a head-on view of oxygen corrosion—foe of the boiler room, thief of power- and steam-generating efficiency. Fortunately this form of corrosion can be checked, simply by adding Santosite* (Monsanto Sodium Sulfite Anhydrous) to boiler feed water and maintaining a ratio of 30 parts to 1,000,000. All residual dissolved oxygen in feed water combines with Santosite to form sodium sulfate, the reaction product with oxygen. Result: no trace of oxygen remains—oxygen corrosion can't start!

Goodbye, Mr. Rat!

After hundreds of years as a world scourge, the rat is nearing the end of his trail of terror and filth. With the coming of Compound 1080, his doom is nearer at hand, as well as that of his army of 1,300 rodent relatives—house mice, field mice, squirrels, gophers and woodchucks, just to mention a few. Outside experiments are also being conducted to test the effectiveness of Compound 1080 in exterminating wolves, foxes, coyotes and other predatory animals. (Because of its high toxicity, Compound 1080 is sold only to licensed operators and to Government Experimental Stations.)

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CHEMICALS AND PLASTICS
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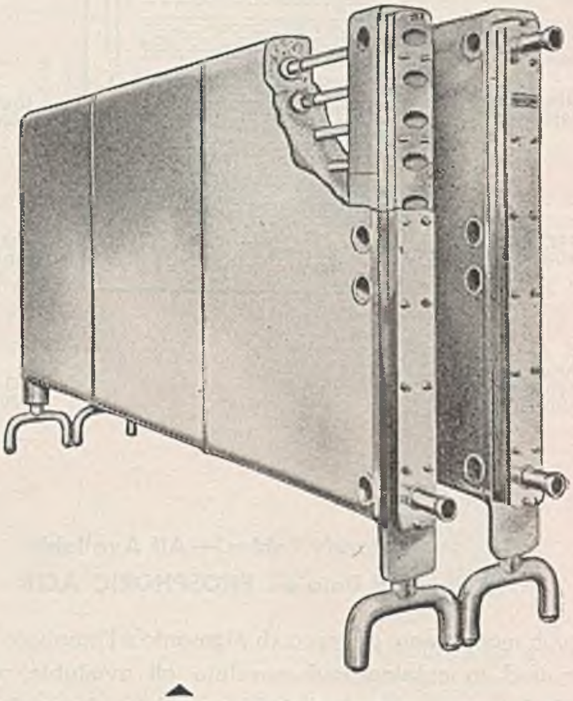
MONSANTO CHEMICAL COMPANY, 1700 South Second St., St. Louis 4, Missouri... District Offices: New York, Chicago, Boston, Detroit, Cleveland, Cincinnati, Charlotte, Birmingham, Los Angeles, San Francisco, Seattle. In Canada, Monsanto Ltd., Montreal, Toronto, Vancouver. *Reg. U. S. Pat. Off.

You get FAST HEATING & COOLING FULL CORROSION RESISTANCE

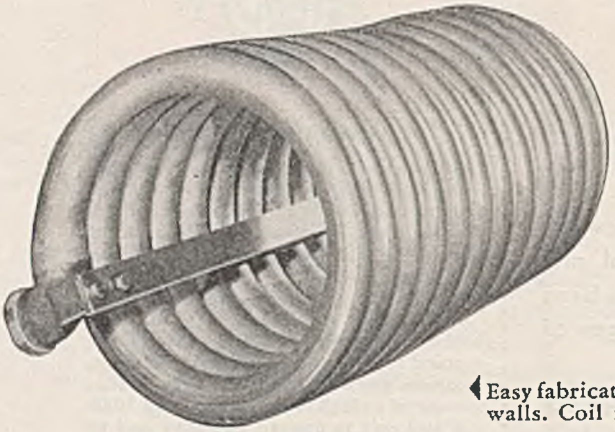
with *Carpenter* Stainless Tubing

● The *uniform walls* of this Stainless Tubing allow you to use gauges that give you faster heating and cooling. And this same uniformity helps to speed fabrication.

On your jobs where you need full corrosion and heat resistance, specify 100% hydrostatically tested Carpenter Stainless Tubing. You'll find it pays—from first cost to less "down time" for tube repairs and replacements. Drop us a line and make use of Carpenter's long experience with Stainless Tubing problems.



▲ On your jobs where sanitary requirements are rigid you'll find this tubing easy to clean and keep clean.



◀ Easy fabrication is one advantage you get because of this tubing's uniform walls. Coil made from 1" IPS Carpenter Stainless Tubing—Type 316.

POLISHED INSIDE *Carpenter* Stainless Tubing

To guard against carry-overs from one process to another, and protect against product contamination, Polished Inside Carpenter Stainless Tubing is often used in food, dairy and chemical production. Available in a wide variety of sizes and analyses.

CARPENTER
STAINLESS TUBING for
—Strength and Rigidity
—Weight Savings
—Corrosion Resistance
—Heat Resistance
—Accuracy
—Fabricating Savings
—Longer Service Life
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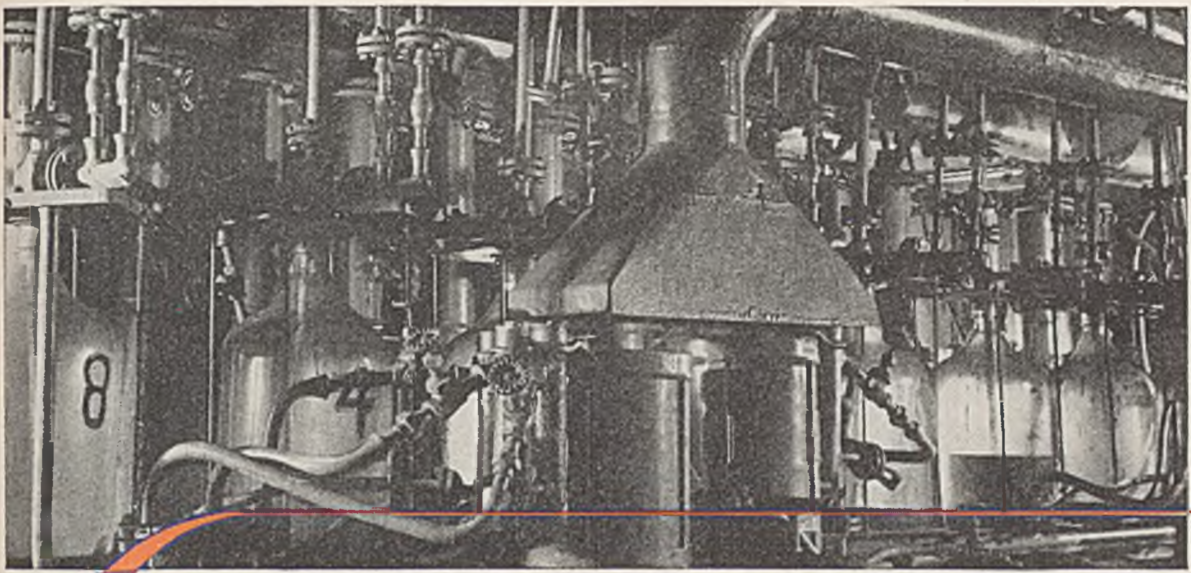
THE CARPENTER STEEL COMPANY • Welded Alloy Tube Division • Kenilworth, N. J.

Carpenter

STAINLESS TUBING



Samples of benzyl chloride are drawn off during distillation, for inspection and test, to assure conformity with Hooker high purity specifications.

For Compounds Containing $C_6H_5CH_2$— Use Hooker Benzyl Chloride

The list of chemicals that can be made with Benzyl Chloride includes almost every compound that contains the $C_6H_5CH_2$—group.

Benzyl Chloride is so reactive that it will give up its benzyl group in many different types of reactions. Friedel Crafts reactions are readily carried out, a typical one being the preparation of diphenyl methane by reacting benzyl chloride and benzene in the presence of aluminum chloride.

It may be reacted with alcohols to produce mixed ethers.

An example of the introduction of the benzyl group into an amino compound is its reaction with aniline to form benzyl aniline.

The benzyl group replaces sodium in reactions of benzyl chloride with sodium cyanide or sodium sulfhydrate.

Esters are readily prepared by reacting the sodium salt of the acid with benzyl chloride.

For uniform results without operating difficulties be sure to use Hooker Benzyl Chloride. Hooker maintains careful control of manufacture and strict adherence to high standard specifications to make sure that all shipments are up to the same uniform high purity.

TYPICAL DATA

BENZYL CHLORIDE
(omega chlortoluene) $C_6H_5CH_2Cl$

DESCRIPTION:
Clear, colorless to light yellow liquid having a pungent odor. Infinitely miscible with alcohol and ether; immiscible with water.

PHYSICAL DATA:

Ml. Wt.	126.5
F. P.	—43°C
B. R.	5° or less incl. 179.4°C

USES:
In manufacture of chemical intermediates, dyestuffs, perfume bases, plasticizers, resins, wetting agents, rubber accelerators, gasoline, gum inhibitors, pharmaceuticals.

For further information on Hooker Benzyl Chloride and other Hooker intermediates ask for Bulletin 320 on your company letterhead.

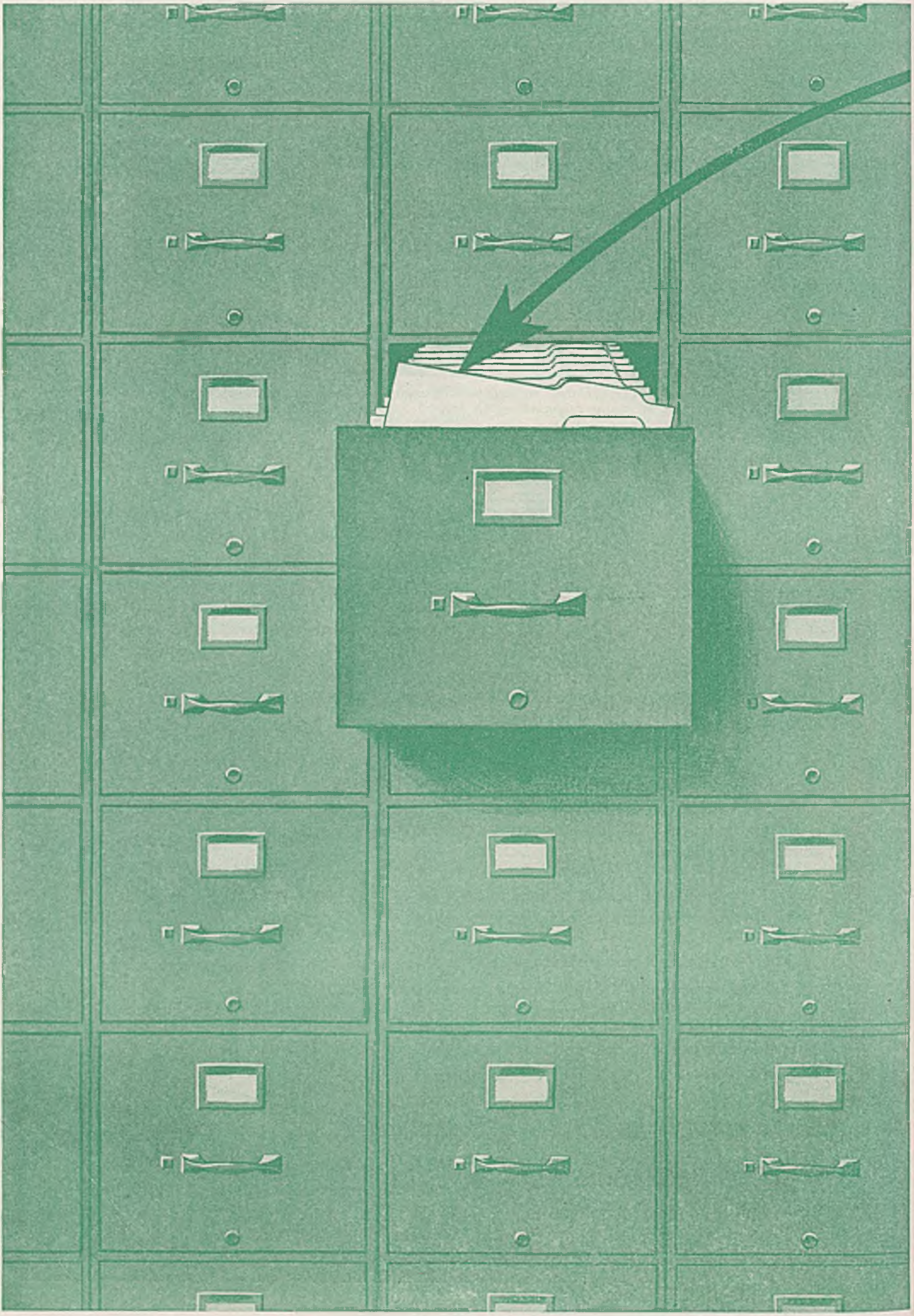
From the salt of the earth

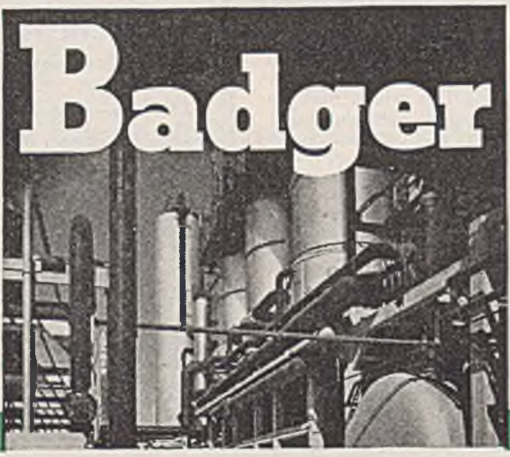
HOOKER
CHEMICALS

HOOKER ELECTROCHEMICAL COMPANY

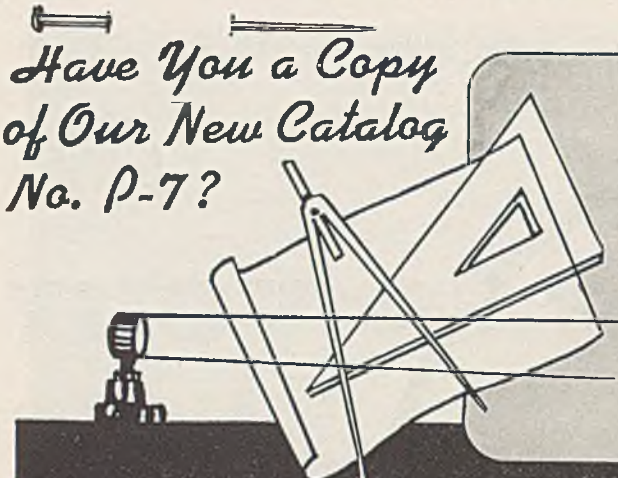
9 FORTY-SEVENTH ST., NIAGARA FALLS, N. Y.
New York, N.Y. Wilmington, Calif. Tacoma, Wash.

Caustic Soda Paradichlorbenzene Muriatic Acid Chlorine Sodium Sulfide Sodium Sulfhydrate




Badger

Have You a Copy of Our New Catalog No. P-7?



DEPENDABLE AUTOMATIC TANK GAUGE ACCURACY

"Right on the Beam"

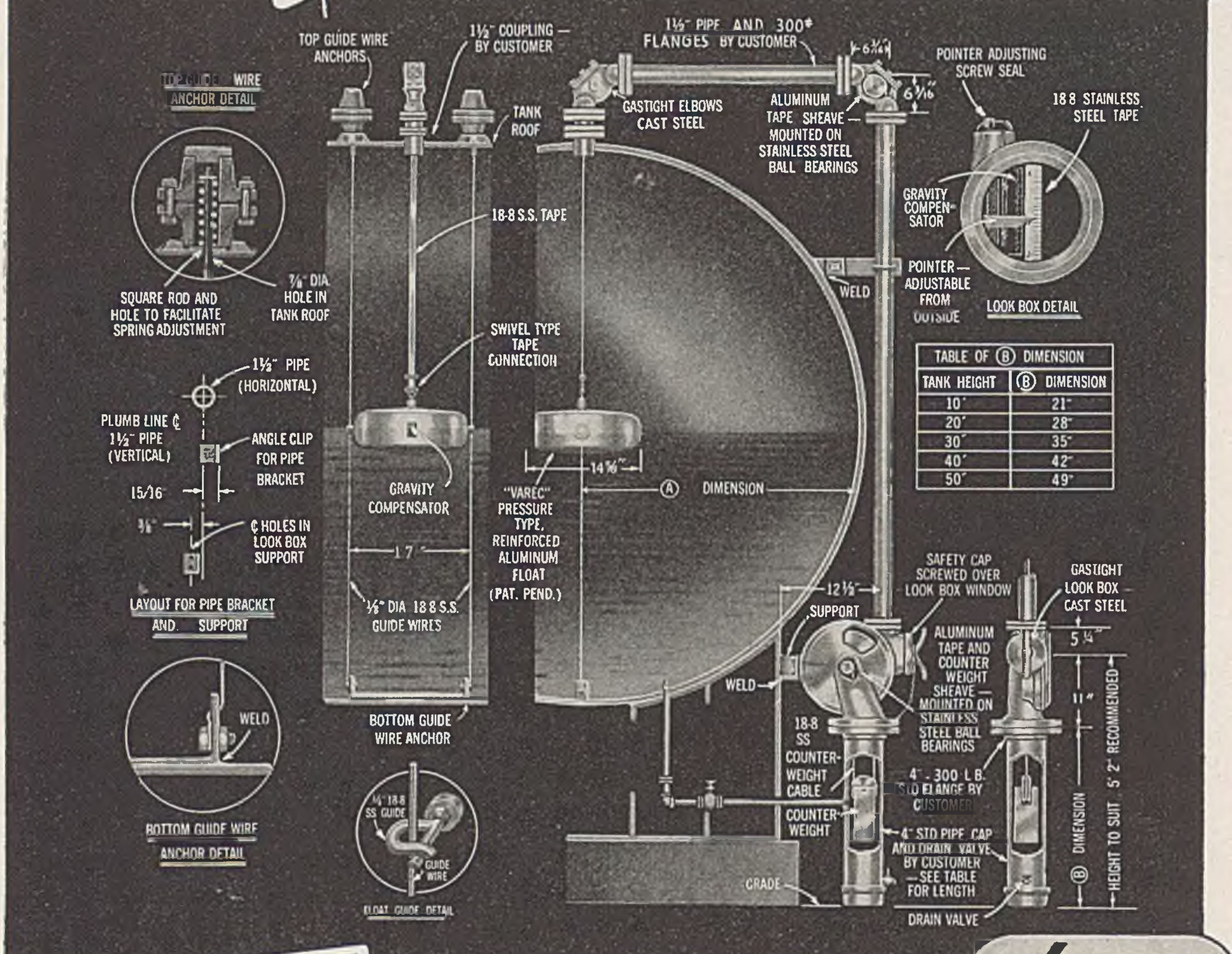


TABLE OF Ⓑ DIMENSION

TANK HEIGHT	Ⓑ DIMENSION
10'	21"
20'	28"
30'	35"
40'	42"
50'	49"

Free **WITH COMPLIMENTS OF "VAREC"**

Use "VAREC" Slide to obtain U.S. Standard dimensions for coarse and fine thread series, U.S, Standard (and other commercial sizes) Woodruff Keys, and American Standard Pipe Threads, plus decimal equivalents, millimeters into Inches, and other pertinent engineering data.

The Pace Setter Since 1928

Dependable Accuracy characterizes the extensive line of "VAREC" Approved Automatic Tank Gauges designed to operate from 0 to 300 P. S. I. on any type tank. Outstanding basic features are the Look Box which may be read from near ground level or from top of tank, aluminum tape sheaves mounted on stainless steel ball bearings, floats of various materials designed for specific pressures, and simplicity of installation and operation. Tape, guide wires, and counterweight cable are 18-8 stainless steel as standard. Look Boxes are equipped with adjustable indicator, window wiper and gravity compensator, enabling the gauger to compensate at the Look Box for any difference in buoyancy of the float due to changes of liquid contents. This exclusive patented "VAREC" feature permits immediate, accurate reading of liquid level directly from the tape.

THE VAPOR RECOVERY SYSTEMS COMPANY
COMPTON • CALIFORNIA, U.S.A.

NEW YORK CITY • CHICAGO, ILL. • CLEVELAND, OHIO
HOUSTON, TEX. • TULSA, OKLA. • AGENCIES EVERYWHERE
CABLE ADDRESS VAREC-COMPTON (ALL CODES)

✓ "VAREC" Equipment is approved by:

Underwriters' Laboratories,
Associated Factory Mutuals' Laboratories
U. S. Treasury Department
U. S. Coast Guard
American Bureau of Shipping
Lloyd's Register U. S. Navy
U. S. Army Engineers

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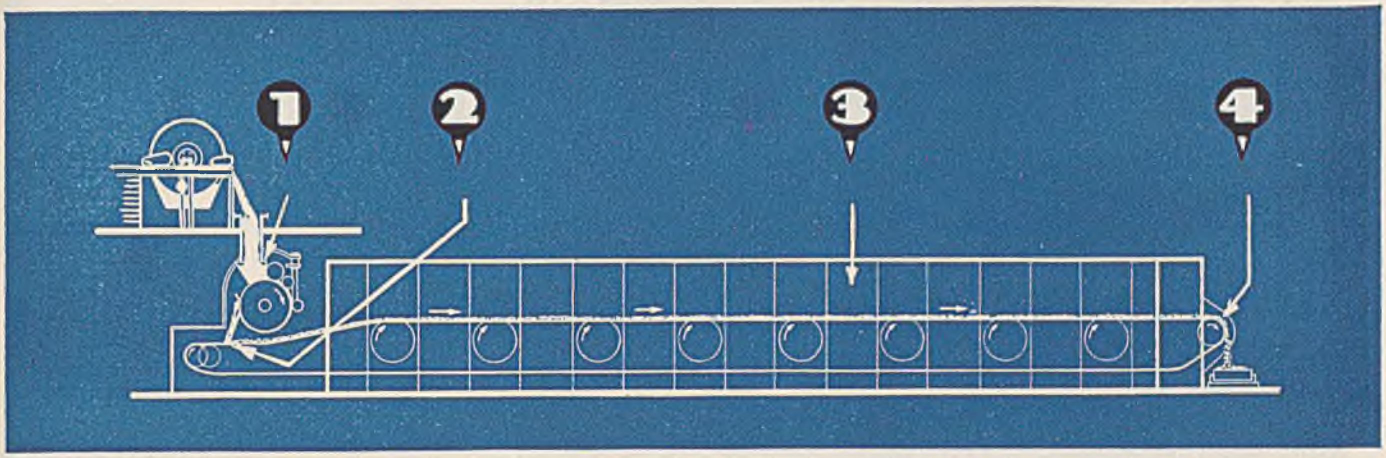
Depending upon which is the governing authority.

Magnesium carbonate dried from moisture content of 565%* (B.D.W.B.) to 1.0% in 29 minutes



This means 5.65 lbs of water per 1.0 lb. dry material

in PROCTOR CONTINUOUS CONVEYOR SYSTEM

In one typical installation of a Proctor individually designed continuous conveyor system, for use in drying magnesium carbonate, here is what takes place: ① Material with moisture content of 565% (B.D.W.B.*) is delivered to pre-forming feed of dryer, from a continuous filter. ② Coming to the hopper of the fin drum feed in this highly moist state, the material is pressed into the grooved surface of an internally heated, revolving fin drum. On this drum, the material is dried sufficiently to be discharged to the conveyor of the continuous dryer, in the form of small sticks of uniform thickness. ③ Loaded to uniform depth on the moving conveyor, the material is conveyed through the drying chambers where heated air at 290°F. is circulated *through* the bed of magnesium carbonate. By forming the material into small, uniform shapes, more rapid diffusion is possible, which accounts for rapid drying and uniformity. ④ After only 29 minutes of drying time, magnesium carbonate, uniformly dried to a moisture content of 1.0% (B.D.W B.), is discharged from the dryer at the rate of 500 pounds (C.D.W.†) per hour

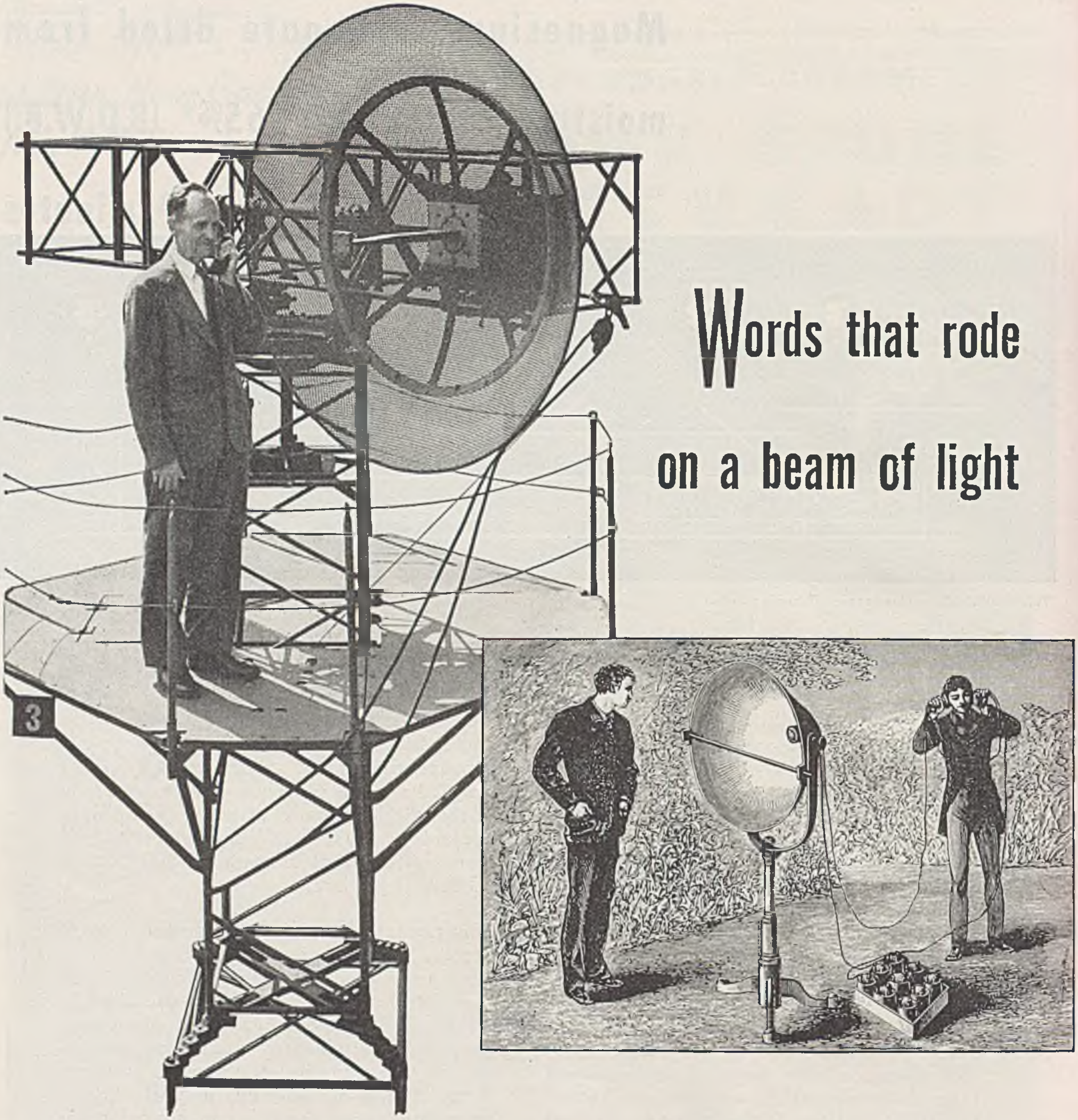
This particular application for one type of Proctor pre-forming feed, combined with a continuous conveyor dryer, illustrates just one installation. These systems are literally tailor-made to meet individual plant and product requirements . . after careful research and study into the specific problem. If the drying of wet-solids is part of your operation, it will pay you to have Proctor engineers consider your problem. Write today.

†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.



Words that rode on a beam of light

If Alexander Graham Bell could look at the microwave antenna in the illustration, how quickly his mind would go back to his own experiments, 67 years ago!

For in 1880 the inventor of the telephone had another new idea. Speech could be carried by electric wires, as Bell had demonstrated to the world. Could it be carried also by a *light beam?*

He got together apparatus—a telephone transmitter, a parabolic reflector, a selenium cell connected to handphones—and "threw" a voice across several hundred yards by waves of visible light, electromagnetic waves of high frequency.

Bell's early experiment with the parabolic antenna and the use of light beams as carriers was for many years only a scientific novelty. His *idea* was far ahead of its time.

Sixty years later communication by means of a beam of radiation was achieved in a new form—beamed microwave radio. It was developed by Bell Telephone Laboratories for military communication and found important use in the European theater. In the Bell System it is giving service between places on the mainland and nearby islands and soon such beams will be put to work in the radio relay.

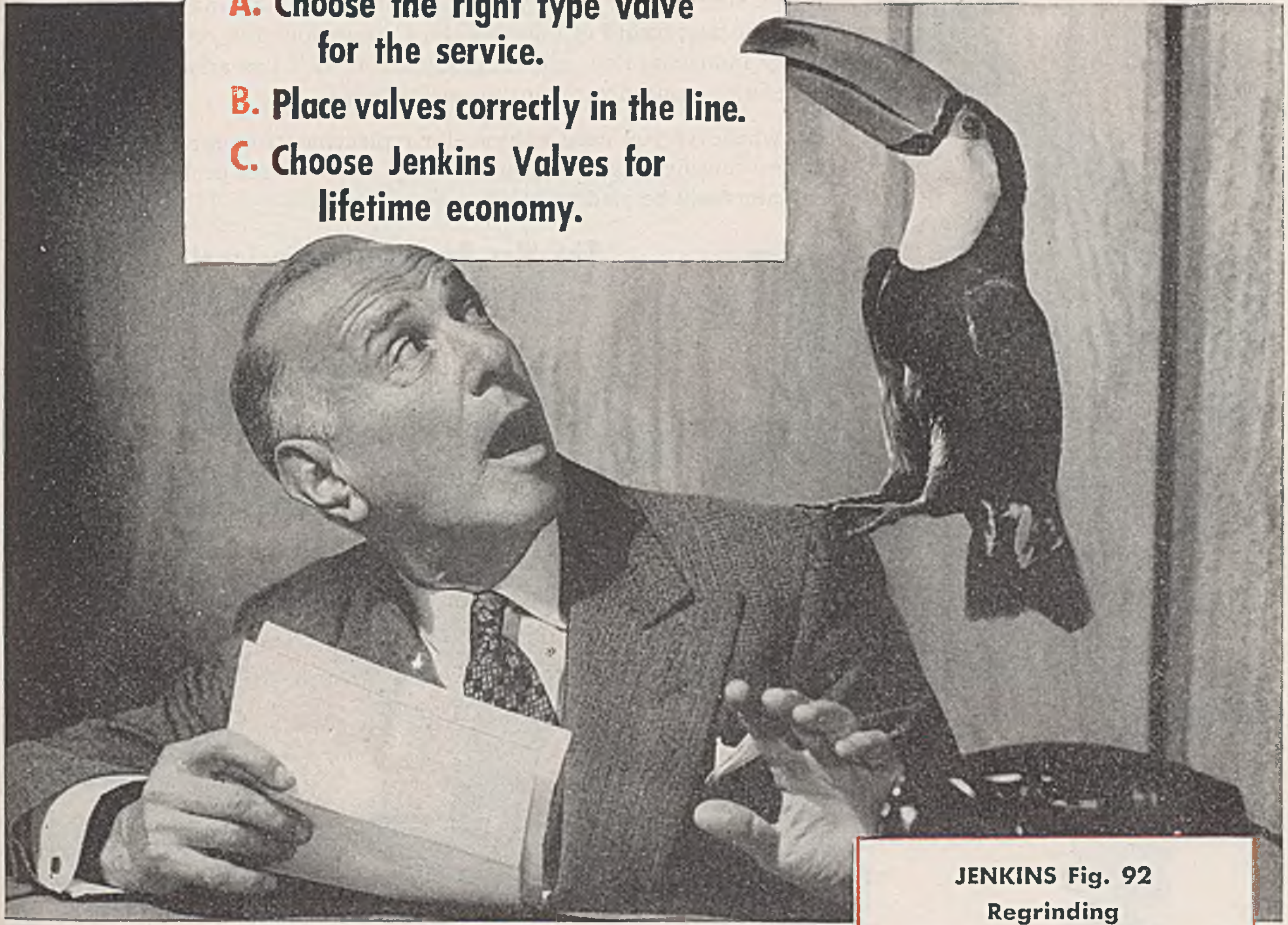
In retrospect, Bell's experiment illustrates once again the inquiring spirit of the Bell System.

BELL TELEPHONE LABORATORIES

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

It's Simple to avoid a Big Bill for valve upkeep!

A. Choose the right type valve for the service.
B. Place valves correctly in the line.
C. Choose Jenkins Valves for lifetime economy.



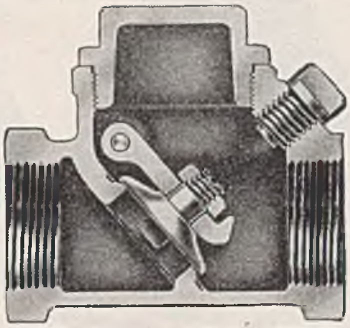
THESE three, simple, basic rules, plus intelligent treatment and care of valves, are paying extra dividends in valve economy to more and more valve users in every industry.

By choosing Jenkins Valves, you get not only valves made with extra endurance that means extra economy, but also expert advice of top-rated valve specialists, Jenkins engineers, on any question of valve selection or placement for any service.

Base your valve buying on this ABC formula for *lowest cost in the long run.*

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

JENKINS Fig. 92
Regrinding
BRONZE SWING CHECK VALVE



125 lbs. Steam 250 lbs. O.W.G.

Designed for service on non-return control systems; especially with Gate Valves, where a comparable full, free flow of steam, oil, water, or gas is required. It is also widely used for condensate and return lines. The high tensile bronze disc is carefully machined to a smooth, tight-fitting finish, can be reground easily without removing valve from line.

ONE OF OVER 600 *EXTRA VALUE* VALVES MADE BY JENKINS *VALVE SPECIALISTS*

LOOK FOR THIS DIAMOND MARK

TRADE JENKINS MARK

SINCE 1864

Jenkins Bros

JENKINS VALVES

Types, Sizes, Pressures, Metals for Every Need

Sold Through Reliable Industrial Distributors Everywhere

Let's look at the Record!

As we start on our 101st year of making valves for industry, we feel that the past record of Powell Valves throughout 100 years of meeting *every* industrial flow control requirement as it has arisen constitutes a definite assurance of future performance.

So, whenever you need valves—for replacements or for new installations—consult Powell. If you have any flow control problems, Powell engineers will be glad to help you solve them.

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

Catalogs on request. Kindly state whether you are chiefly interested in Bronze, Iron, Cast Steel, or Corrosion-Resistant Valves.

Fig. 2051—150-pound Stainless Steel "Y" Valve. Has flanged ends, bolted flanged yoke, outside screw rising stem and plug type disc.

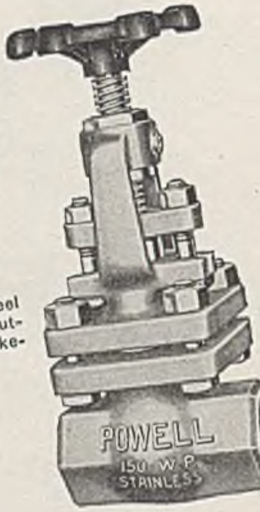


Fig. 1978—150-pound Stainless Steel Globe Valve with screwed ends, outside screw rising stem, bolted yoke-bonnet, and plug-type disc.

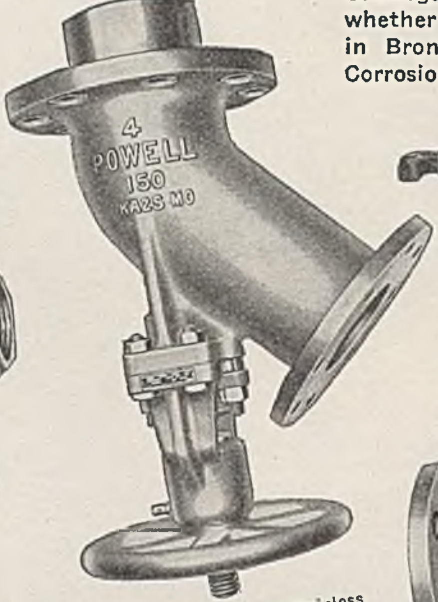


Fig. 2309—150-pound Stainless Steel Flush bottom Tank Valve, for attaching to metal tanks and autoclaves. In this design, disc rises into tank to open valve.

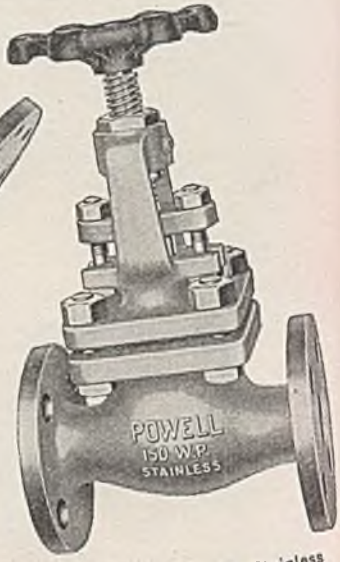


Fig. 1969—150-pound Stainless Steel Gate Valve. Has flanged ends, outside screw rising stem, bolted flanged yoke-bonnet and taper wedge solid disc.

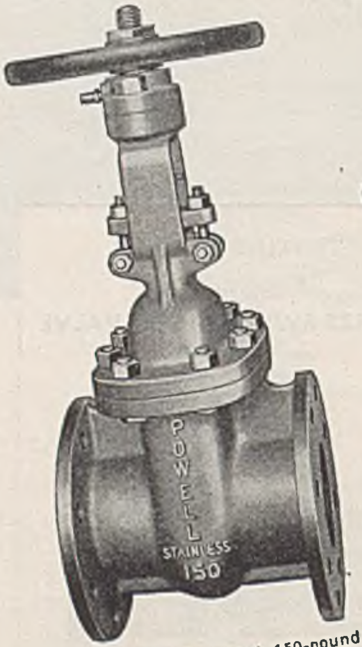


Fig. 2453 G—New Standard 150-pound Stainless Steel Gate Valve, with outside screw rising stem, bolted flanged yoke-bonnet and taper wedge solid disc.

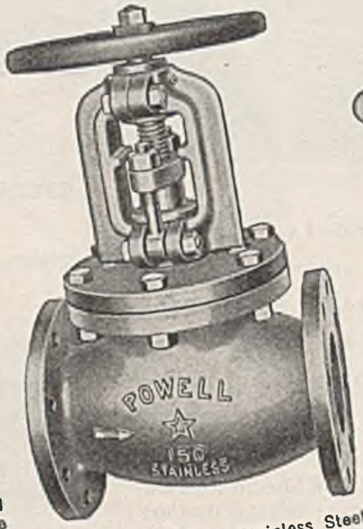
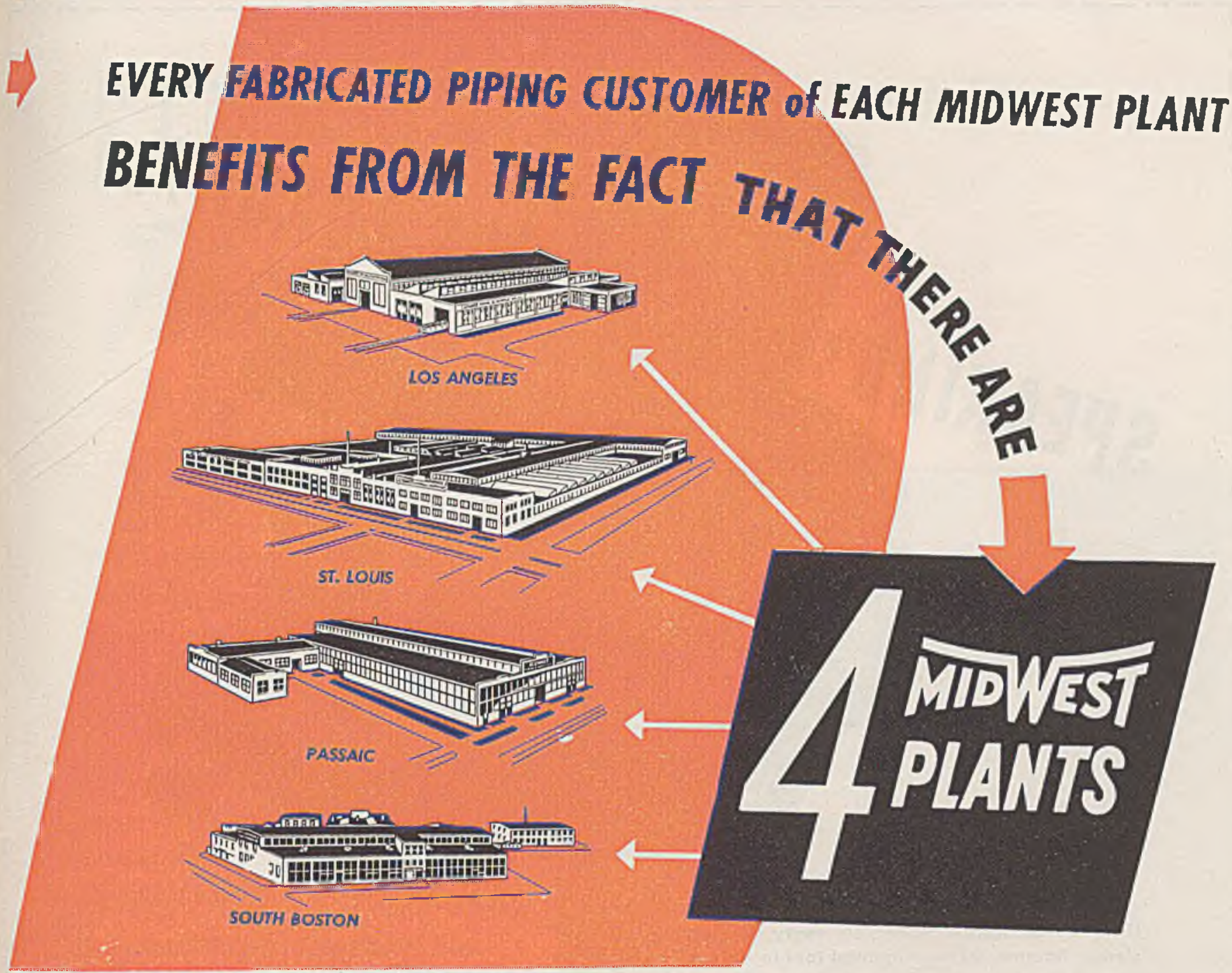


Fig. 2429—150-pound Stainless Steel O. S. & Y. Globe Valve. Has flanged ends and outside screw stem.

Fig. 1847—200-pound Stainless Steel Swing Check Valve. Screwed ends, screwed-on cap and regrindable, renewable disc.

POWELL VALVES



Strategically located in various parts of the country, all of the four Midwest plants are of definite benefit to every Midwest customer.

Undoubtedly the most important advantage is the better piping that results from the continuous exchange of information and experience between the four plants. For example, if Passaic develops a new and valuable technique or method, the information is made available at once to St. Louis, Los Angeles, and South Boston. When Los Angeles finds a better way to control grain size in forged lap joints, the other plants are immediately informed. Regardless of which plant fabricates your piping, you get the benefit of the combined experience of all four plants.

Other advantages are greater flexibility in meeting delivery requirements . . . a better understanding of regional conditions . . . source of supply close to the job.

Midwest is logically your first source of piping—whether you want a simple bend, a welded header, or a complete and complex piping job for a large plant fabricated and erected with undivided responsibility.

MIDWEST PIPING & SUPPLY COMPANY, INC.

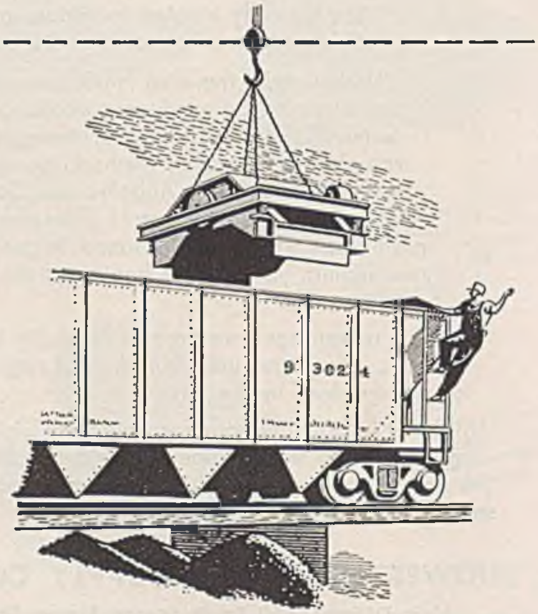
Main Office: 1450 South Second Street, St. Louis 4, Mo.

Plants: St. Louis, Passaic (N. J.) and Los Angeles • Subsidiary: Lumsden & Van Stone Co., South Boston 27, Mass. • Sales Offices: New York 7—30 Church St. • Chicago 3—645 Marquette Bldg. • Los Angeles 33—520 Anderson St. • Houston 2—229 Shell Bldg. • Tulsa 3—533 Mayo Bldg. • Atlanta 3—Red Rock Bldg. • South Boston 27—426 First St.

4 PLANTS ARE BETTER THAN 1

PIPING FABRICATORS AND CONTRACTORS


SPEAKING
OF LUXURY...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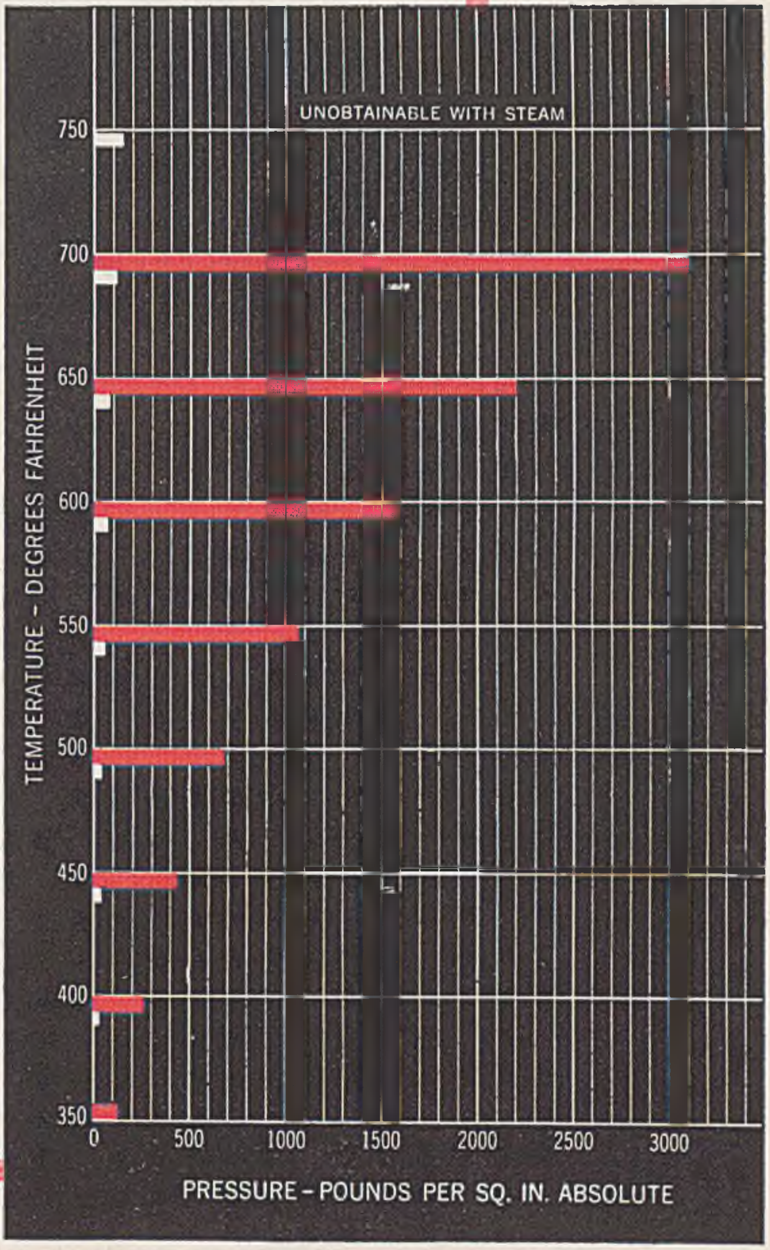
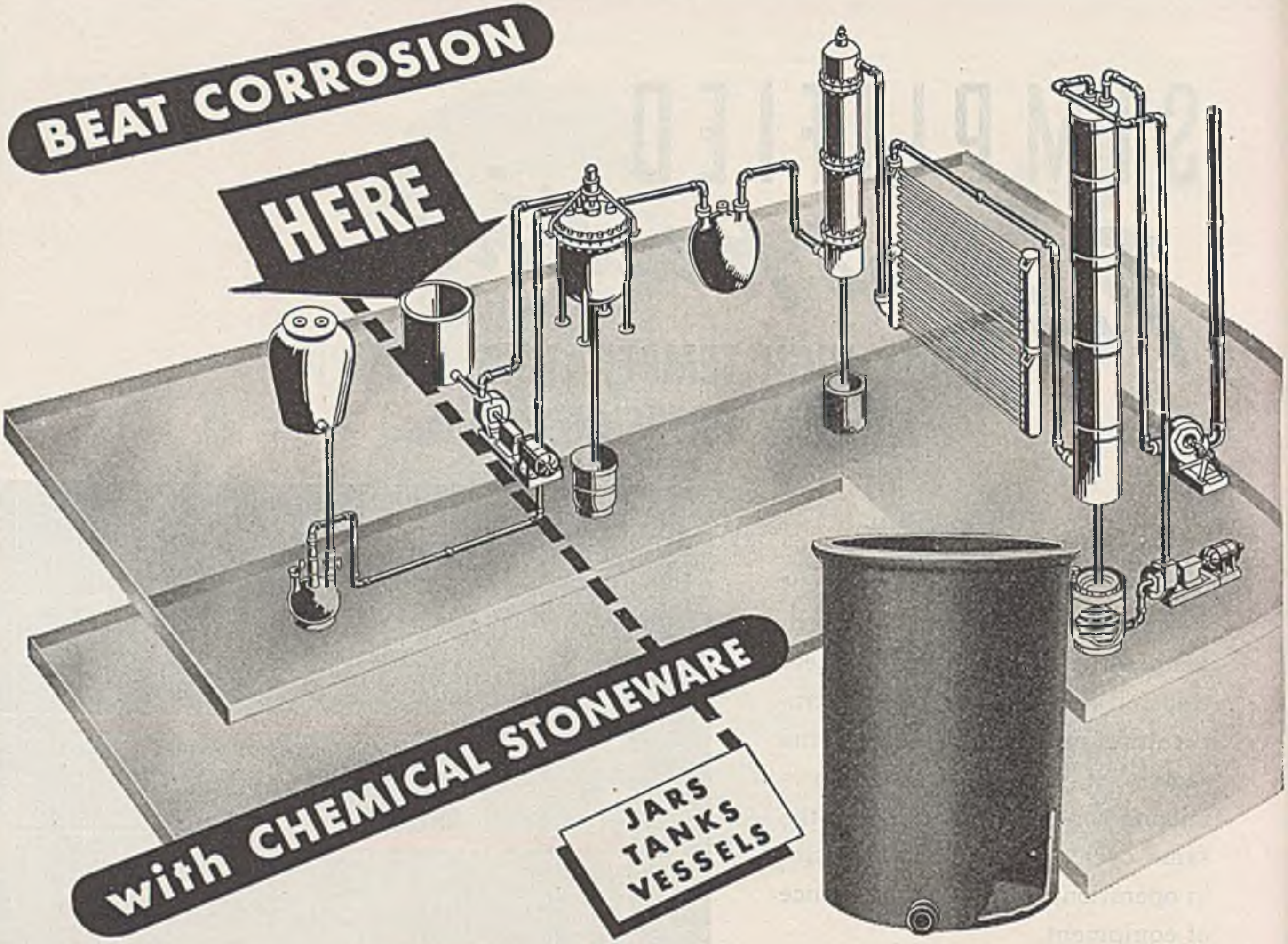

UNOBTAINABLE WITH STEAM
TEMPERATURE - DEGREES FAHRENHEIT
750
700
650
600
550
500
450
400
350
0
500
1000
1500
2000
2500
3000
PRESSURE - POUNDS PER SQ. IN. ABSOLUTE


BEAT CORROSION
HERE
with CHEMICAL STONEWARE
JARS
TANKS
VESSELS

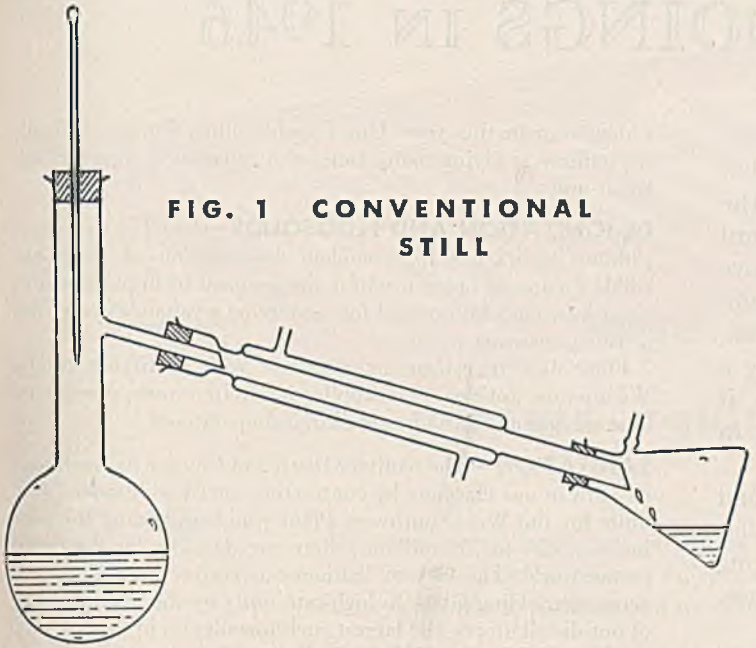


FIG. 1 CONVENTIONAL STILL

Which Still Do You Choose?

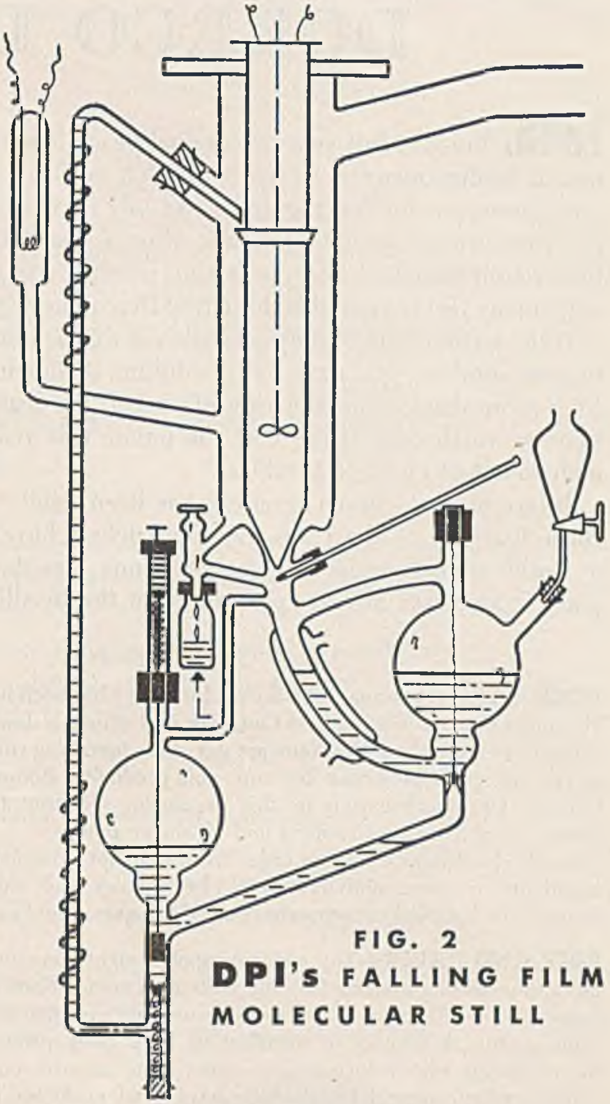


FIG. 2 DPI's FALLING FILM MOLECULAR STILL

FOR COMPLETE RESEARCH YOU NEED BOTH!

The ordinary still (fig. 1) is a handy laboratory tool. It does many jobs well. But as you know, it has definite limits.

DPI's Falling Film Molecular Still (fig. 2) takes over at the point where ordinary distillation methods stop. Molecular distillation—short-path distillation in exceptionally high vacuum—makes it possible for you to fractionate many substances "undistillable" by earlier methods. In general, these substances include natural and synthetic materials which are in a liquid state above 80° C, have low vapor pressures, and whose molecular weights are over 300.

Any laboratory concerned with investigative and preparative work in chemistry today should find the Falling Film Molecular Still—or other DPI laboratory-scale molecular stills—an indispensable aid.

For detailed information on how molecular distillation might aid in your research, we invite your letter telling us your needs or problems. DPI men who have pioneered in high-vacuum techniques will give careful consideration to your request.

DISTILLATION PRODUCTS, INC.

745 RIDGE ROAD WEST, ROCHESTER 13, NEW YORK

Pioneering in Molecular Distillation and High Vacuum Research

TEAR OFF HERE

REMINDER

For information about molecular stills, write to:

DISTILLATION PRODUCTS, INC.

745 Ridge Road West
Rochester 13,
New York

DORRCO DOINGS IN 1946

1946, the first full year of nominal peace, has been one of readjustment. It started with high hopes of that great peace production the world so badly needed. The pressure groups brought set-back after set-back until production was shot; and the Nation rebelled and gave what many feel is a mandate for a free Democracy again.

If the termination of the coal strike, as this is written, proves another sign that the pendulum is starting a long swing back from the rule of special privilege, it may be worth what it has cost the public this year in man-days lost by labor troubles.

Internationally much progress has been made; and those listening to the United Nations debate have felt a world education in Human Relations was taking place, which was not so apparent from the headlines.

* * *

GOLD—A broad resurgance in the gold industry has been noted. The most notable instance is a Canadian mill which is doubling capacity to more than 4000 tons per day, thus becoming runner-up to the great Hollinger for top, gold-producing honors in Canada. Our contribution to this expansion—18 tray thickeners, 20 agitators, 3 classifiers and 18 sludge pumps.

In the Philippines, a large order from Benguet Consolidated highlights renewed activity there. In Mexico and Central America, increased silver prices have acted as a spur to gold as well.

PULP AND PAPER—This year we supplied eight new continuous recausticizing systems for pulp mills with an aggregate daily capacity of 2500 tons and are modernizing old systems at four other plants. A number of installations have been made, too, for producing satisfactory process water from impure sources.

Two rather unusual installations have been made for black ash treatment. In one, black ash is to be leached and washed continuously for soda recovery prior to recausticizing. In the other, the carbon residue is to be washed, after acid treatment, preparatory to activation.

SAND—Many new classifiers indicate the trend towards well-washed, high-specification sand. Three 250 ft. dia. thickeners, in a single long basin, will recover wash water for re-use in West Virginia and will be the largest thickener installation in the East.

CEMENT—Renewed activity everywhere is evident. Four new American plants have adopted our closed-circuit grinding system on the raw end with at least two more to follow. Additional systems are being supplied to cement makers in China, Colombia, Chile and Panama.

CHEMICALS AND PLANT ENGINEERING—The large number of brine purification jobs reflects the continued heavy demand for chlorine and caustic soda. Largest clariflocculator to date is a 125 ft. unit in Texas, to treat upwards of 2000 gals. per min.

Testing and plant engineering hit an all-time peak. Three types of projects predominated: the treatment of nickel ores by the Caron process for South America and the East Indies; alumina projects for the United States, Russia and Australia; and chemical fertilizer plants for this country and England.

SUGAR—Enforced lack of maintenance during the war has made modernization a keynote this year. Cane sugar has shown an unprecedented demand for continuous juice clarifiers and vacuum mud filters. New cane varieties have created new clarification problems. This year we built the largest clarifier in our history

Most of the tonnage of beet sugar in the United States is made by our Continuous Carbonation System, several new units of which went in this year. Our Rapid-Cooling, Rotary, Lafeuille Crystallizer is giving many times the capacity of conventional batch units.

DE-IONIZATION AND FLUOSOLIDS—Our D-I System, in addition to its use for complete de-ionization of water and edible syrups, is being used for the removal of impurities from sugar-bearing solutions and for recovering a valuable syrup from a fruit processing waste.

FluoSolids investigations continue with gratifying results. We are now working on its application to limestone, precipitated lime sludges and various metallurgical operations.

SANITATION—The Sanitary District of Chicago has reaffirmed its faith in our clarifiers by contracting for 24 additional 126 ft. units for the West-Southwest Plant which will bring the nominal capacity to 700 million gallons per day—by far the largest in the world. The City of Baltimore is converting 18 of its 30 acres of trickling filters to high-rate units by the addition of 30 of our distributors—the largest such installation in this country. The Cities of Savannah, Georgia; Dallas, Texas; and Long Beach, California are typical of other large cities which we have served this year.

In Puerto Rico we are supplying equipment and erection supervision for 10 new sewage plants and for the new water treatment plant of the City of San Juan. At Jackson, Michigan, extensive field tests are demonstrating conclusively the economy and efficiency of the shallow-bed, trickling filters, which we have advocated, as compared with deep-bed types.

ABROAD—Our associated companies, especially in England, are going strong and the Continent is coming back fast. With the necessary equipment or services supplied either from Europe or America, we have been active in Europe, Asia, South America and Africa—largely in petroleum, sewage, potash, paper, cement, coal, copper and gold.

* * *

The industrial unrest and unbalanced production have given us great problems to meet. Like many others in both consumer and durable goods industries, we shall end this year with greatly enlarged unfilled orders due to the lack of labor, material and shipping facilities for export.

A month in Germany last Summer emphasized the problems faced there, and attendance at a quadripartite session brought home, as no words could, the difficulties of international relations and the great efforts being made by all to solve them. The almost infinite patience needed, I believe, is there.

Members of our staff, who have been scattered in Europe, Asia and South America this year, are united in feeling much progress is being made. To our friends and to the Dorr staff everywhere, we send New Year's greetings with the belief that the year 1947 will see a crystallization of the efforts that have been made and a clearer course charted for a United World.

John V. N. Dorr

570 Lexington Ave., New York 22

DORRCO

ANOTHER edge moor achievement in process equipment fabrication

This Edge Moor horizontal autoclave with quick-opening door is *another* Edge Moor achievement in process equipment fabrication . . . a direct result of Edge Moor experience, facilities and proficiency.

Edge Moor is equipped to furnish *any type* of heavy-wall welded fabrication to your individual designs, specifications or requirements. Materials include:

- CARBON STEELS
- STAINLESS STEELS
- CLAD STEELS
- NICKEL STEELS
- MONEL
- HERCULOY
- HIGH CHROME
- 18-8 ALLOYS
- NICKEL
- INCONEL
- NICHROME
- EVERDUR

Edge Moor Shops have complete facilities for stress-relieving, annealing and X-ray . . . and are approved by leading insurance companies for fusion welding to meet all codes and tests. We shall be pleased to place our experience and facilities at your disposal when you are considering additional plant equipment. Write for literature *today*.

Edge Moor Iron Works, Inc. • Main Office and Works: Edge Moor, Delaware
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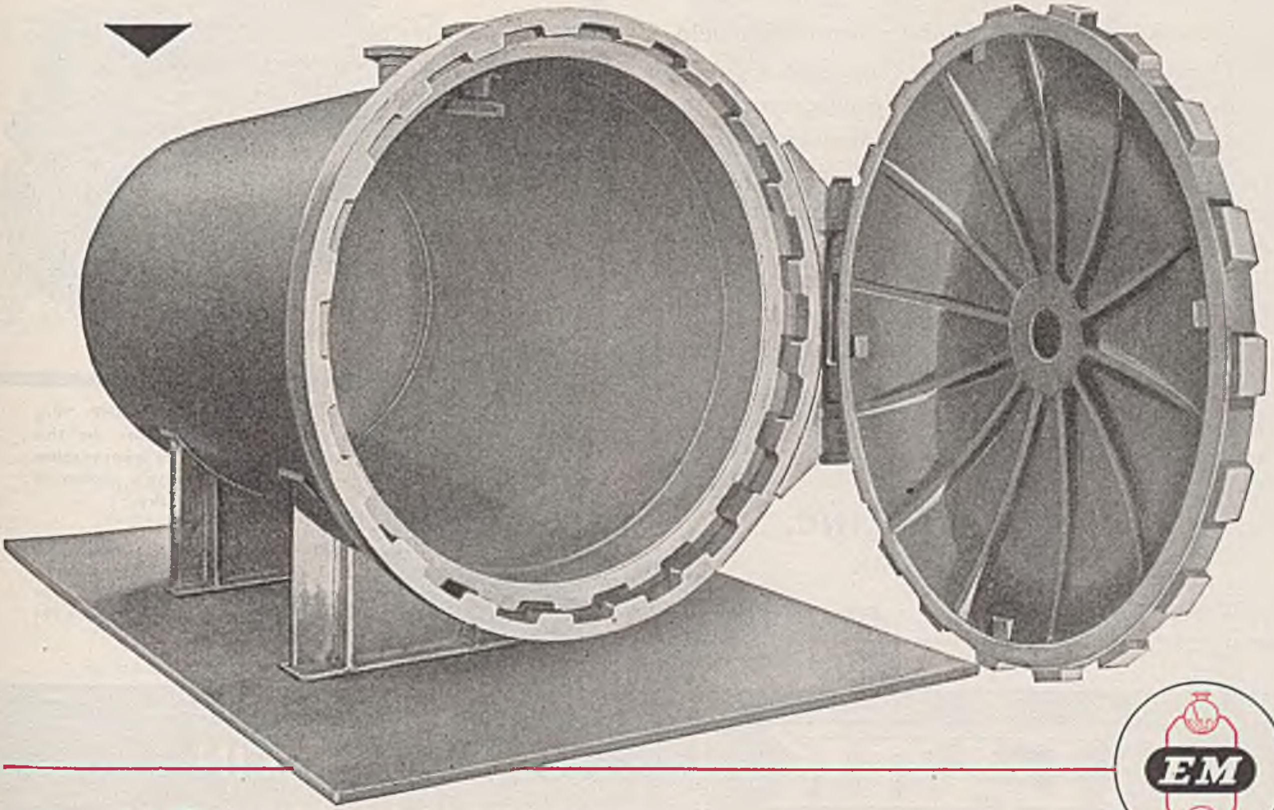
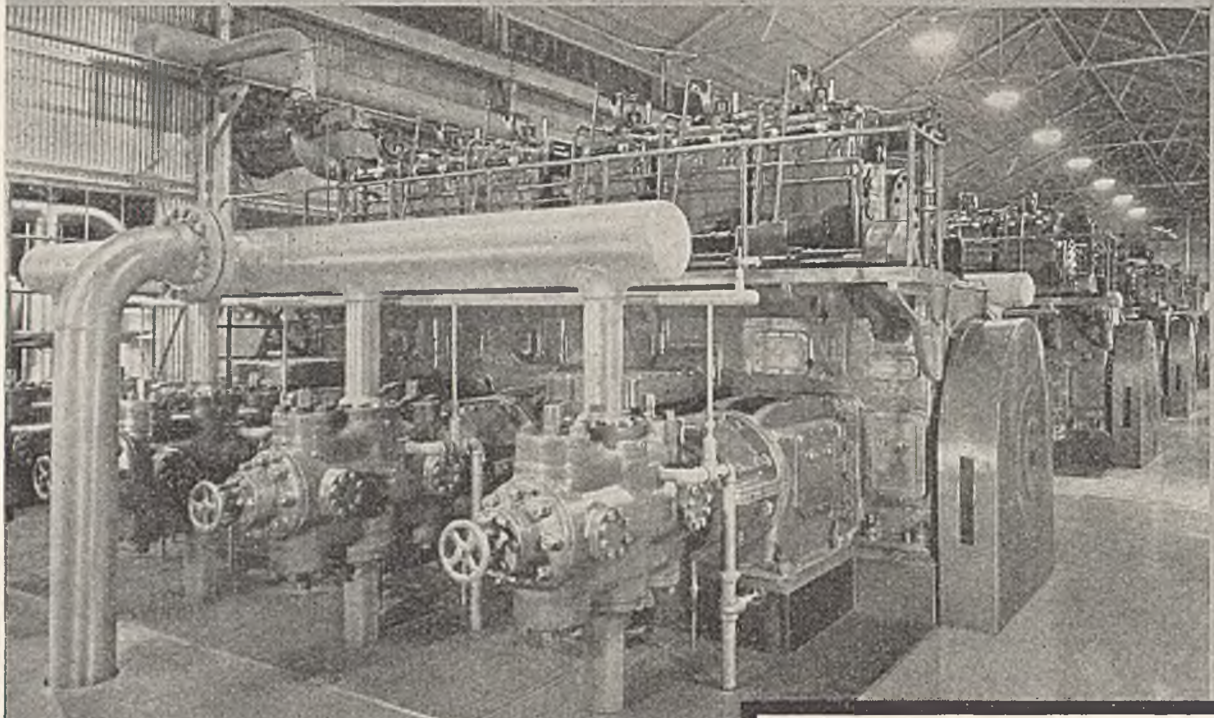


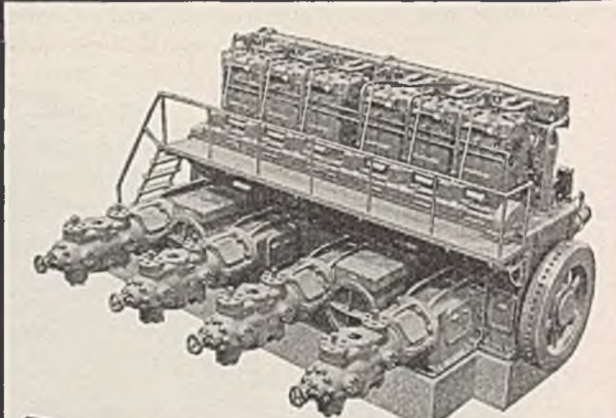
EM 1867

edge moor fabricators of process equipment

THE CLARK "BIG ANGLE"

Most horsepower per unit of space





● This is the king of the heavy-duty compressor field, the new Clark BA-17 Right Angle Compressor.

The BA-17 represents the highest development of the long line of Clark 2-Cycle gas-engine-driven compressors. It was designed to fill the need for greater economy in high pressure pipe line pumping and large scale pressure maintenance.

It doubles the horsepower per cylinder previously available in gas-engine-driven compressors—200 BHP instead of 100 BHP—the most compact, heavy-duty compressor ever built.

This results in much lower foundation and building costs and lower maintenance costs.

CLARK BROS. CO., INC.
OLEAN, NEW YORK

New York • Tulsa • Houston • Chicago • Boston • Washington
Los Angeles • London • Buenos Aires • Caracas, Venezuela

The Clark "Big Angle" BA-17

A GAS-ENGINE DRIVEN COMPRESSOR DELIVERING 200 BHP PER CYLINDER

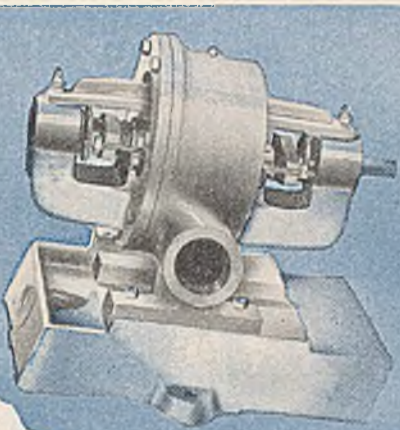
(Above) Clark 1200-BHP "Big Angle" Compressors in the Tennessee Gas and Transmission Pipe Line Company's station at Winchester, Kentucky.

•

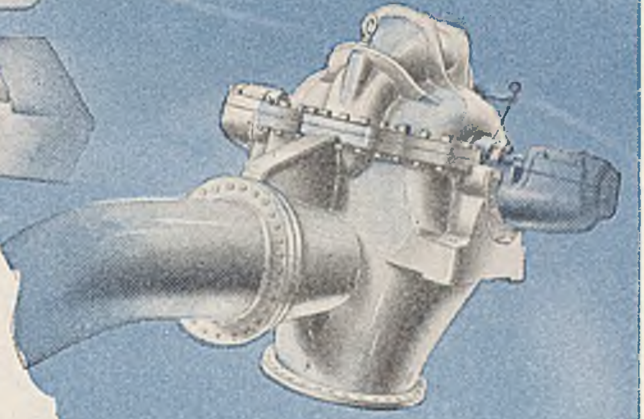
For complete specifications and data on the BA-17, including typical installation design for modern pipe line station, ask for Catalog BA-17.

CLARK
ONE OF THE DRESSER INDUSTRIES

SETS THE PACE IN COMPRESSOR PROGRESS



Westco Turbine Pumps



Fairbanks-Morse Centrifugal Pumps

How much does it cost to make a Pump?

It costs a lot of money to make any pump—especially if you want to be a leader, not a follower, and to build a pump so efficient, so dependable that it will be second to none.

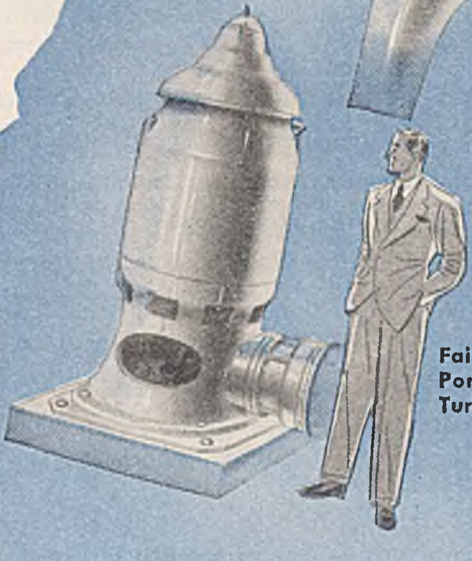
You pay the expense of maintaining well-staffed laboratories for product investigation and research—for continuous search for high efficiencies, better applications—and for the thorough testing of your finished product.

You pay the expense of providing production facilities and techniques; you pay for new materials, new methods which, with the cost-reducing benefits of mass production, assure your customers of greatest satisfaction.

Finally, you've the problem of making it easy for your customers to reach you for sales, service and consultation; you must network the country with distribution centers manned by experts.

Yes, all this costs a lot of money. No wonder, then, that there are so few pump manufacturers with this valued background. Among them, Fairbanks-Morse is an unquestioned leader in all phases of liquid-moving service . . . For all pumping problems, first see your Fairbanks-Morse dealer or call at the nearest Fairbanks-Morse branch office.

Fairbanks-Morse Propeller Pumps



Fairbanks-Morse and Pomona Deepwell Turbine Pumps

FAIRBANKS-MORSE

A name worth remembering

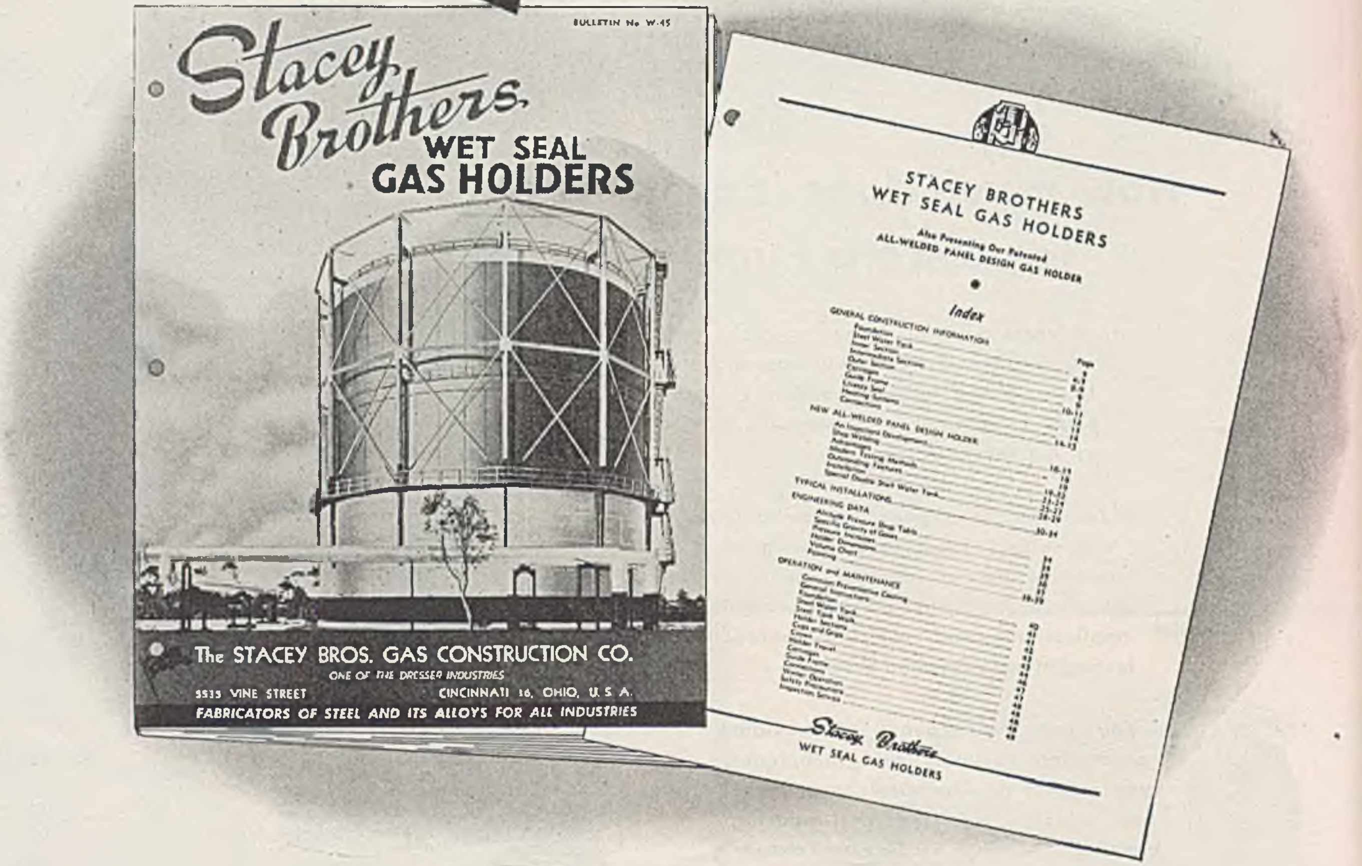
DIESEL LOCOMOTIVES • DIESEL ENGINES • MAGNETOS • GENERATORS • MOTORS • PUMPS
SCALES • STOKERS • RAILROAD MOTOR CARS and STANDPIPES • FARM EQUIPMENT

NOW

you can get

COMPLETE INFORMATION

in this one 52-page book



BULLETIN No. W-45

Stacey Brothers
WET SEAL
GAS HOLDERS

The STACEY BROS. GAS CONSTRUCTION CO.
ONE OF THE DRESSER INDUSTRIES
5535 VINE STREET CINCINNATI 16, OHIO, U. S. A.
FABRICATORS OF STEEL AND ITS ALLOYS FOR ALL INDUSTRIES

STACEY BROTHERS
WET SEAL GAS HOLDERS
Also Presenting Our Patented
ALL-WELDED PANEL DESIGN GAS HOLDER

Index

Stacey Brothers
WET SEAL GAS HOLDERS

If you need additional gas-holder capacity—or if you now operate a wet seal holder—*you can't afford to be without this book.*

In it, you'll find detailed construction information, plus operation and maintenance hints—and a wealth of important engineering data.

One complete section is devoted to the famous patented Stacey Brothers All-Welded Panel Design Gas Holder—the most important single construction advance in more than a generation. You'll get *all* the facts—based on our experience in building over 60,000,000 cu. ft. of all-welded capacity.

Your copy of this valuable book will be mailed to you without obligation. Simply write us on your company letterhead, stating the types and capacities of holders you now operate—or plan to install.

STACEY BROTHERS GAS CONSTRUCTION CO.
One of the Dresser Industries
5535 VINE STREET • CINCINNATI 16, OHIO

Stacey Brothers
ALL-WELDED GAS HOLDERS

WESTVACO QUALITY

U.S.I.

REVERE
COPPER AND BRASS INCORPORATED

General Mills, Inc.

GENERAL ELECTRIC

WESTINGHOUSE

Westinghouse

FINE HEYDEN CHEMICALS

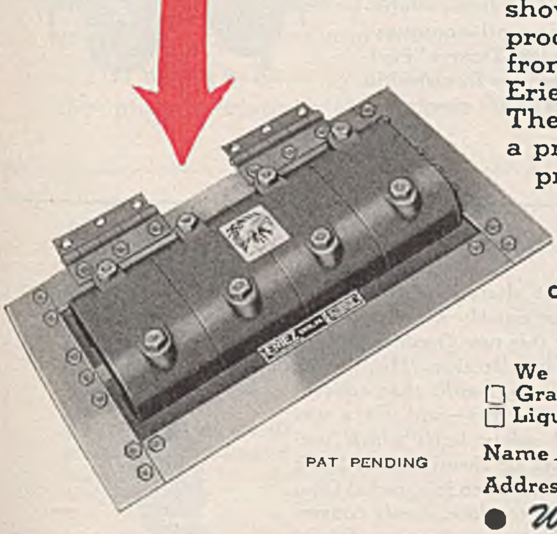
ARMOUR STAR

REPUBLIC STEEL
REG. U.S. PAT. OFF.

More Eriez Protected Marks of Quality!

THE TRAMP IRON MENACE IS ELIMINATED
BY ERIEZ *Non-Electric Permanent* MAGNETS!

AGAIN Eriez *Non-Electric Permanent* Magnets prove their worth among the leaders in the processing industries . . . The well-known marks of quality in chemical processing shown above, represent but a few of the hundreds of industrial processors who have licked the problem of tramp iron removal from their processing lines by installing the type and size Eriez Magnets best suited to their production requirements. These Eriez installations are writing off their cost and showing a profit. They eliminate fire hazards from tramp iron sparks, protect products from contamination, and prevent costly machinery damage and production shutdowns. Let us help you solve your tramp iron troubles. Clip and mail the coupon below, today.



PAT PENDING

CLIP AND MAIL TODAY

We are interested in removing tramp iron or ferrous particles from the following materials: ____

We would like to know more about installation of ERIEZ on: IEC-2

☐ Gravity Conveyors ☐ Mechanical Conveyors ☐ Pneumatic Conveyors
☐ Liquid Pipelines Magnetic Trap ☐ Equipment or Processing Machines

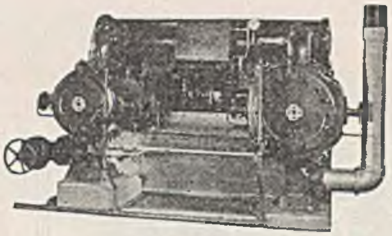
Name ____
Address ____ City ____ State ____

● *When It's Magnetic Protection . . . See Eriez First*

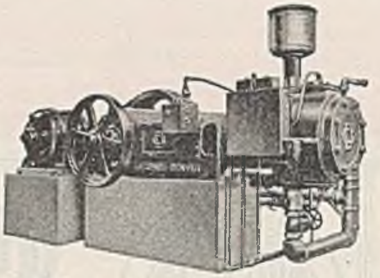
The above are but a few of the many hundreds of industrial companies who have Eriez Magnetic Protection.

Eriez
EAR' EEZ

ERIEZ MANUFACTURING CO.
116 EAST 12th ST. ERIE, PENNA.



The air cylinders in this Gardner-Denver "HA" Horizontal Compressor are especially designed for highest volumetric efficiency and lowest horsepower requirements. Its duoplate valves are cushioned for high delivery capacity, high compression efficiency and lowest power consumption. The class "HA" compressors are available in capacities from 316 to 2012 cubic feet displacement per minute.



Is dust a problem in your plant? This Gardner-Denver Class "RX" Horizontal Compressor is dustproof. And its special design permits complete water jacketing of all valves, air passages and cylinder heads to remove the heat of compression—increasing efficiency and cutting horsepower. The Class "RX" Horizontal Compressors are furnished in sizes from 89 to 1292 cubic feet displacement per minute.

shopping for **EXTRA** value?

To get your money's worth in air compressors, centrifugal pumps or concrete breakers, look for the *special* features that help you do a better job at less cost. Every Gardner-Denver product on this page has such features—and we'll gladly give you complete information about any one of them. Write Gardner-Denver Company, Quincy, Illinois.

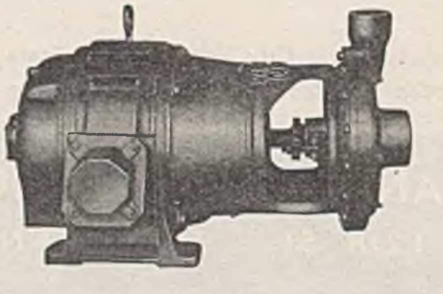
GARDNER-DENVER

SINCE 1859

In this Class "WB" 2-stage Vertical Compressor, Gardner-Denver engineers departed from conventional air compressor design to give you more volumetric efficiency with greater capacity. "WB" Compressors—furnished in capacities from 142 to 445 cubic feet displacement per minute—have efficiencies comparable to those of large horizontal compressors.

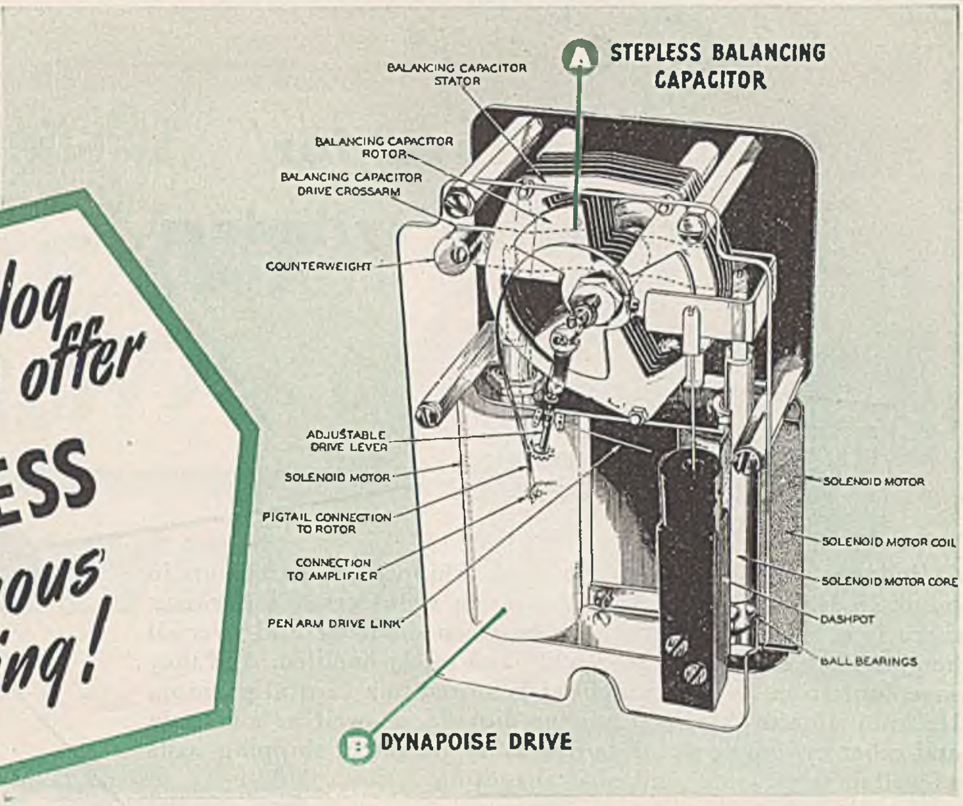
Here's a modern portable air compressor that's mighty handy to have around the plant! Complete water jacketing of its cylinders means dependable operation under constant load—cooler air—lubricating oil economy. Gardner-Denver "Portables" are furnished in sizes to suit every need.

In this Gardner-Denver Close Coupled Centrifugal, see how pump and motor are combined to form a complete, compact unit. These pumps can be installed in any position and are designed for capacities up to 250 gallons per minute, and heads up to 250 feet.



Plant alterations go forward more quickly when your men use this new Gardner-Denver Paving Breaker. The B87 is easier to handle than conventional types—and has a special safety latch which prevents air throttle from being opened when it is moved from place to place. Easily convertible to a sheeting driver.

Only Dynalog Instruments offer STEPLESS continuous balancing!



. . . AND HERE'S THE MEASURING UNIT THAT PRODUCES IT

Of all the unique improvements featured in the new *Foxboro Dynalog Controller*, the Dynapoise Balancing Unit is by far the most revolutionary. It is the heart of the Dynalog principle . . . providing electrical movement and stepless balancing in their simplest possible forms. Only motions of small magnitude are involved. There are no complicated, or delicate mechanisms to wear or get out of order. The unit is ruggedly constructed and thoroughly protected.

The new Foxboro Dynalog Controller offers the proven advantages of both the Foxboro Dynalog Recorder and the new M-40 Controller. It has the absolutely continuous sensitivity and instantaneous response of the Dynalog principle plus the dependably-accurate control feature of *Permaligned* Construction found in the M-40 Controller.

Investigate the advantages of this Dynalog Electronic Controller for processes in your plant. Resistance bulb controllers are available now . . . thermocouple type, soon. Write for Bulletin 397. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U. S. A.

A — STEPLESS BALANCING CAPACITOR . . . a simple, rotating variable air capacitor provides friction-free, completely continuous balancing. No slidewire – no moving or intermittent contacts.

High Sensitivity . . . permanent positive balancing action on bridge unbalances of less than 15 micro-volts.

B — DYNAPOISE DRIVE . . . a powerful, poised, double-solenoid type device, directly coupled to balancing capacitor, moving only when instrument is rebalancing. No rotating motor with reducing gears. No brushes or bearings.

The Dynapoise drive with its short stroke eliminates mechanical reduction and permits instantaneous response to changes in measured variable. No fast-moving parts to stop and start. Only six moving parts including all linkage and pen arm. Each solenoid core has 3 ball bearings at the bottom to minimize friction with sides.

HIGH BALANCING SPEED . . . 3 seconds for full travel of pen or pointer.

FOXBORO
REG. U. S. PAT. OFF.

ELECTRONIC INSTRUMENTATION

What to look for in choosing cylinders

design

Cylinders should be designed with the shippers' requirements in mind. In Hackney Anhydrous Ammonia Cylinders, for instance, there is a balanced relationship between diameter and over-all height. They can be easily, quickly and safely handled. And they save floor space as they can be safely stored in a vertical position. Hackney liquid chlorine, sulphur dioxide, as well as ammonia and other cylinders, are designed to assure lower shipping costs as well as faster, safer and easier handling.

light weight and strength

Strength and light weight should be balanced. One should not be sacrificed for the other. In Hackney Cylinders you are assured of a lightweight cylinder, yet one of adequate strength. This is made possible by the Hackney Deep Drawing Process, which assures uniform sidewall thickness and eliminates all excess material. Then, too, the physical qualities of Hackney Cylinders are improved by special heat-treating after complete fabrication.

appearance

While this feature may seem a factor of less importance in industrial selling, a wise shipper sees that his container reflects the high quality of his product. The Hackney Seamless Cylinder is handsome in appearance, for the cold drawing process results in a smooth, eye-appealing finish.

write for full details

Be sure to get the whole story on Hackney Seamless Cylinders. They are designed and constructed to give lowest transportation costs, full protection to product, ease of handling and ample resistance to transportation and handling abuse.

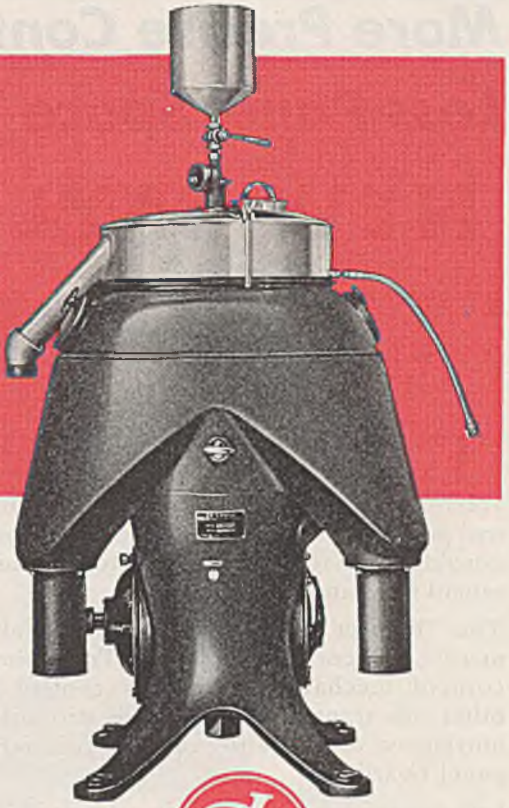
Hackney
MILWAUKEE

Pressed Steel Tank Company

Manufacturers of Hackney Products

Main Office and Plant: 1451 South 66th Street, Milwaukee 14
1313 Vanderbilt Concourse Bldg., New York 17
208 S. La Salle St., Room 2075, Chicago 4
558 Roosevelt Bldg., Los Angeles 14
213 Hanna Bldg., Cleveland 15

CONTAINERS FOR GASES, LIQUIDS AND SOLIDS



Now available for Refineries of

ONE CAR/DAY CAPACITY . . .

DE LAVAL

Engineered

SYSTEMS

DE LAVAL engineered systems for refining vegetable oil are now available for plants of one carload per day capacity. This is in addition to the refineries of from 2 to 24 carloads per day—or even more—announced previously.

De Laval systems are laid out in such a way that time-saving details, and exacting engineering standards, make possible higher yields of vegetable oil. They are, moreover, unusually free from trouble in operation.

The practical touch of the De Laval oil refining experts is exemplified in the way the systems are designed to occupy a minimum of floor space.

● Details will be sent on request.

Note these Features

1 Centralized Control permits addition of reagents, increase or decrease of capacities from one point. A single switch stops flow.

2 Oil and reagent pumps are driven by one electric motor.

3 Automatic flow controls are installed throughout the entire system.

4 System can be operated by one man who has time to spare for other duties.

5 Results are always uniform owing to precision control.

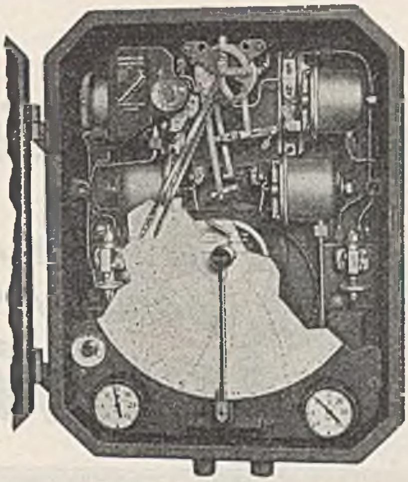
THE DE LAVAL SEPARATOR COMPANY
165 Broadway, New York 6 427 Randolph St., Chicago 6
DE LAVAL PACIFIC CO., 61 Beale St., San Francisco 19
THE DE LAVAL COMPANY, Limited
PETERBOROUGH
QUEBEC MONTREAL WINNIPEG VANCOUVER

DE LAVAL
SYSTEMS FOR REFINING VEGETABLE OIL

COMPLETELY ENGINEERED
SIMPLE TO OPERATE—

More Precise Control... Less Panel Space With

NEW TAYLOR "TRANSET"



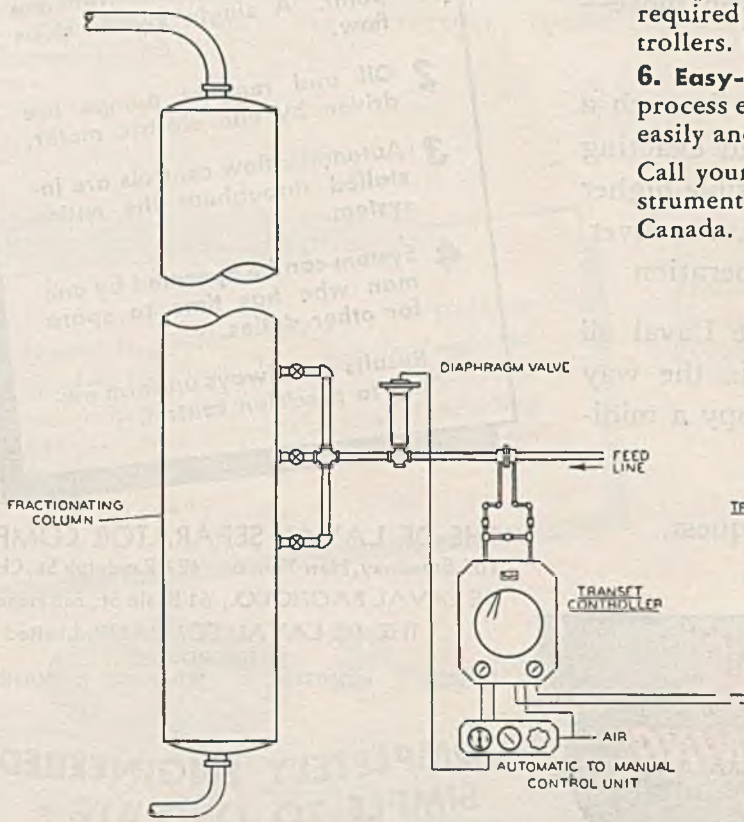
"TRANSET" is a new Pneumatic Transmission System particularly adapted to applications involving long lead lines between transmitter and control panel and where compactness of control panel is a consideration for the control of temperature, pressure, rate of flow, and liquid level.

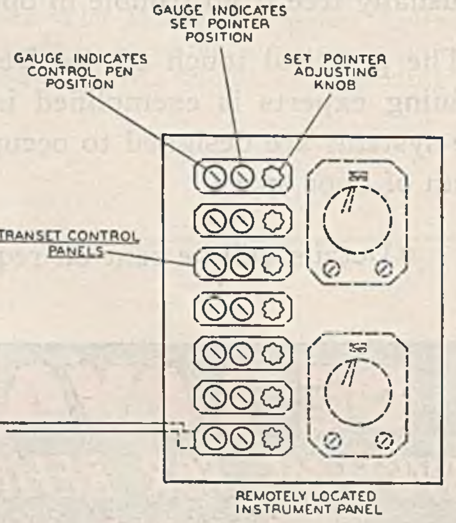
The "Transet" Controller is really a Fulscope Pneumatic-Set Recording Controller-Transmitter. Left hand control mechanism regulates control valve while other side transmits air pressure, proportional to pen movement, to indicating receiver remotely located on panel board.

Left gauge of receiver unit is calibrated in same units of measurement as controller chart and thus provides indication of controlled variable. Right gauge, connected in pneumatic-set line and calibrated in same units as controller chart, indicates set pointer position. Thus, when both pointers of the receiver unit coincide, the pen and set pointer of Transet will be together and process will be at desired control point. Here is what Transet gives you:

1. **More Precise Control:** Eliminates or greatly reduces time lag in the control circuit because Transet Controller can be at or near the point of measurement.
2. **Pneumatic Control at Its Best:** The simplicity and dependability of Taylor Fulscope air-operated controllers extended to remote pneumatic transmission.
3. **Field Tested and Time Proven:** No experiment; simply new combinations of standard control features.
4. **Standard Case Construction:** Contains controller, transmitter and pneumatic-set mechanisms. Also allows space for spring or explosion-proof electric chart drive.
5. **Less Expensive Panels and Control Rooms:** You can put *seven* Transet receiver units in same space required by *two* conventional recording receiver-controllers. (See sketch below.)
6. **Easy-To-Read Dials** on compact panels enable process engineer to check all related process variables easily and quickly.

Call your Taylor Field Engineer, or write Taylor Instrument Companies, Rochester, N. Y., or Toronto, Canada.

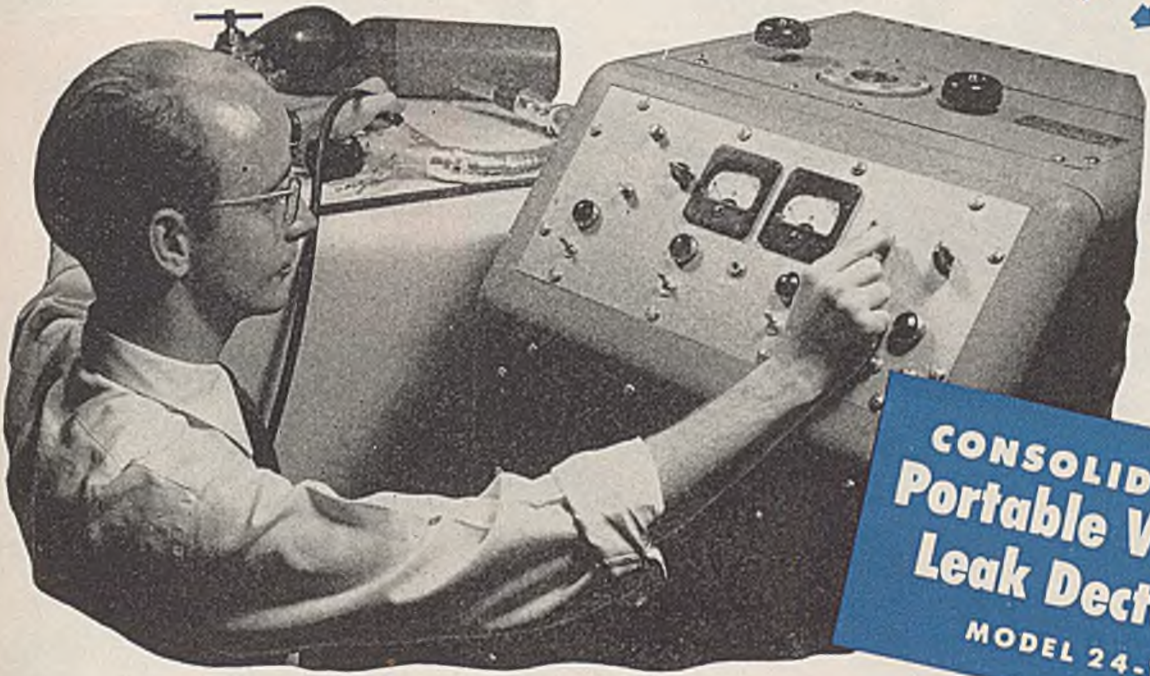




TAYLOR INSTRUMENTS MEAN ACCURACY FIRST

QUICKLY LOCATES LEAKS...

as small as $\frac{1}{100,000,000}$ cc. per second



CONSOLIDATED'S
Portable Vacuum
Leak Dectector
MODEL 24-101

Prevent Long and Expensive Shutdowns

Wherever there is a vacuum or pressure system operating inefficiently due to leakage, or wherever production equipment is being tested for leakage, a Consolidated Leak Detector should be on the job. Simple to operate, it is extremely accurate and fast in detecting and measuring leaks. It is a new tool that will save you much time and many dollars lost due to costly leaks.

The operation of the Consolidated Leak Detector is based on the Mass Spectrometer principle. Essentially, it consists of an ionization chamber set up to measure helium as it passes through the system. By introducing non-contaminating helium into suspected areas of leakage, the smallest leak will be indicated on the Leak Rate Meter and set the Audio Alarm into operation. One man can operate this instrument.

Many adaptations for specific leakage tests can be made by your engineers or ours. Write Dept. 104 today for additional information.

- **PORTABLE**
  22" x 25" x 43", wt. 300 lbs., mounted on rubber-tired ball-bearing casters.
- **SENSITIVE**
  Selection of six ranges of Leak-Rate Meter readings.
- **ACCURATE**
  Measures leakage rate to .00000001 cc. per second.
- **SIMPLE TO OPERATE**
  Audible and visible alarm for one-man operation.
- **STANDARD POWER**
  115 V. 60 cycles A. C., operates wherever ordinary lighting circuit is available.
- **ECONOMICAL**
  Uses only 850 watts and negligible amounts of helium and liquid air. No water is needed.
- **SIMPLE TO MAINTAIN**
  All electrical and vacuum components are standard and very readily accessible.

Consolidated Engineering Corporation

Designers and Manufacturers of Analytical Measurement Equipment

620 NORTH LAKE AVENUE • PASADENA 4, CALIFORNIA


PURE

◀ CARBON TWELVE as it appears under an electron microscope, magnified 100,000 diameters.

CARBON

CARBON TWELVE... A carbon available in carload lots which approaches the quality of a fine C. P. chemical. It is carbon in its purest form, and it is available *now*, in carload lots. Carbon Twelve is ready for new consumers and new applications, and at a much lower cost than most industrial carbons.

These are some of the many qualities of Carbon Twelve:

Its ability to prevent caking recommends it to those industries using hygroscopic materials.

Its chemical purity recommends it as a reagent to the carbon disulphide and electrode industries.

Its fine particle size and large surface area recommend it as a catalyst carrier in both liquid and gaseous systems.

Its low thermal conductivity, lower than that of the most widely used insulators, including ground cork, recommends it as a low temperature insulating material.

Conversely, it can be used in inert atmosphere at high temperatures which would melt other insulators.

Its fluidity provides easy application, especially in closed, cylindrical forms.

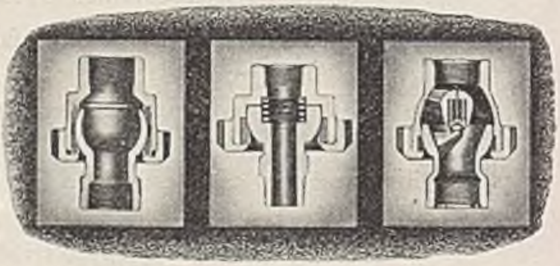
Carbon Twelve is 99% pure carbon. It is available now, at a great economy, in carload or L.C.L. lots. Unequaled production facilities assure a constant supply. The Research and Development Department of Godfrey L. Cabot, Inc., is ready to explore with you the many possibilities of Carbon Twelve.

CABOT

GODFREY L. CABOT, INC.

77 FRANKLIN STREET, BOSTON 10, MASS.


VIBRATION GIVES THE PITCH IN A TUNING FORK
but gives trouble in fluid lines

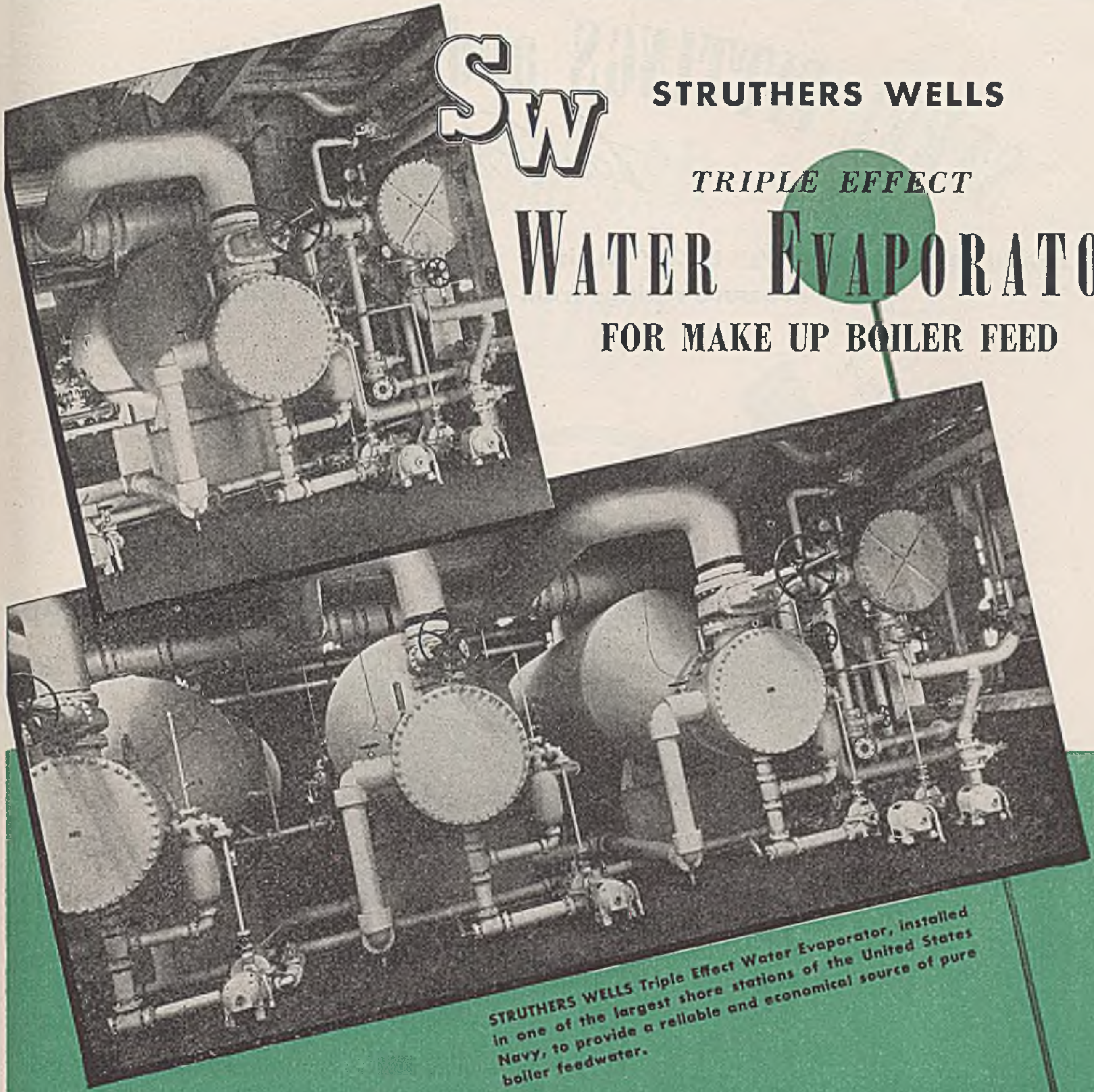


STRUTHERS WELLS

TRIPLE EFFECT

WATER EVAPORATOR

FOR MAKE UP BOILER FEED



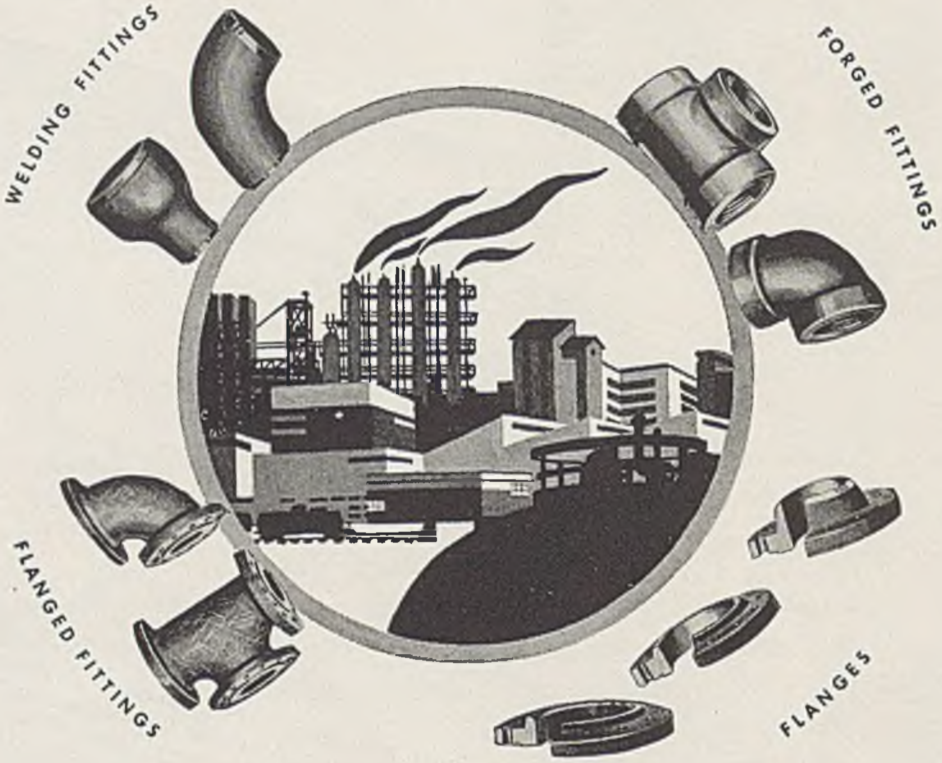
STRUTHERS WELLS Triple Effect Water Evaporator, installed in one of the largest shore stations of the United States Navy, to provide a reliable and economical source of pure boiler feedwater.

● Designed to operate on either fresh water or sea water feed, with provision for thermal descaling of tubes, and arranged to permit continued operation with one or more effects cut out, this installation has a normal rated capacity in excess of 100,000 gallons per day of pure distilled water.

In the modern power plant, STRUTHERS WELLS make-up evaporators provide sound basic design together with tried and proven improvements which assure a maximum of performance and a minimum of maintenance, making them fitting companions for STRUTHERS WELLS Feedwater Heaters.

STRUTHERS WELLS CORPORATION

PROCESS EQUIPMENT DIVISION • WARREN, PENNA.
PLANTS AT WARREN, PENNA. and TITUSVILLE, PENNA.


WELDING FITTINGS
FORGED FITTINGS
FLANGED FITTINGS
FLANGES

How a supported catalyst can cost you less

The answer is, let Porocel Corporation put your catalyst on activated bauxite.

Our carrier—Porocel—with a price range of 2½ to 4½ cents per pound, costs much less than other supports (frequently high-priced synthetic materials). Its rugged, granular character eliminates the need for costly forming steps—permits direct impregnation by simple, inexpensive techniques. The result is savings of 20-50% in initial cost of the ready-to-use catalyst.

Porocel is inert in the great majority of cases. The degree of purity in low-iron, low-silica Porocel means almost complete freedom from unwanted side reactions. Hence, Porocel catalysts exhibit clean-cut reactions and long life. Result? Low unit operating costs.

With a surface area of about 225 square meters per gram and porosity averaging 55% of its total volume, Porocel is capable of adsorbing large quantities of many inorganic salts or other compounds. Impregnation of the active ingredient is uniform and widely dispersed over areas easily reached by gaseous and liquid reactants—most important in surface catalysis.

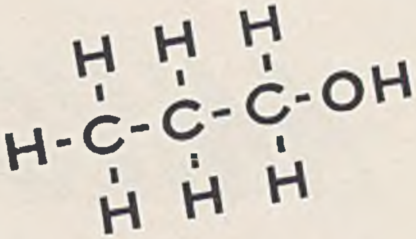
Catalysts are made in mesh sizes ranging from 2/4 to 20/60 or in special grades when desired. And these tough, uniform particles withstand wide ranges of temperature, pressure and flow—stand up under severe handling.

As pioneer developers of bauxite-supported catalysts, we have produced efficient materials for others. Now, let us show you how economically it can be done for you. *Outline the details to: Attapulgus Clay Company (Exclusive Sales Agent), Dept. C, 260 South Broad Street, Philadelphia 1, Pa.*

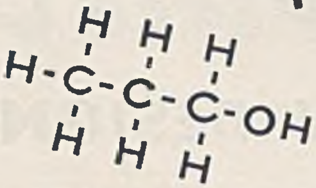
POROCEL
CORPORATION

ACTIVATED BAUXITES • SUPPORTED CATALYSTS • CATALYST CARRIERS • ADSORBENTS • DESICCANTS

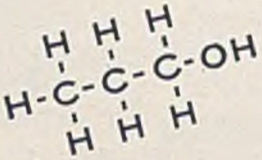
CELANESE OFFERS n-PROPYL ALCOHOL IN VOLUME



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$

The Celanese chemical plant at Bishop, Texas, is now offering n-propyl alcohol in drum or tank car lots for early delivery. If you are looking for processing advantages in your manufacturing; for improvements in your products; or for shortcuts in your production, the advantages of this straight chain hydrocarbon are worth investigation.

PHYSICAL PROPERTIES

MOLECULAR WEIGHT		60.06
COLOR		water white
ODOR		characteristic alcohol-like odor
SPECIFIC GRAVITY	20°/4° C	0.804
DISTILLATION RANGE	ASTM	2° including true boiling point
WEIGHT PER GALLON	20° C	6.7 lbs.
SOLUBILITY		soluble in water, alcohol, ether and practically all other organic solvents
FLASH POINT	open cup	32.2° C
BOILING POINT	1 atm.	97.2° C
FREEZING POINT		−127° C
VAPOR PRESSURE	100° F or 37.8° C	0.9 lbs. per sq. in.

n-propyl alcohol possesses excellent solvent power and miscibility—can also be used as a replacement for other alcohols now in critical supply. Call or write for additional information. *Celanese Chemical Corporation,* division of Celanese Corporation of America, 180 Madison Avenue, New York 16, N. Y.

PROPIONALDEHYDE

A Celanese Chemical with Possibilities for You

Here is a Celanese chemical with great industrial possibilities. Propionaldehyde—hitherto obtainable only in laboratory amounts—is now being produced by Celanese, and can be supplied in quantities large enough for pilot plant operation.

Furthermore, you can depend on Celanese for a steady supply of this aldehyde, when you are ready for full-scale production. Write for further information.

FORMALDEHYDE · ACETALDEHYDE · ACETIC ACID · METHANOL
ACETONE · ORGANIC PHOSPHATES · PLASTICIZERS · INTERMEDIATES

*Reg. U. S. Pat. Off.

ANNOUNCING

A NEW DESIGN IN FILTER PRESS CONSTRUCTION!

THE YOUNGSTOWN MILLER VERTICAL STACK FILTER PRESS represents a radically new design in filter press construction, wherein the plate and frame are combined in one casting and placed in a vertical stack.

Cleaning and removal of the cakes is accomplished quickly and easily simply by starting with the top member and latching it in an elevated position. This permits the filter paper and cake to be pulled forward out of the press. Succeeding members are similarly handled until the entire press is clean.

Of cast iron construction, the YM Filter Press is suitable for the filtration of many liquids, only a few of which are alkid resins, solvents, paint, varnish, molasses, honey, fruit syrups, soaps, liquid shampoos, shaving lotions; fish, linseed, castor and essential oils; cutting oils and coolants.

Filtering area—31 sq. ft.
Available cake space 2 cu. ft.

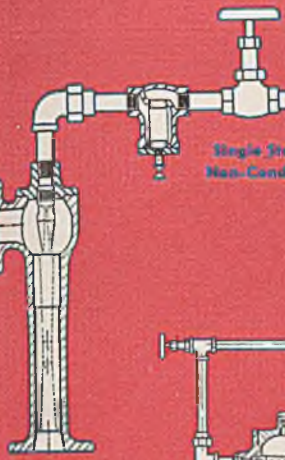
THE YOUNGSTOWN MILLER CO.
SUBSIDIARY OF WALTER KIDDE & COMPANY, INC.
Belleville, New Jersey

...a Kidde *product*

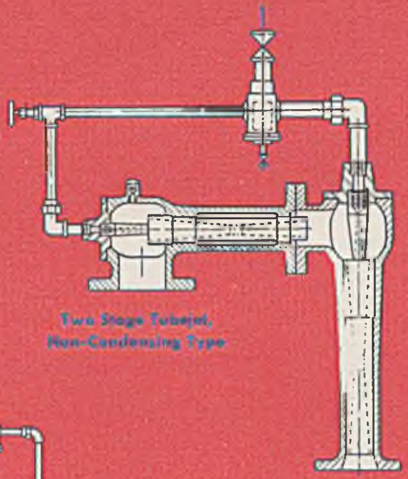
STEAM JET AIR EJECTORS
Engineered to Your Needs

Our complete line of Tubejet Steam Jet Air Ejectors is illustrated to demonstrate that the selection of the correct unit for an individual job requires more than some people may think. It requires years of experience in successful installations to correctly solve the "never before encountered" problems of today's new methods and industries. Radojet now Tubejet are the oldest names in steam jet air ejectors, known to the most people in the world today; we have the most experience because we believe we have made the most installations. If there is any vacuum problem within the scope of ejectors which we have not already met and solved, we don't know of it. You can safely rely on our advice, whether your problems are new to you or to the world. Bulletin on request, catalog in preparation; write to us now.

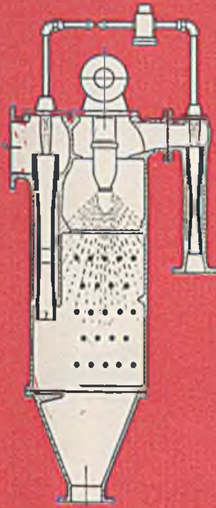
C. H. WHEELER MFG. COMPANY
1806 SEDGLEY AVENUE, PHILA. 32, PA.
REPRESENTATIVES IN MOST PRINCIPAL CITIES



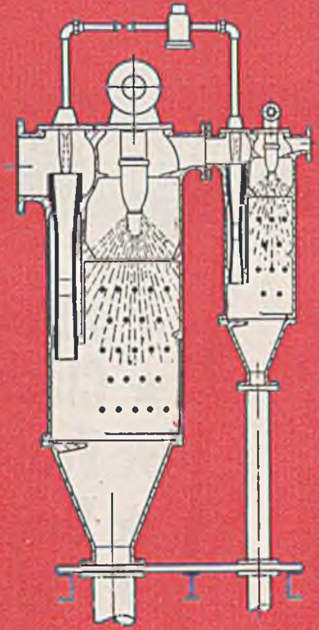
Single Stage Tubejet,
Non-Condensing Type



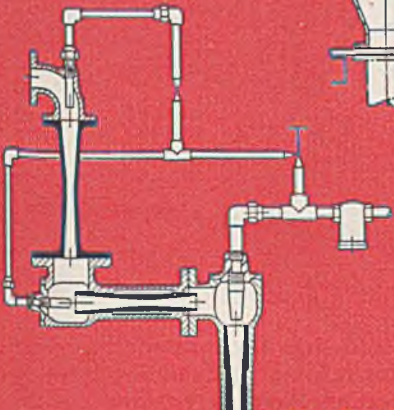
Two Stage Tubejet,
Non-Condensing Type



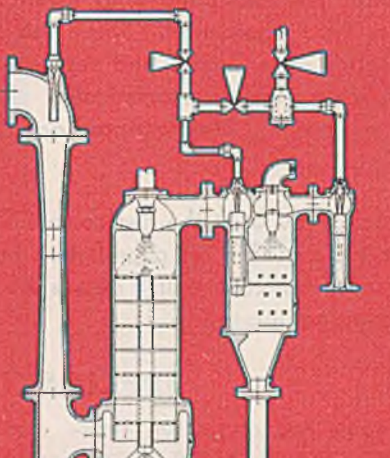
Two Stage Tubejet with
Barometric Inter-Condenser



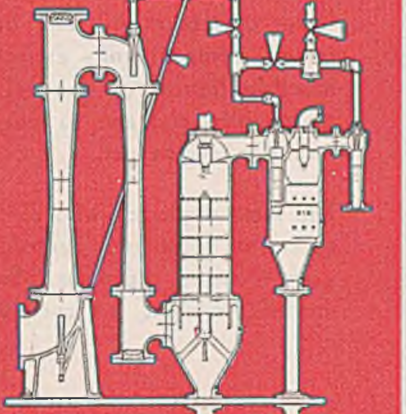
Two Stage Tubejet with Barometric
Inter- and After-Condenser



Three Stage Tubejet,
Non-Condensing Type



Three Stage Tubejet with
Two Barometric Condensers



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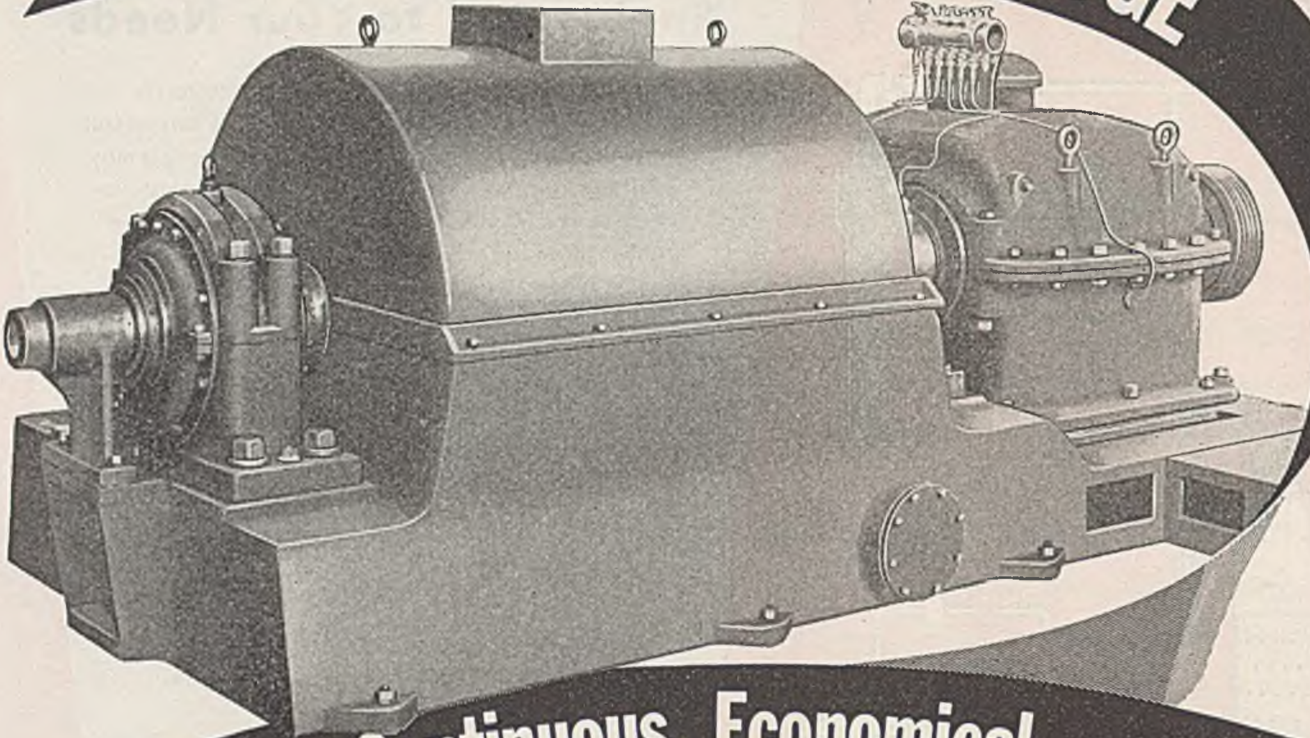

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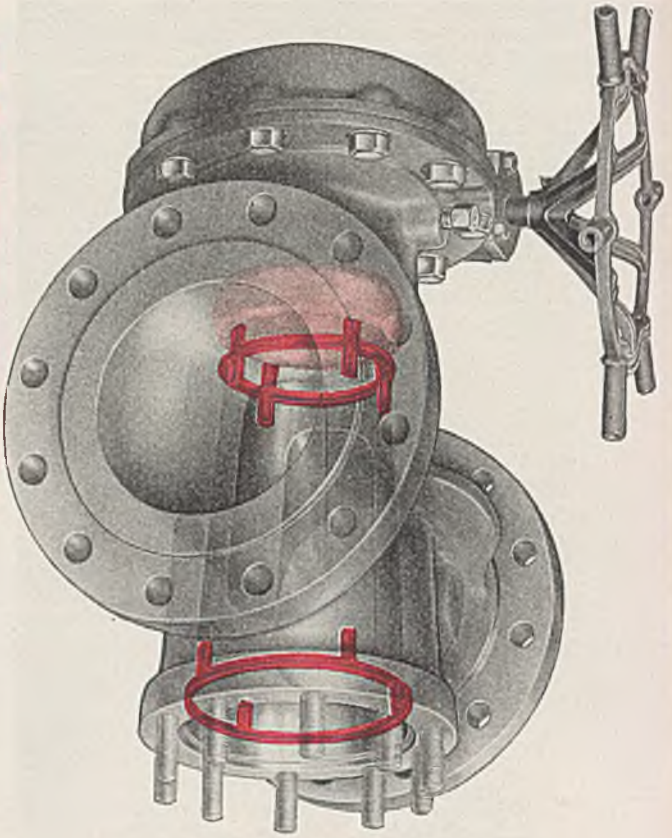

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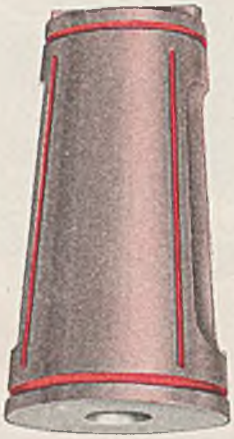

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New Bulletin No. V-200 describing the various types of Nordstrom Lubricated Valves, with specifications and prices, will be sent upon request.

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LUBRICATED VALVES

As We See It . . .

Controlling Inflation. Lightbown, Verde, and Brown give service test data on Butyl inner tubes starting on page 141. Butyl's superior air-retaining properties resulted in improved tire life, and, on aging, the original physical properties of Butyl tubes were retained better than in tubes made from natural rubber. The paper has an easy style; you will probably enjoy reading it even if your interest in the subject is no greater than that of an automobile owner.

Optic Topic. With no disrespectful intent we "give you the bird" in another of this issue's papers—and what is more, in full color. Beetles, buttons, and old automobiles are displayed also in full spectral glory. These objects are part of the color page insert illustrating an article on page 147 by Buc, Kienle, Melsheimer, and Stearns. The subject is the phenomenon of bronzing in surface coatings, and the illustrations on the insert show some of the color effects that are discussed in the accompanying text. Interface and interference bronze are described and differentiated. Equations are presented that predict adequately the spectrophotometric curve of interface bronze. The authors' theoretical analysis explains the phenomenon as a function of such elements as the angles of incidence and refraction, the elastic constant of various components, the fraction of energy reflected, and various refractive indices and extinction coefficients. The authors state that these principles offer a sound basis for achieving some control of bronzing in coatings through formulation adjustments. They do not, however, extend their paper to include comparative data on any such actual work.

On the same general subject an I&EC report titled "Colorful Thoughts", appearing on page 8 A (advertising section), will be of interest to many who read the bronzing article. The report goes back to a philosophical discussion of color. Through an ingenious triangular diagram, man's definition and understanding of color through chemical composition, optical measurement, and psychological reaction are integrated into a system that has a logical place for all well known methods of expressing color.

Basic Answer. Steel mills probably began singing the Limehouse Blues when wartime demands for high calcium limestone took away much of their supply of this material, which they had been using for neutralization of waste pickle liquor. The acid wastes still had to be neutralized, however, so readily available dolomitic lime was investigated in order to find how satisfactory a substitute it provided. Hoak, Lewis, Sindlinger, and Klein report the results of this work starting on page 131. Their final balance sheet rates the pros and cons of dolomitic lime as being about equal to those of high calcium lime; the former is 14 to 24% cheaper per unit of basicity but requires a longer reaction time, an excess of lime, or a higher reaction temperature for equivalent neutralization per unit time, and yields a bulkier sludge. In view of the limited supply capacity of high calcium limestone, it is possible that the magnesia-containing substitute may become a permanent choice for the waste disposal job.

Fat of the Land. R. L. Demmerle, one of our own staff, has contributed to this month's collection the article starting on page 126. The subject is the Emersol process, a method for the industrial separation of fatty acid fractions from natural fats through crystallization from a solvent. The article is intentionally written from a broad perspective that compares the newer method with the century-old pressing technique. It should provide an interesting and authoritative survey of an industrial chemical field. It is designed to be read by those who like to keep up with all fields of chemical technology. We hope to present similar staff articles written with the same purpose in future issues of INDUSTRIAL AND ENGINEERING CHEMISTRY.

Alcohol Rubber. One who is in a position to know commented in a prepublication review of our lead-off paper on butadiene from alcohol, authored by Toussaint, Dunn, and Jackson, "It is the only really quantitative and authoritative information on the basic reaction involved in the alcohol-butadiene program." Our reviewer, a chemical engineer of national eminence, undoubtedly gained this favorable impression of the article in part because it searches out the heart of the process development. The paper covers those experiments in which were determined the actual yields, efficiencies, and critical process relations in industrial types of equipment. It is this crucial stage of investigation that shows how many slips and lost drops can be expected in transferring a process from the cup of laboratory chemistry to the lip of engineering feasibility.

Many more articles containing, as does this one, data on chemical engineering process fundamentals should be incorporated in the industrial chemical literature. Without them the scientific record of applied chemistry developments will be as unsatisfying as a detective novel with the last chapter missing.

Plant auxiliary equipment is the subject under discussion in Brown's column on equipment and design. Corrosion-resistant filters made through powder metallurgy methods, a semisensitive balance for rapid production methods, motor speed controls, and electrical rectifiers are the specific items discussed. Most of them are new and may have substantial applications in chemical plants.

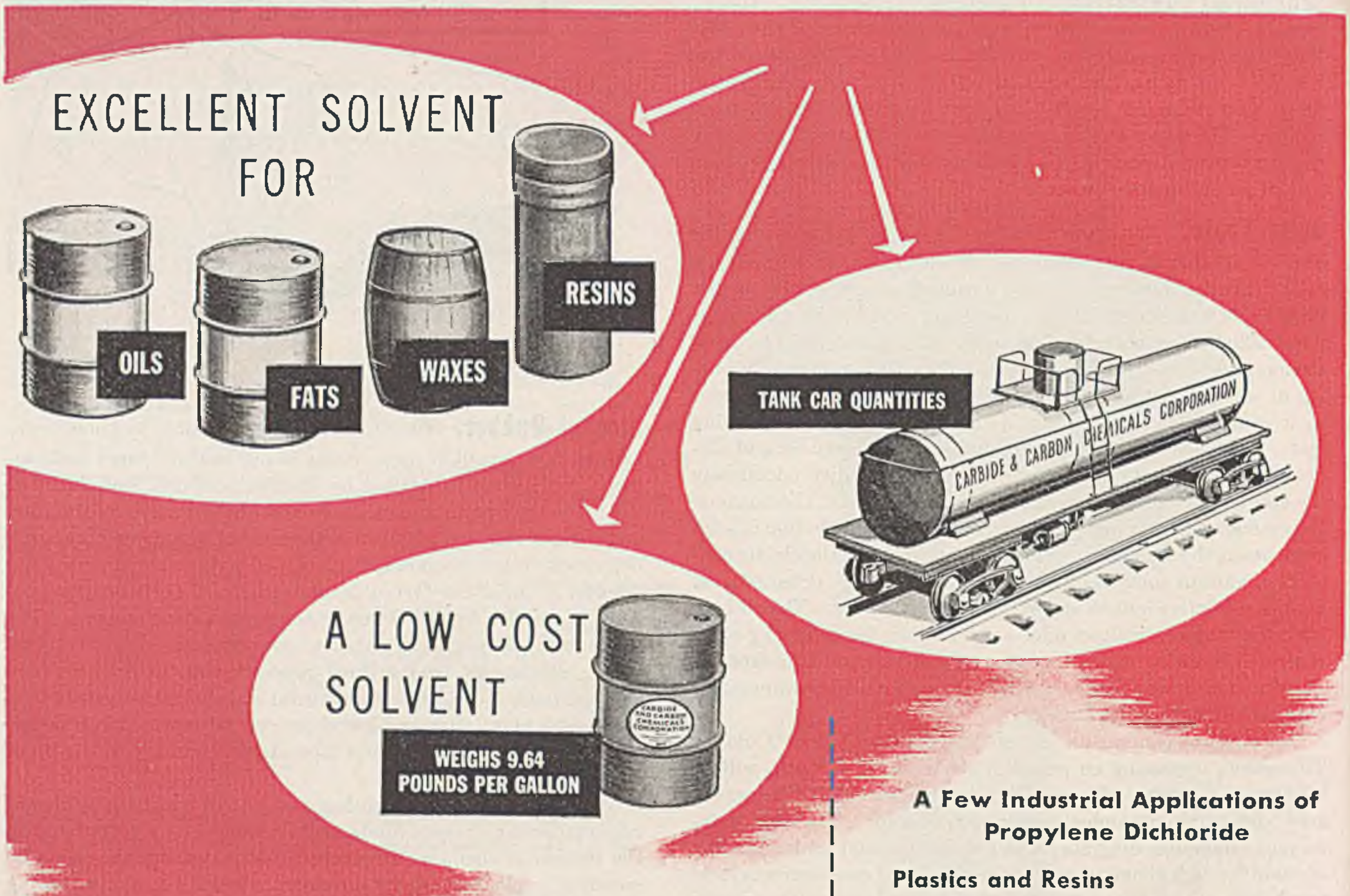
A temperature controller that is essentially a Wheatstone bridge circuit is suggested by Munch where expenditures must be kept low. The design advantages of the instrument are enumerated.

Economics as well as corrosion rates determine the proper choice of chemical plant construction material. Fontana cites illustrative examples to point out the wise choice and emphasizes the necessity for the process development engineer's being aware of the corrosion problem and making suitable tests during developmental phases of the work. Units for expression of corrosion rates are also discussed.

Suggestion systems come in for their share of attention in von Pechmann's column. Some danger points are cited and policies are suggested to ensure that pitfalls are avoided in the operation of the plant suggestion system.

D. O. Myatt

Propylene Dichloride



Propylene Dichloride — which can be supplied in drum and tank-car quantities—is an ideal solvent for many industries. Propylene Dichloride resembles ethylene dichloride in its solvent properties and in general its applications are similar. Propylene Dichloride is a clear, colorless liquid that boils at 96.3°C. As this compound is resistant to oxidation by air, and hydrolysis by water, it can be handled in common construction metals.

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INDUSTRIAL and ENGINEERING
Chemistry

WALTER J. MURPHY, Editor

Declassification and the AEC

PROBABLY no other commission or agency of the Government in the long history of this country has had so many prayers offered for its success by so many people as has the Atomic Energy Commission. No one would accuse *The New York Times* of an overstatement when, in an editorial commenting on the assumption of atomic energy control by civilians, it remarked that the commission has as important a job as has been entrusted to any group of men in our history.

The commission has inherited grave responsibilities—it also has acquired a number of headaches.

When we are inclined to criticize, and may our criticism always be constructive, let us remember both the responsibilities and the headaches that were passed on to the commission on the final day of 1946. It has been asked to pioneer in uncharted fields. The existence of the commission will have a momentous effect internationally—at least until such time as an all-inclusive world atomic energy agency is created.

The commission must consider first things first. Unquestionably it is aware of criticism concerning the slowness in declassifying certain scientific information and data on nucleonics accumulated in the war years and since V-J Day. Much of this criticism comes from scientists who participated directly in the Manhattan Project.

Part of the criticism that has been voiced concerning the slowness of declassification may be unwarranted, while some may be entirely justified. We must remember that even if security were not the factor that it very definitely is in the field of nucleonics, the huge amount of material accumulated would alone make the task of dissemination a most difficult assignment.

Our experiences with the military and civilian authorities responsible for releasing such information have, in the main, been quite satisfactory. We know at first hand about many of the very elaborate plans for detailed publication now being carried out. We think we know, certainly we should know, some of the mechanical and editorial problems inherent in the declassification and publication of scientific material on a scale greater than anything previously visualized in scientific circles. We are experiencing at first hand some of these difficulties in making ready for publication in the March issue of INDUSTRIAL AND ENGINEERING CHEMISTRY the Fluorine Symposium presented at the September meeting of the SOCIETY in Chicago last year.

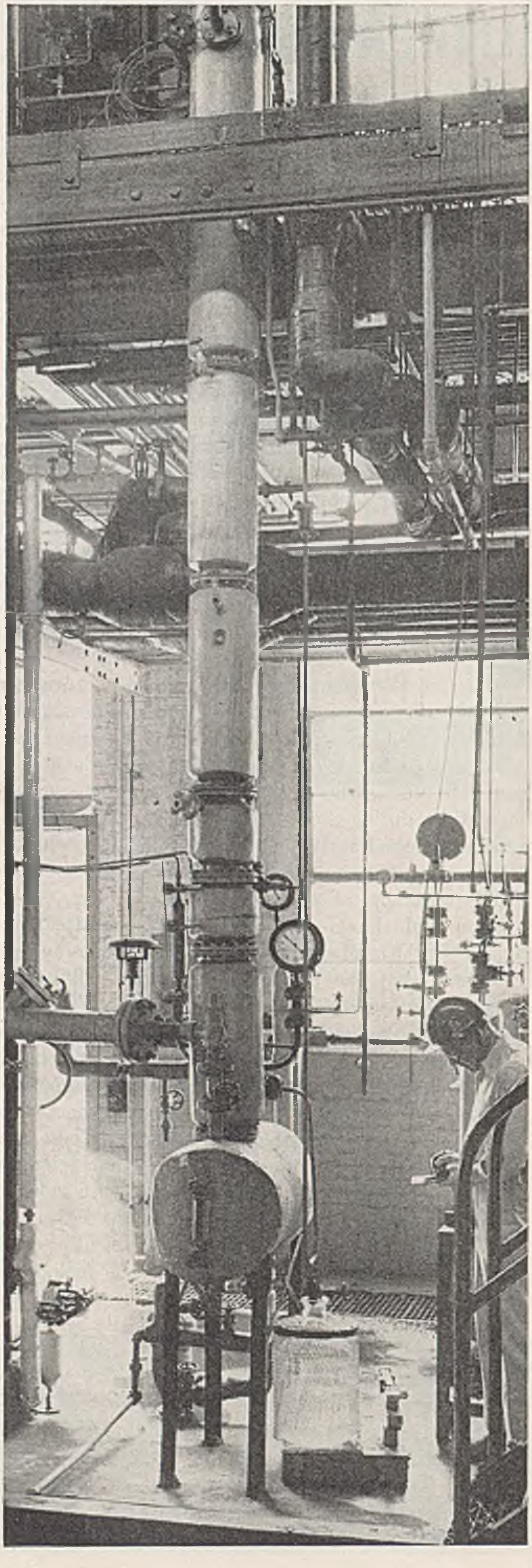
Scientific workers in other countries are offering for publication manuscripts on a variety of subjects in the nucleonics field. These workers are under no obligation to withhold their manuscripts until American scientists are permitted to disclose and record work performed under secrecy orders during the past several years. As a consequence, American scientists are in a most disadvantageous position as regards possible priority of scientific publication. To the scientist this is important —more important than monetary reward.

Many of the scientists who pioneered the work on nucleonics are extremely young. To them especially the matter of publication is of the utmost importance. Most have no backlog of publications in other fields and feel that others who were not under extreme secrecy regulations during the war years in many ways are receiving preferential treatment. Such thoughts, whether justified or not, do not make for good morale.

The make-up of the new Atomic Energy Commission and the General Advisory Committee, appointed on December 12 to assist the commission, is a guarantee that the publication problem will be approached in a highly sympathetic manner. The members of both bodies are fully aware of the legitimate aspirations of the scientists who made the atom bomb possible and who now are understandably impatient with regulations that hamper the fastest development of peacetime applications of nuclear energy. These, and indeed all scientists, properly believe that scientific advances are achieved most readily and with greatest rapidity when no artificial barriers are erected to prevent the widest possible dissemination of scientific data.

The problem has many sides. Let us look at it calmly and objectively. Above all, let us as scientists try to see that credit is given where it rightly belongs.

The lot of editors of scientific journals will not be an enviable one for the next few years. We, like the Atomic Energy Commission, will face some headaches in our attempts to reach just decisions on priority of publication. Assistance in making these decisions will be appreciated. In the final analysis, however, the innate honesty of the scientists involved will assure correct decisions in the overwhelming majority of cases.



Production of Butadiene from Alcohol

W. J. TOUSSAINT, J. T. DUNN,
AND D. R. JACKSON[1]

Carbide and Carbon Chemicals Corporation,
South Charleston, W. Va.

UNTIL the necessity arose of replacing our supply of natural rubber, investigation of the production of butadiene for synthetic rubber was of relatively minor importance in this country. In Russia where this eventuality was more apparent, the Lebedev process (*2*) for producing butadiene from ethanol was developed, and many details of the operations were published, exclusive of the specific nature of the catalyst. Much earlier Ostromislensky had obtained butadiene, in small but interesting amounts, from ethanol and acetaldehyde over catalysts which might be broadly described as having dehydrating properties. Moreover, much information of more or less pertinence had accumulated in both the academic and patent literature on the reaction of alcohols and carbonyl compounds over various catalysts; but little progress was indicated in the preparation of diolefins by these reactions.

Intermittently over a long period the authors and others in this laboratory worked on the project of making butadiene. A significant advance was made when Quattlebaum (*1*) found that crotonaldehyde and ethanol gave butadiene more readily than did ethanol and acetaldehyde, and concluded that Ostromislensky's process, and Lebedev's also, had as the key step the reaction of ethanol and crotonaldehyde according to the following scheme:

$$CH_3{-}CH_2OH + CH_3{-}CH{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3{-}CHO + H_2O \quad (1)$$

The Ostromislensky process depended upon the conversion of acetaldehyde to crotonaldehyde (Equation 2) and the Lebedev process further required the formation of acetaldehyde from ethanol (Equation 3):

$$2CH_3{-}CHO \longrightarrow CH_3{-}CH{=}CH{-}CHO + H_2O \quad (2)$$

$$CH_3{-}CH_2OH \longrightarrow CH_3{-}CHO + H_2 \quad (3)$$

After this theory was presented, attention was concentrated on a study of Equation 1, and silica gel was eventually found to be a good catalyst for that reaction. In an attempt to improve the characteristics of this catalyst, it was found that certain metal oxides not only produced butadiene from the crotonaldehyde but also converted acetaldehyde and ethanol to butadiene with considerable improvement over other known catalysts. It was found further that the addition of copper gave good results in the Lebedev type of process, if sufficient acetaldehyde were maintained in

---

[1] Present address, Wyandotte Chemicals Corporation, Wyandotte, Mich.

During the war emergency a substantial part of the butadiene for manufacturing synthetic rubber was produced from ethanol. The development of this process was facilitated by the recognition that crotonaldehyde is the intermediate in the Ostromislensky reaction, in which ethanol and acetaldehyde are converted to butadiene. Initially a process was developed for converting crotonaldehyde and ethanol to butadiene with a catalyst of silica gel, but suitable modification of the catalyst afforded equally efficient production of butadiene from acetaldehyde and ethanol. Further, by incorporating dehydrogenating components in the catalyst, the Lebedev type of process was effected for converting ethanol more directly to butadiene. The preferred catalyst for the acetaldehyde-ethanol reaction consisted of silica gel impregnated with tantalum oxide. With this catalyst efficiencies of about 67% from ethanol as the ultimate raw material were obtained in the laboratory, and the results were substantially reproduced in plant operation. Zirconia supported on silica gel was considered as a possible replacement catalyst, since zirconia was more readily available and the yield of butadiene was only somewhat less than that obtained with the tantalum catalyst. The by-products from the process comprise a multiplicity of hydrocarbons, aldehydes, ketones, esters, ethers, alcohols, etc. The more important of these—namely, ethylene, butenes, ethyl ether, and butanol—were recovered on a plant scale in a quality suitable for utilization.~~The photograph on the opposite page shows a still used for the recovery of butadiene and of reactants.

the feed to inhibit hydrogenation of the butadiene. Most attention, however, was given to the development of the Ostromislensky process, since it seemed to offer greater certainty of successful large-scale operation within the limited time which then remained available for study.

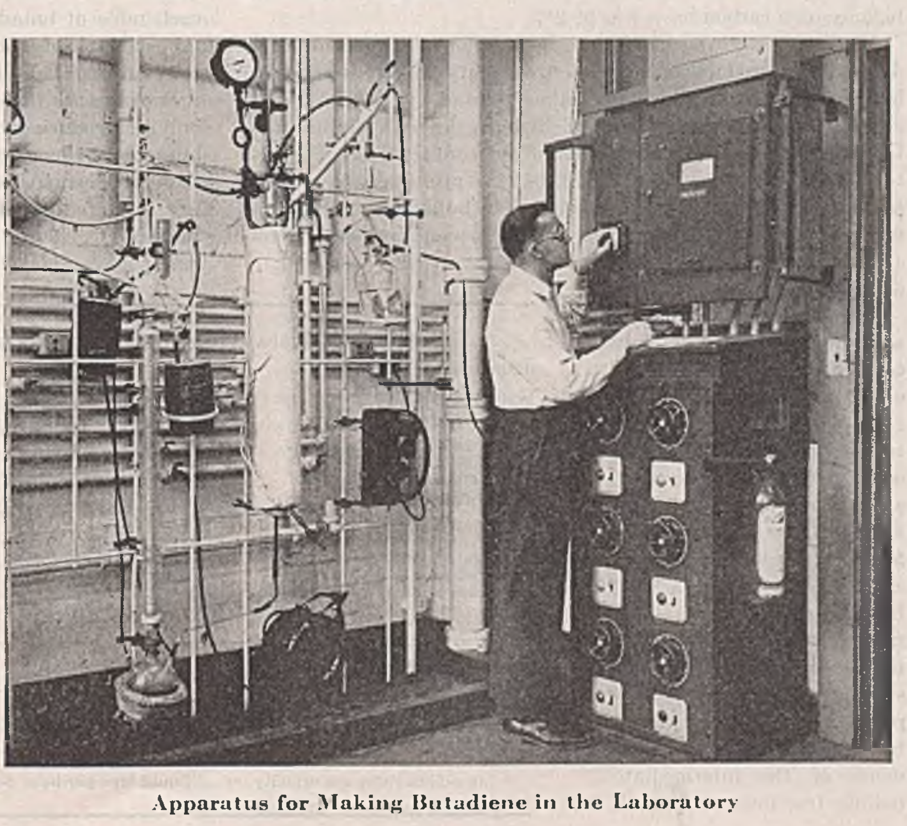
BUTADIENE FROM ETHANOL AND CROTONALDEHYDE

At one time during these investigations the most promising method for the commercial production of butadiene seemed to be the reaction of ethanol and crotonaldehyde over a catalyst of purified silica gel. In laboratory scale experiments the results had been improved to the point where butadiene was obtained from crotonaldehyde with an efficiency of 63%. In order to confirm these results in commercial types of equipment and to gain further information on the process, the study was continued in a large laboratory scale converter and still. The converter was a 3-inch by 24-foot stainless steel tube heated by boiling Dowtherm; it contained 18 feet of silica gel purified by treatment with nitric acid. The still consisted of a 6-inch, 22-tray bubble cap column on a 17-gallon kettle.

From these studies data are presented in Table I from two series of experiments: one (experiments 17–21) in which the molar ratio of ethanol to crotonaldehyde in the feed material was 3 to 1, and the other (experiments 22–28) in which the ratio was 6 to 1. The effect of the larger excess of ethanol was to conserve the more valuable reactant, crotonaldehyde, although with some sacrifice in the efficiency from ethanol. The calculations of efficiency and single-pass yield were made on the assumption that the butadiene was derived solely from the crotonaldehyde introduced, and the acetaldehyde solely from the ethanol, according to Equation 1. ("Single-pass yield" is used to denote the per cent yield of product based on a specific reactant or reactants fed; "efficiency" refers to the per cent yield based on the reactant consumed.) This gave an efficiency from ethanol to acetaldehyde in one series in excess of 100%, which is accounted for by hydrolysis of the crotonaldehyde. The other items in the efficiency were calculated approximately; the gas consisted largely of propylene and ethylene, and the high boiling oils and tar were considered to be condensation products of crotonaldehyde; the percentage unaccounted for includes by-products of intermediate boiling point as well as loss.

In experiments 17 to 21, inclusive, with a 3 to 1 molar ratio of ethanol to crotonaldehyde, the approximate composition of the feed in mole per cent was: ethanol, 36–39; crotonaldehyde, 12–13; water, 52–48. The feed rate varied between 3.84 and 4.04 gallons per hour per cubic foot of catalyst. At 360–370° C. the average single-pass yield of butadiene from crotonaldehyde was 27.6%, and of acetaldehyde from ethanol, 12.4%. The molar ratio of acetaldehyde to butadiene in the products varied between 1.24 and 1.53. For the five runs the material balance on a carbon basis was 97.6%.

For experiments 22 to 28 ethanol and crotonaldehyde were employed in a molar ratio of 6 to 1 in a feed of the following approximate composition, in mole per cent: ethanol, 42; croton-



Apparatus for Making Butadiene in the Laboratory

Table I. Butadiene from Ethanol and Crotonaldehyde

	Expt. 17–21		Expt. 22–28	
	Lb./hr./ cu. ft. of catalyst	% by wt.	Lb./hr./ cu. ft. of catalyst	% by wt.
Converter feed, av.[a]				
Ethanol	14.30	50.0	15.62	58.1
Crotonaldehyde	7.35	25.8	3.98	14.8
Acetaldehyde	0.04	0.2	0.03	0.1
Water, etc.	6.85	24.0	7.30	27.0
Total	28.5	100.0	26.9	100.0
Converter make, av.[a]				
Ethanol	12.55	44.0	14.13	52.6
Crotonaldehyde	4.39	15.4	1.97	7.3
Acetaldehyde	1.75	6.1	1.29	4.8
Butadiene	1.57	5.5	1.25	4.6
Gaseous	0.1	0.4	0.1	0.4
Oil and tar	0.25	0.9	0.1	0.4
Water, etc., loss (by difference)	7.9	27.7	8.1	29.9
Total	28.5	100.0	26.9	100.0
Duration, hours	112		199	
Temperature, ° C.	360–370		350–365	
Pressure, lb./sq. in. gage	8–16		8–13	
Single-pass yield				
% from ethanol to acetaldehyde	12.4		8.5	
% from crotonaldehyde to butadiene	27.6		40.6	
Efficiency, % crotonaldehyde to				
Butadiene	68.6		80.8	
Gas (>90% olefins)	4.1		5.9	
Oil and tar	11.5		5.3	
Oxidizable in tails	1.6		1.3	
Unaccounted for	14.2		6.7	
Total	100.0		100.0	
Efficiency, % ethanol to				
Acetaldehyde	102		88.8	
Unaccounted for	...		11.2	
Total	...		100.0	

[a] Average for each series.

aldehyde, 7; water, 51. The feed rate was substantially the same for all experiments, 3.60 to 3.72 gallons per hour per cubic foot of catalyst. Based on crotonaldehyde fed, the single-pass yield of butadiene varied from 34.0–37.9% at 350–355° C. to 47.2–48.5% at 363–370° C. The average single-pass yield of acetaldehyde from ethanol was calculated to be about 9.5% at 363–370° C., and about 7% at 350–355° C. The average ratio of acetaldehyde to butadiene was 1.28. For these runs the material balance on a carbon basis was 98.2%.

In all of these experiments the ratio of acetaldehyde to butadiene in the products was greater than unity, largely because of hydrolysis of crotonaldehyde rather than dehydrogenation of ethanol. The addition of acetaldehyde to the feed mixture was therefore investigated as a means of overcoming this. The extent of hydrolysis was diminished, but the principal effects were a lowering of the yield and efficiency to butadiene and an increased yield of by-product oils and tars, which apparently resulted from aldehyde condensations.

The gaseous by-products were rather simple, largely ethylene with some propylene; but considerable difficulty was experienced in determining the nature of the other by-products. Accurate analyses for ethanol and crotonaldehyde were not feasible for each experiment, and for this reason a wide fraction containing these materials was recycled with make-up reactants in successive runs in each series of experiments. Ethyl acetate and hydrocarbons were components of the intermediate boiling fractions, and small amounts of butanol and crotyl alcohol were also identified. Components of the higher boiling materials were not separable, either as obtained or after hydrogenation, although isomeric dihydrotolualdehydes were indicated as present.

Most of our studies were made at approximately atmospheric pressure, the pressure drop through the catalyst and distillation system being about 8 to 16 pounds gage. However, a few experiments were made with a converter pressure of 50 pounds gage. The feed mixture contained ethanol and crotonaldehyde in a molar ratio of 6 to 1. The production ratio was increased about 55% over that obtained at atmospheric pressure, other conditions being the same, but the ultimate efficiency from ethanol to butadiene was decreased appreciably. There was an excessive increase in oil formation as well as an indication of greater hydrolysis of crotonaldehyde to acetaldehyde.

Butadiene from the large scale experiments was refined in the still system modified to provide cooling of the condenser by methanol, which circulated through a carbon dioxide–acetone mixture. The make was passed through a scrubber supplied with 10% aqueous caustic soda to remove acetaldehyde. The following fractions were taken off in sequence: fraction 1, 4.7 pounds; fraction 2, 7.9 pounds; and fraction 3, 9.8 pounds. Fraction 1 contained 94% of butadiene by determination as the tetrabromide, and fractions 2 and 3 had a purity of 98.5% as indicated by freezing point, if the impurity is assumed to be butene. The chief impurity of the first fraction was probably propylene. A test for monoalkylacetylenes was negative.

BUTADIENE FROM ETHANOL AND ACETALDEHYDE

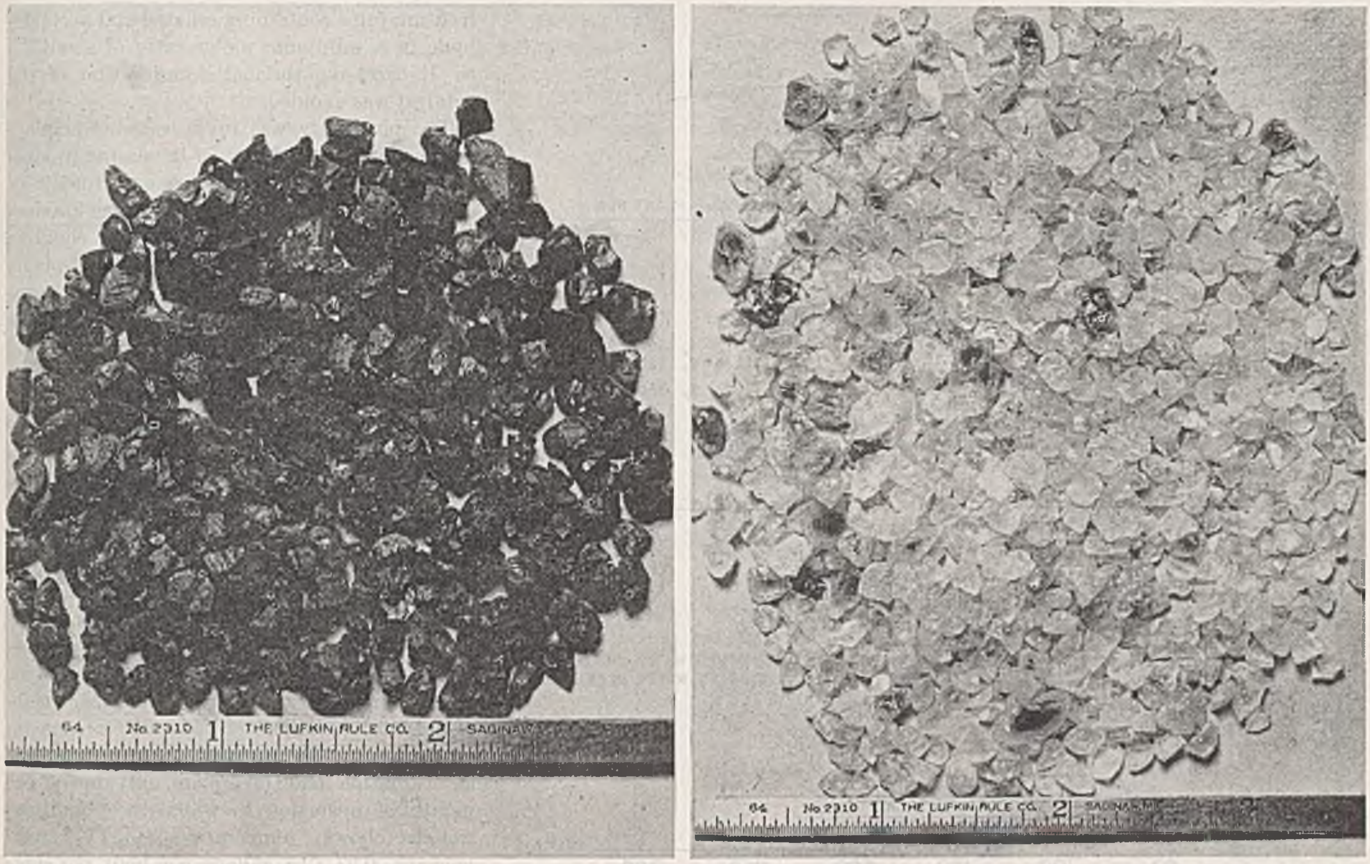
In an attempt to improve the performance of the silica gel catalyst with ethanol and crotonaldehyde, it was found that by incorporating certain metal oxides, notably those of tantalum, zirconium, and columbium, much smaller amounts of acetaldehyde and correspondingly larger amounts of butadiene resulted. With a catalyst of 2.4% tantalum oxide on silica gel at 325° C., a space velocity of 0.7 liter of liquid feed per hour per liter of catalyst, and a molar ratio of 6 moles of ethanol to 1 mole of crotonaldehyde in the feed, all but 7% of the crotonaldehyde was reacted. The product contained only 0.3 mole of acetaldehyde for each mole of butadiene produced and 1.25 moles of butadiene for each mole of crotonaldehyde fed, and the production ratio was 5.5 pounds of butadiene per hour per cubic foot of catalyst.

Such results indicated that these catalysts were capable not only of producing butadiene from ethanol and crotonaldehyde, but also of converting acetaldehyde to crotonaldehyde. It therefore seemed likely that acetaldehyde could be used in the feed mixture instead of crotonaldehyde, and this was found to be the case. The use of such catalysts with ethanol and acetalde-

Table II. Preparation of Butadiene from Ethanol and Acetaldehyde

Experiment No.	TCS-1		TCS-2		TCS-3		TCS-4		TCS-5	
Temperature, ° C.	310		320		320		320		320	
Molar ratio, EtOH/AcH	3.0		3.0		3.0		3.0		3.0	
L.h.s.v.[a]	0.56		0.58		0.58		0.55		0.58	
Single-pass yield from EtOH and AcH, %	25.5		25.2		24.7		28.1		24.2	
Production ratio, g./hr./l. of catalyst	68		62		64		66		59	
Materials, moles	In	Out	In	Out	In	Out	In	Out	In	Out
Ethanol	24.00	17.70	23.93	17.76	23.87	17.00	23.75	17.56	23.69	17.22
Acetaldehyde	7.98	2.37	7.98	2.82	8.08	2.95	7.97	2.93	8.01	2.95
Butadiene	...	4.08	...	4.01	...	3.94	...	4.45	...	3.84
Unidentified (b.p. 9–95° C., aq.)	...	1.79	1.76	2.26	2.24	4.30	3.39	3.89	3.84	5.31
Water	6.0	16.1	7.27	19.7	6.24	17.3	5.96	16.7	5.54	...
Efficiency from EtOH to butadiene, %	64.7		65.0		57.3		71.8		59.4	
Efficiency from AcH to butadiene, %	72.7		77.7		76.8		88.2		75.9	
Av. ultimate efficiency from EtOH, %	65		67		65		68		67	

[a] Liquid hourly space velocity, cc. of liquid feed per hour per cc. of catalyst.



Sample of Catalyst after Reaction Period (*left*) and Sample after Reactivation by Oxidation of the Carbonaceous Deposit with Air (*right*)

hyde demonstrated an increasing efficiency in the order columbium, zirconium, and tantalum; a minimum expectancy of 61% efficiency from ethanol was established for the over-all process, in which acetaldehyde would be produced from ethanol by the conventional copper catalyst, and the butadiene separately from ethanol and acetaldehyde over a tantalum oxide-silica gel catalyst. Because of extensive plant experience in producing acetaldehyde, the investigation could fortunately be limited, to a large extent, to the step of producing butadiene.

Much of this work was in laboratory scale equipment, which enabled more rapid progress in attacking many of the questions to be answered. Here again the analytical problems in determining the efficiency were complex; while confidence was gradually acquired in the data of single experiments, more satisfying assurance could be placed in a series of experiments in which the recovered reactants were repassed several times over the catalyst with make-up feed materials.

Data from a series of such experiments with a catalyst of 2.5% tantalum oxide on silica gel are given in Table II. The butadiene fraction, after refining by distillation and treatment with aqueous hydroxylamine to remove acetaldehyde, contained the following: propylene, 1.8%; butene, 2.2%; vinylacetylene, 0.011%; butadiene, 96%. Based on four-carbon materials only, the butadiene purity was about 98%. The efficiencies from ethanol and acetaldehyde to butadiene are calculated for the individual experiments of the series on the basis of the following equation:

$$CH_3{-}CH_2OH + CH_3{-}CHO \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O \quad (4)$$

The average ultimate efficiencies from ethanol are calculated from the amounts of ethanol consumed as such, and of acetaldehyde referred to ethanol; acetaldehyde is obtainable at 92% efficiency from ethanol.

Experiments of this nature established the possibility of obtaining an efficiency of 65-70% without credit for the by-products. They formed a basis for the conditions which were recommended for the operation of the butadiene plants. These conditions were intentionally mild with regard to presumed or known deteriorating effects on the catalyst, while sufficient productivity was maintained.

A difficult problem involved the amount of tantalum oxide to use in the catalyst. The supply of ore was limited, and careful conservation was further necessitated because of other important wartime uses. Fortunately only a low percentage on the silica gel was required to give catalysts of good activity; however, the activity varied with concentration as did the decline of activity with use. Variation of promoter concentration did not cause large effects in the efficiency of utilizing ethanol (Table III); but in view of the tremendous quantities of alcohol involved, it was necessary to be as economical as possible in the use of this raw material. It was decided that all of these factors were best satisfied by a catalyst of about 2% tantalum oxide, and this was generally installed in the plants.

The molar ratio of ethanol to acetaldehyde and the temperature were highly significant and were, to some extent, compensating factors affecting the efficiency, the operating cycle, and the nature of the by-products. As shown in Table IV, the efficiency was better at 325° C. with a feed mixture of 3 moles of ethanol to 1 of acetaldehyde than it was at 300° or 350° C.; with a mixture of 2 moles of ethanol to 1 of acetaldehyde it was better at 350° than at 325° C. With the latter proportion of reactants and the same space velocity the efficiency was inferior at 375° C.

The effect of molar ratio and temperature on decline in activity with use—a factor of much importance in determining the operating cycle—was even more striking, as shown by Figure 1.

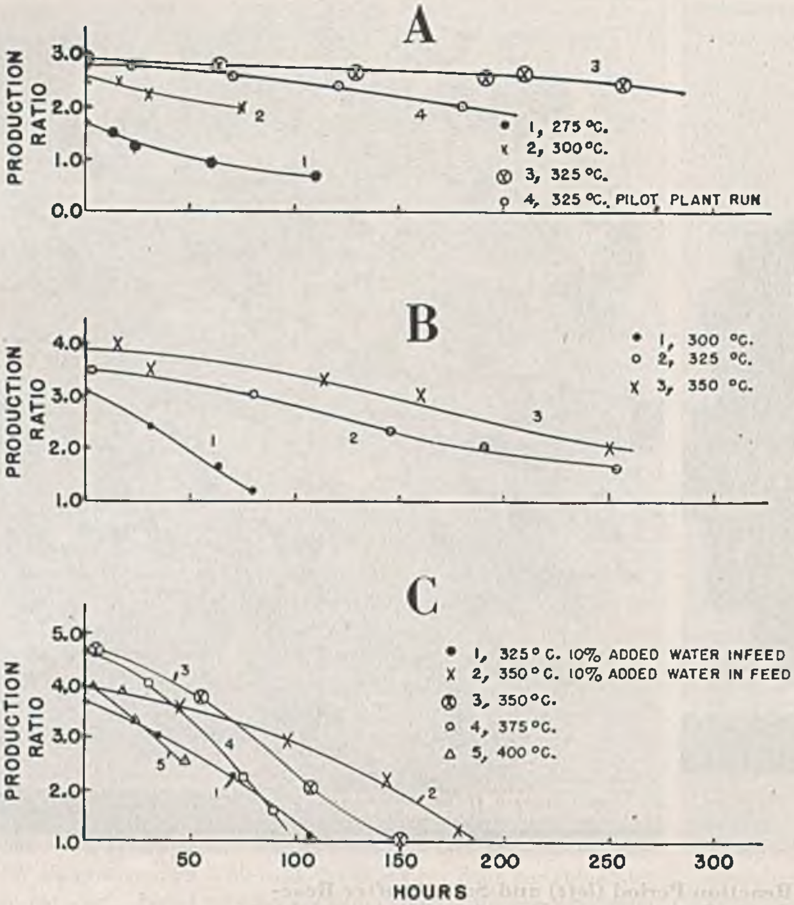


Figure 1. Production Ratio (Pounds of Butadiene/Hour/Cubic Foot of Catalyst) *vs.* Time of Operation (Hours) at a Space Velocity of 0.33

Feed molar ratio, ethanol to acetaldehyde: *A*, 3 to 1; *B*, 2.5 to 1; *C*, 2 to 1

With a mixture containing 3 moles of ethanol to 1 of acetaldehyde, the decline in production ratio with time was very slow at a temperature of 325° C. (curve 3, Figure 1*A*) but was considerably accelerated at 300° C. Correlation with pilot plant production is shown by curve 4. Good agreement was reached, although recovered feed, containing diluents, was used in part of the pilot plant run. With a molar ratio of 2.5 to 1, similar effects were noted, except that somewhat higher temperatures were required for best results (Figure 1*B*).

With a molar ratio of 2 to 1 a considerable increase was noted in initial productivity due to the higher aldehyde concentration. This also resulted in a rather rapid loss of activity through fouling, even at 350° C. (curve 3, Figure 1*C*). The addition of 10% of water to the feed lowered the rate of decrease and the initial production ratio, so that the average productivity was hardly affected. The addition of water did not prevent rapid fouling at 325° C. High temperatures (375° and 400° C.) were even less satisfactory at the space velocity used.

In securing the maximum over-all productivity, the time spent in burning off carbonaceous deposits must also be taken into consideration. Further, the larger the amount of this deposit the longer would be the time required for its removal, since this step is highly exothermic and the catalyst is very sensitive to temperatures in excess of 500° C. In practice it was considered undesirable to exceed a temperature of 400° C. By using steam as a diluent during much of the burn-off period and by operating with feed mixtures containing ethanol and acetaldehyde in a minimum molar ratio of about 2.5 to 1, excessive thermal deterioration of the catalyst was avoided.

The possibility was investigated of employing pressure as a means of increasing production. At 80 pounds gage in experiments of about 30-hour duration, the average production ratios for the period were about equal to those from similar experiments at atmospheric pressure, but the subsequent carbon burn-off was about ten times as large. At the elevated pressure the amount of carbonaceous deposit was reduced by increasing the ratio of ethanol to acetaldehyde in the feed, although it remained greater relative to the butadiene production than at atmospheric pressure. Similar effects were noted for a smaller increase in pressure (15 pounds gage).

Because of the large number of by-products, only the more significant and readily isolable ones were determined in the laboratory experiments. Knowledge of the other components progressed with the larger scale operations, which provided increased facilities, manpower, and quantities of material for such investigations. The data of Table V represent an evaluation made on a plant unit during one month of operation in which the conditions were as follows: temperature, 343° C.; space velocity, 0.37 (2.8 gallons per hour per cubic foot of catalyst); and molar ratio of ethanol to acetaldehyde, 2.75 to 1. Significant amounts of butyraldehyde, methyl ethyl ketone, ethyl acetate, and acetic acid, which are made in the formation of acetaldehyde, are included in the values in Table V.

The major by-products comprise ethyl ether, ethylene, hexenes and hexadienes, ethyl acetate, pentenes and

Table III. Effect of Concentration of Tantalum Oxide

(Temperature, 320° C.; feed ratio EtOH/AcH, 3/1)

Experiment No.	1[a]	2	3	4	5	6
Tantalum oxide, %	0.0	0.6	2.0	5.5	5.5	2.0
L.h.s.v.	0.58	0.58	0.58	0.58	1.0	0.33
Production ratio, g./hr./l. of catalyst	6	37	66	96	160	47
Single-pass yield to butadiene from EtOH and AcH, %	2.3	15.0	27.3	35.0	27.9	31.0
% efficiency to butadiene from:						
Ethanol	..	60.9	61.2	52.1	50.3	...
Acetaldehyde	..	68.8	80.4	80.0	79.3	...
Ethanol, ultimate	..	62	67	61	60	...

[a] Temperature, 365° C.

Table IV. Effect of Molar Ratio and Temperature

Experiment No.	1[a]	2	3	4[b]	5[b]	6	7	8[a]
Feed ratio, EtOH/AcH	3:1	3:1	3:1	2.5:1	2.5:1	2:1	2:1	2:1
Temperature, ° C.	300	325	350	325	350	325	350	375
Catalyst, Ta_2O_5, %	2.0	1.3	1.3	2.0	2.0	0.8	1.3	2.0
L.h.s.v.	0.33	0.58	0.58	0.33	0.33	0.50	0.58	0.33
Single-pass yield to butadiene from EtOH and AcH, %	28	21	23	22.1	28.8	23	32	31
Production ratio, g./hr./l. of catalyst	42	58	64	34	47	53	91	49
% efficiency to butadiene from:								
Ethanol	58.9	57.8	50.8	58.4	54.8	58.6	57.4	43.5
Acetaldehyde	69.5	78.5	78.0	72.6	80.2	67.6	78.2	72.8
Ethanol (ultimate)	61	64	59	62	63	60	64	53

[a] Efficiency determined after 60 hours of operation at these conditions.
[b] Efficiency determined after 168 hours of operation at these conditions.

Table V. Products from Ethanol and Acetaldehyde

Product	% of Ethanol Consumed	Product	% of Ethanol Consumed
Methane	0.14	Butyraldehyde and methyl ethyl ketone	0.30
Carbon monoxide	0.08	Hexenes-hexadienes	3.97
Carbon dioxide	0.03	Ethyl acetate	1.17
Ethylene	3.91	Ethyl acetal	1.25
Ethane	0.09	Crotonaldehyde	0.1
Propylene	1.69	Butanol–crotyl alcohol	1.25
Propane	0.12	Butyl acetate	0.11
Butadiene	63.9	Vinylcyclohexene	0.15
Butene	1.41	Hexanol	0.16
Butane	0.01	Hexaldehyde	0.54
Methyl ethyl ether	0.30	Acetic acid	1.36
Pentenes	0.44	Unidentified products	3.8
Pentadienes	0.46	Loss	5.1
Ethyl ether	8.0	Total	100
Ethyl vinyl ether	0.15		

Table VI. Zirconia Catalyst

Experiment No.	1	2	3
Catalyst, ZrO_2, %	2	1.4	1.6
Feed ratio, EtOH/AcH	3:1	3:1	3:1
Temperature, ° C.	325	305	325
L.h.s.v.	0.58	0.33	0.33
Production ratio, g./hr./l. of catalyst	55	37	45
Single-pass yield to butadiene from EtOH and AcH, %	20	24	29
% efficiency to butadiene from:			
Ethanol	50	53	50
Acetaldehyde	77	68	77
Ethanol (ultimate)	59	57	59

Table VII. Butadiene from Ethanol

Feed mixture, moles	
Ethanol	15.8
Acetaldehyde	5.3
L.h.s.v.	0.32
Production ratio, g./hr./l. of catalyst	51
Temperature, ° C.	325
Products, moles	
Butadiene	3.4
Butenes (estd.)	0.2
Hydrogen	1.8
Acetaldehyde	1.9
Ethanol	9.0
Efficiency[a], %	64

[a] With debit for acetaldehyde at 92% efficiency from ethanol.

pentadienes, acetic acid, and butanol. The hexadienes consist mainly of 1,3-cyclohexadiene, 2,4-hexadiene, and 3-methyl-1,3-pentadiene with small amounts of 1,3-hexadiene. The hexenes were not identified but are believed to be both branched and straight-chain isomers. The pentadienes comprise both piperylene and isoprene in a ratio of about 6 to 1. The pentenes isolated and identified thus far consist of 2-pentene, 2-methyl-2-butene, and 2-methyl-1-butene, and the presence of 1-pentene and 3-methyl-1-butene is indicated. The butene mixture contained about 35% of 1-butene, 44% of *trans*-2-butene, 21% of *cis*-2-butene, and 0 to 3% of isobutene. Equilibrium apparently does not exist among the straight-chain butenes, since these values do not correspond with those of Voge and May (*3*). The presence of an excess of 1-butene indicates that this isomer is formed preferentially on the catalyst.

Several of the by-products were utilized. These included ethylene, butene, ethyl ether, and butanol (and crotyl alcohol); they correspond to about 15% of the alcohol consumed. The details of the operations were worked out through the cooperation of many individuals connected with the project. Isolation of the other components in a practical manner was more difficult; the high boiling oils, in particular, seemed of importance only as fuel, but fortunately they were relatively small in amount.

Other oxides supported on silica gel which are capable of promoting the formation of butadiene from ethanol and acetaldehyde are those of zirconium, columbium, thorium, uranium, and titanium, in order of decreasing activity. Zirconia on silica gel, the second most favorable catalyst, gave results of intermediate character between those of columbium and tantalum oxides. It was considered as a replacement catalyst for the butadiene plants in case the supply of tantalum became inadequate. The maximum efficiency obtained was 59% from ethanol to butadiene. A few selected experiments are given in Table VI. Butene formation was somewhat greater than with catalysts of tantalum oxide, and the purity of the butadiene in the C_4 fraction ranged from 91 to 95%. A favorable synergistic action was sought from combinations of the oxides of tantalum, columbium, and zirconium, but such effect was not definitely established.

BUTADIENE FROM ETHANOL

There is considerable fascination in the idea of passing ethanol alone into a converter and obtaining butadiene as the major product without the use of supplementary equipment for providing acetaldehyde. This is apparently what was originally intended in the Lebedev process, in which improved results were subsequently obtained by recycling acetaldehyde.

Attempts to produce satisfactory results were generally unsuccessful with our preparations of the Lebedev catalysts. However, the addition of cadmium oxide (*1*) to the silica base catalysts gave butadiene with an efficiency of 45 to 50% at temperatures of 300° to 350° C. Somewhat better results were obtained when copper was employed, but the amount of recycle acetaldehyde was critical, since otherwise appreciable hydrogenation of the butadiene occurred. Table VII shows the results of one experiment in which one fourth volume of supported copper catalyst (*4*) was employed with a silica gel–supported tantalum oxide catalyst; the butadiene, after removal of acetaldehyde, was about 95% pure. An increase of the copper catalyst to half the mixture resulted in a purity somewhat below 90%.

CONCLUSIONS

The ethanol-acetaldehyde process was adopted since it seemed to offer the greatest and the most certain advantages under the rapid development imposed by the war emergency. The ethanol-crotonaldehyde process did not provide a higher production of butadiene per gallon of alcohol consumed, and it would have required a larger amount of equipment and a greater number of operating personnel. The present studies in the development of this process probably had their greatest value in indicating the right path to the successful development of the ethanol-acetaldehyde process. The Lebedev type of operation might have matured into a slightly superior process in some respects, but it presented, a priori, the disadvantage of compromise in the choice of conditions for two distinct reactions: dehydrogenation of ethanol and conversion of ethanol and acetaldehyde to butadiene; also the complications of a larger and more variable amount of by-product butene seem certain in plant operation. The ethanol-acetaldehyde process fulfilled its mission in providing a large supply of butadiene in the shortest possible time from what was a surplus material at that time.

ACKNOWLEDGMENT

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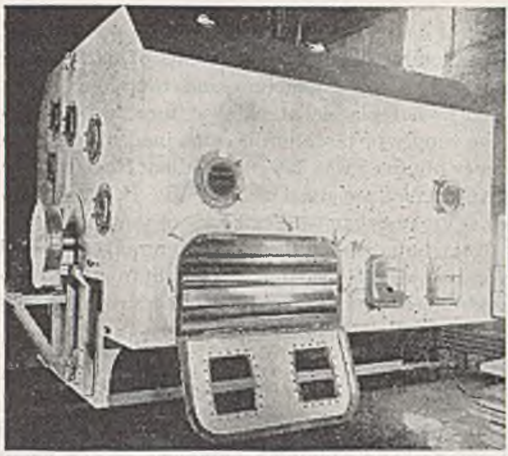
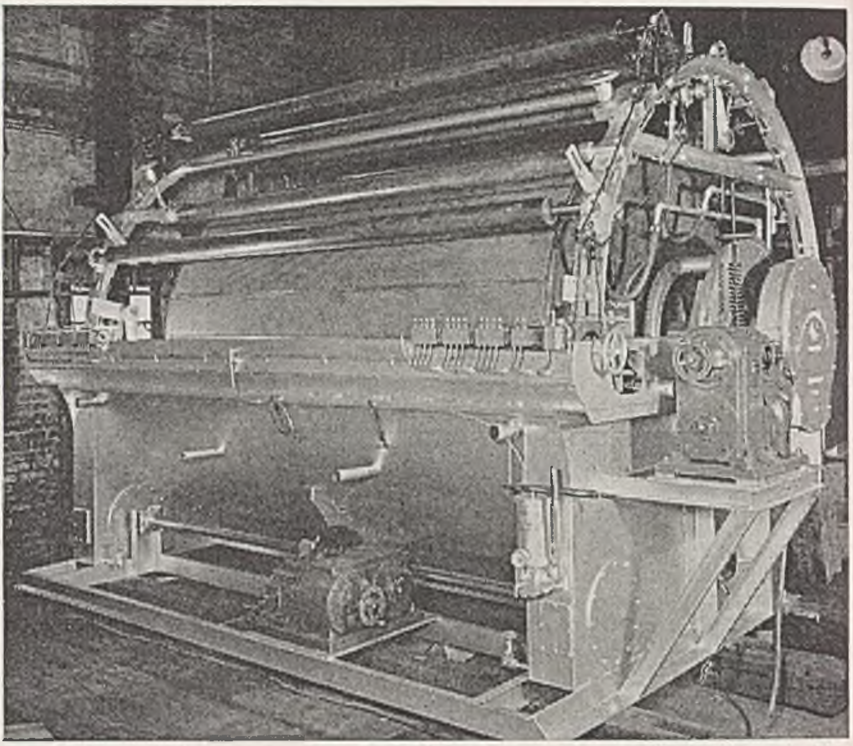
LITERATURE CITED

(1) Quattlebaum, W. M., Toussaint, W. J., and Dunn, J. T., *J. Am. Chem. Soc.*, submitted for publication.
(2) Tallalay, A., and Tallalay, L., *Rubber Chem. Tech.*, 15, 403 (1942).
(3) Voge, H. H., and May, N. C., *J. Am. Chem. Soc.*, 68, 550 (1946).
(4) Young, C. O., U. S. Patent 1,977,750 (1934).



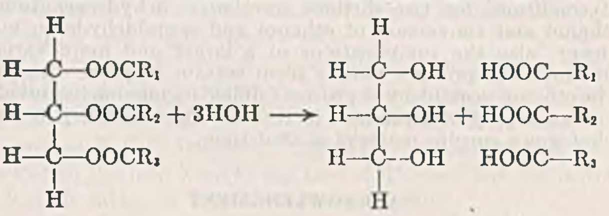


Preinstallation View (*right*) of Rotary Vacuum Filter Used in the Fatty Acid Separation Step of the Emersol Process. The Unit as Installed (*above*) Is Enclosed in a Hood to Prevent the Escape of Methanol Vapors into the Atmosphere. The filter Was Specially Designed for this process by Filtration Engineers, Inc.

EMERSOL PROCESS . . . *A Staff Report*

RICHARD L. DEMMERLE, Associate Editor

UNTIL recently the fatty acid field has been more of an art than a science; therefore, tradition and custom have played an important part in determining the nomenclature employed in the discussion and specifications of the products themselves. The natural fatty acids are, with few exceptions, monobasic aliphatic compounds consisting of an even-numbered hydrocarbon chain and terminating in a carboxyl group (*5*). Their principal occurrence is in the form of mixed glyceryl esters, the major portion of natural fats, from which the free acids are obtained by the following hydrolysis known as splitting:



$$\begin{array}{l} \mathrm{H_2C{-}OOCR_1} \\ \mathrm{HC{-}OOCR_2} + 3\mathrm{HOH} \longrightarrow \\ \mathrm{H_2C{-}OOCR_3} \end{array} \begin{array}{l} \mathrm{H_2C{-}OH} \\ \mathrm{HC{-}OH} \\ \mathrm{H_2C{-}OH} \end{array} \begin{array}{l} \mathrm{HOOC{-}R_1} \\ + \mathrm{HOOC{-}R_2} \\ \mathrm{HOOC{-}R_3} \end{array}$$

Although the reaction is reversible, it is kept going forward by the presence of a large excess of water, and is accelerated by mineral acids, soaps, and sulfonic acids, the most famous of which is the Twitchell reagent (*3, 6*). Since the esters are usually of the mixed type containing more than one fatty acid group, the reaction produces a mixture of several fatty acids which, with some purification, is used directly in soap manufacture.

A substantial market exists, however, for the separate solid and liquid fractions of this mixture, often referred to as commercial stearic acid and red oil. Interest in this separation was first evinced over a century ago by candle manufacturers who endeavored to make a superior nonwilting product by using only the hard stearic acid instead of the whole tallow or hog grease. Uses for red oil or oleic acid had not been developed at that time; therefore, after the fat was split and the solid fraction removed, the liquid fraction was discarded. The picture is vastly different today, however; oleic acid actually exceeds its companion acid in the many industries they enter, such as the manufacture of fine soaps, cosmetics, textiles, lubricants, plastics, and pharmaceuticals. The 1945 production figures (*11*) were 54,206,000 pounds of commercial stearic acid and 74,140,000 pounds of commercial oleic acid.

This article discusses the preparation of commercial stearic and oleic acids by the two principal methods of separation now employed—the continuous Emersol process, based on fractionation of the acids from a polar solvent, and the conventional batch method of mechanical pressing. The latter, which has remained approximately at its initial level of development for the past hundred years, makes use of the fact that saturated acids with a chain of C_{10} or longer exist in the solid phase at room temperature whereas the unsaturated acids remain in the liquid state. By this process the palmitic and stearic acids, saturated compounds of C_{16} and C_{18} lengths, are separated from oleic and linoleic acids (both C_{18}), containing one and two double bonds, respectively. Actually, the commercial stearic acid produced by this method is a mixture of stearic and palmitic acids, for many years considered to be pure stearic acid and used as such by the industry. Although the composition of this product may vary somewhat, best engineering practice is achieved when the ratio is approximately 45 parts of stearic to 55 parts of palmitic acid (Figure 1). Because the trade has become accustomed to this 45-55 mixture, the Emersol plants in existence have confined themselves principally to making this traditional product, although they are capable of producing fractions high in either stearic or palmitic acid content.

As would be expected, the purity of a fatty acid sample is reflected by the temperature at which it crystallizes; use is made of this relation in the universally employed titer test of the American Oil Chemists Society and the AMERICAN CHEMICAL SOCIETY. In reality, the titer is the maximum temperature reached during the transformation to the solid phase due to the heat of crystallization at the solidification point. In the case of commercial stearic acid, this measurement is expressed as degrees Fahrenheit, and for the better grades containing only 3% oleic acid, it ranges between 131° and 132° F. With products containing as much as 17% oleic acid, this reading may drop to 127° F. or lower. The titer of the oleic acid fraction, on the other hand, is expressed in degrees centigrade by convention, varying from 0° for the purer samples to 18° C. for those high in saturated acid.

In addition to titer, acid number and color and iodine values are used as valuable means of determining the purities of the various fatty acid products.

SEPARATION BY MECHANICAL PRESSING

This method consists briefly of chilling the mixture of the fatty acid products of the fat splitting reaction and subjecting the resulting cakes to mechanical pressure to express the liquid acids. Successful operation depends on keeping the composition of the solid acid constituents at a level of approximately 45% stearic and 55% palmitic acid. Although this so-called eutectic mixture is the one usually found in nature, some basic stocks vary in composition and have to be blended. This ratio should be maintained because it is conducive to the formation of a crystal structure which, upon chilling, affords the most complete separation of the liquid and solid fractions when pressure is applied. Because of this consideration the mechanical method has been limited in the main to the production of the 45-55 mixture commonly known as commercial stearic acid.

The cakes for the mechanical pressing operation are formed by cascading the melted mixed acids from the splitting reaction, after purification by distillation, into a series of flat aluminum pans about 2 feet × 1 foot × 2 inches in size, and chilling them slowly to 36° F. The solidified fatty acid cakes are then removed from the pans, wrapped in burlap, and stacked in hydraulic presses where the initial pressing takes place. Although this step removes a substantial portion of the liquid acids, a considerable amount remains behind because of mechanical entrainment and the collapse of the cake during this cold pressing. To remove these residual liquid fatty acids, the cakes are remelted, recast, and repressed in successive hot pressing operations at temperatures around 100° F. The total number of pressings to which a given lot is subjected is used to indicate the purity of the solid product; hence the trade refers to single-pressed, double-pressed, and triple-pressed commercial stearic acids (*9*).

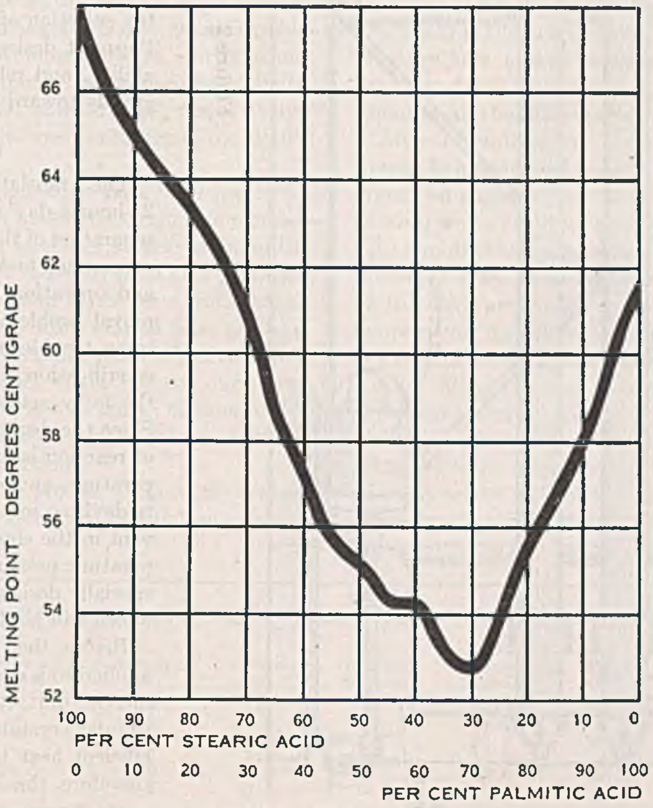


Figure 1. Typical Melting Point Curve for Commercial Stearic Acid

The liquid acids separated during the cold pressing operation constitute the red oil of industry but must be purified if a better grade of oleic acid is desired. The expressed fraction of the subsequent hot pressings, however, contains large quantities of the solid acids in solution and for the sake of economy must be blended with the original feed for reprocessing. This recycling amounts to about 40% of the weight of the total acids in process and as such contributes considerably to the cost.

Some other disadvantages of the older process are also apparent. Being a batch method, its labor requirements are considerably larger than those of an Emersol plant of equivalent capacity; the actual figures are twelve or fourteen operators to two. Its dependency upon the maintenance of a fixed ratio of palmitic to stearic acids greatly limits the pressing method with respect to the utilizable raw materials and the products obtainable from them. In addition, the several disjointed manual operations inherent in this process give rise to excessive product losses and, consequently, an untidy plant.

For many years fatty acid processors had been aware of these faults of their method and in some instances had started investigations to find an improved, less wasteful process to separate mixed fatty acids. Fractional distillation (*1*), an apparent answer to the problem, had been used to produce several saturated acids commercially but was not feasible to separate compounds of equal chain lengths (C_{18}) from one another because of their almost identical boiling points.

THEORETICAL CONSIDERATIONS

Before initiating work on the Emersol process, Emery Industries had investigated the possibility of developing any one of a number of laboratory methods of separation into a production scale. The Twitchell lead soap procedure was studied and, although useful for analytical purposes, was shown to have no commercial value. Attempts to remove the liquid fraction from partially crystallized mixed acids by means of water and an emulsifying agent also proved fruitless. Likewise, the use of a selective solvent for the same purpose was unsuccessful because it did not overcome the disadvantage of the mutual solubility of the acids in one another.

It became apparent that what was needed was a means to cause the solid acids to separate from a polar solvent solution of the mixed acids in an insoluble form that could be removed by filtration. Further investigations indicated that this could best be accomplished by lowering the temperature of the solution to the point at which practically all of the solid acids were crystallized (*2*).

SELECTION OF SOLVENT

The major problem in the development of the Emersol process was the selection of the most efficient solvent, from both a technical and economic viewpoint, and the determination of the optimum concentration at which it should be used. The actual choice of the

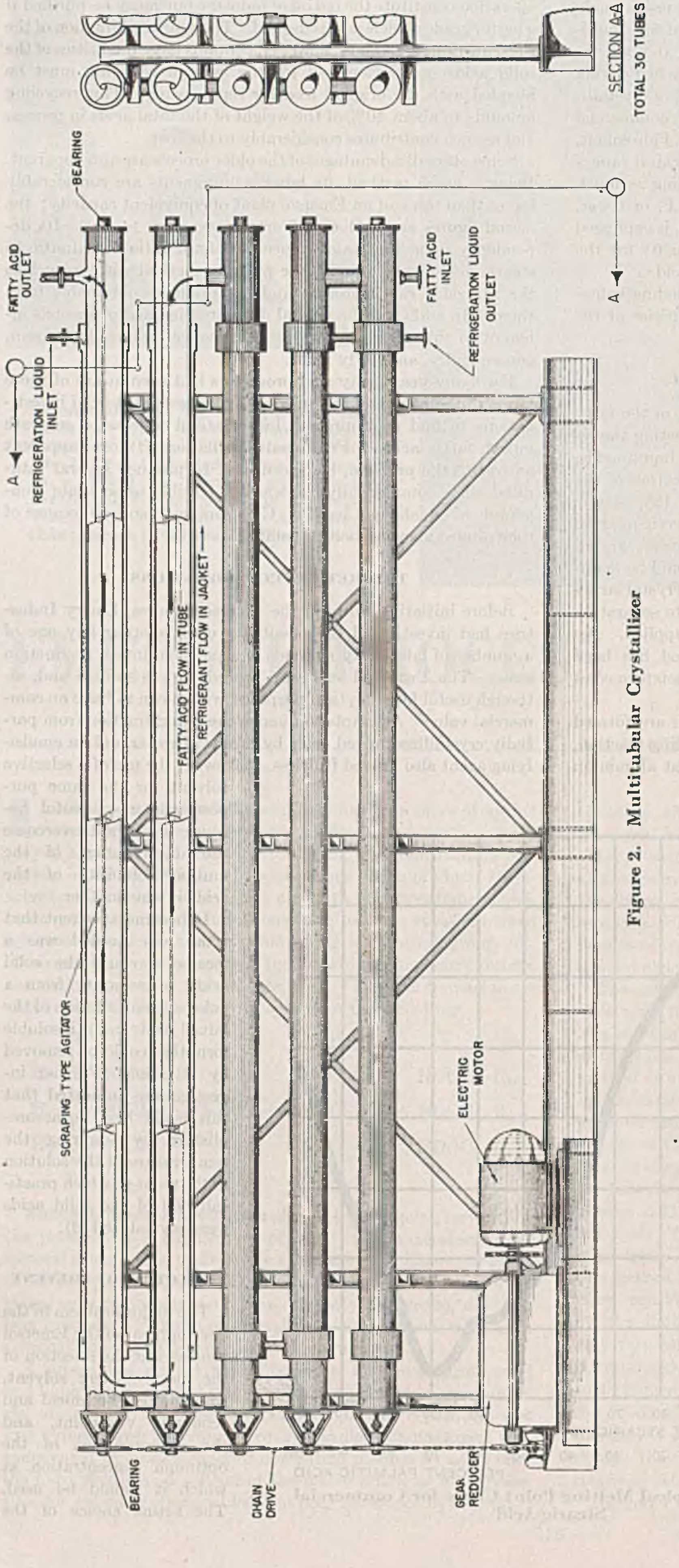


Figure 2. Multitubular Crystallizer

solvent depended upon many factors; not the least of them was the type of crystal structure it imparted to the solid acids during chilling. Petroleum ether and chlorinated hydrocarbons, for instance, gave flat, pearly, plate-type crystals, which because of their structure had bad filtering and solvent washing characteristics. More desirable were the granular needlelike crystals which could be formed in acetone, methanol, and ethanol solutions.

It developed subsequently that water-miscible solvents containing not more than 15% water were the best media from which to crystallize the solid acids, provided the total acid concentration was not greater than 30%. When this figure was exceeded, the precipitate tended to form a slimy mass, and it was observed that a water content of more than 15% did not afford complete separation of the acids.

Another consideration was the temperature to which the solvent solution of the mixed acids had to be cooled to effect complete crystallization of the solid components. This was especially important from an economic point because refrigeration is one of the major costs in a solvent crystallization process. Study again showed that, as far as this matter was concerned, ethanol, methanol, and acetone were preferable to the other solvents tested.

Stability and ease of removal were the final criteria that the chosen solvent had to meet. Low boiling solvents, while satisfactory for laboratory testing, introduced serious toxicity hazards and large solvent losses in plant operations. On the other hand, the complexity of the removal of high boiling solvents, because of the vacuum evaporation necessary to prevent the subjection of the products to high temperatures, precluded their usage.

Final evaluation of all these factors dictated the selection of 90% methanol as the solvent with the most desirable qualities. Its low cost, availability, and relative ease of recovery contributed greatly toward this decision (7).

DESIGN PROBLEMS

The translation of these developments into a 24-hour-a-day continuous process capable of 95% separation of the liquid and solid acids was a time-consuming task with many difficulties in design and operation to be overcome. The solvent removal problem of the Emersol process presented some trouble at first because of the possibility of esterification reactions between the methanol and the fatty acids during the course of distillation. Since the degree of product formation in this type of reaction is directly dependent upon time, temperature, and concentration, it became necessary to devise a means of removing the bulk of the solvent in the shortest time and at the lowest temperature possible. This was accomplished by a specially designed countercurrent stripping column which will be described later in the article.

Before the foregoing developments could be applied to a continuous, uniformly operating commercial unit, it was necessary to design a multitubular crystallizer (Figure 2) that would ensure efficient heat transfer. The rate of cooling and therefore the rate of crystal formation was important economically as well as practically because it determined the size of the unit, the amount

Table I. Typical Raw Materials and Emersol Product Processed from Them

Raw Material	Titer, ° C.	Iodine Value	Acid Product	Yield, %	Titer	Iodine Value
No. 1 tallow	42.4	52.2	Com. stearic	51	129.5° F.	6.0
			Oleic	49	2.0° C.	...
White grease	38.7	62.5	Com. stearic	38	128.7° F.	6.0
			Oleic	62	2.0° C.	...
Yellow grease stearin	45.2	44.7	Com. stearic	52	129.5° F.	6.0
			Oleic	48	2.0° C.	...
Garbage grease	37.5	68.4	Com. stearic	35	127.6° F.	6.0
			Oleic	65	2.0° C.	...
Linseed oil	...	185	Solid acids	14	44.7° C.	87.0
			Liquid acids	86	...	195.0
Soybean oil	...	129.3	Solid acids	15	48.5° C.	50
			Liquid acids	85	...	144
Sardine oil	...	160.0	Solid acids	25	...	30.0
			Liquid acids	75	...	201.0

of solvent required and, to a certain degree, the type of crystal formed. If this rate was too fast, precipitation rather than crystallization tended to occur and slow filtration resulted. The crystallizer tubes were equipped with internally rotating blades to scrape the walls and thereby ensure a clean surface to afford efficient heat transfer. These blades had to be designed in such a manner as to prevent any blockage of flow and crystal deposition upon the scraper. An optimum rotational velocity for the scraper also had to be determined; too great a speed resulted in the breaking of the crystals and too low a speed impeded heat transfer.

Because of the corrosive nature of both hot and cold solutions of fatty acids in methanol, it was necessary to use Type 316 stainless steel or aluminum throughout the process as construction materials.

THE PROCESS

The transition from the laboratory to the pilot plant stage culminated in the expansion of the latter to a semicommercial plant. This unit, capable of producing 20 tons of finished products per day, evolved from the development work started some years earlier, and was the forerunner of two commercial plants at Cincinnati with capacities of 30 and 40 tons, respectively. The recently completed large unit was constructed by Blaw-Knox Company.

The Emersol process is extremely flexible, both with regard to raw materials and products. It can make high-grade commercial stearic acid or fractions very high in either stearic or palmitic acids alone, as well as a 2° C. titer (or lower) oleic acid product. Its possible raw materials (Tables I and II) cover a wide range, including tallow, greases and stearin from animal fats, garbage grease, linseed oil, soybean oil, sardine oil, palm oil, cottonseed oil, and ucuhuba fat. The versatility of the process, due to its precise control of the crystallization temperature, enables it to be used to fractionate within families of fatty acids as well as to separate the solid and liquid compounds.

The commercial operation of the process (Figure 3) begins with the purification of the feed stock by distillation, a step necessary to remove the color, odor, neutral fat, and unsaponifiable materials. Because the eventual separation is physical, these undesirables must be eliminated here to prevent their appearance in the final products. The belief has been expressed, however, that it may be possible to split very high grade fats by the autoclave technique and obviate the distillation purification.

The fatty acids and methanol are proportioned by positive displacement pumps discharging through flowmeters to the crystallizer. During passage of the mixture to the latter unit, a small quantity of crystal promoter is introduced into the steam. This agent, usually the neutral fat of one of the acids being processed, aids in the formation of filterable crystals, provided its concentration does not exceed 3.5% and remains preferably at a level of about 1%. If the amount of neutral fat is excessive, large crystals are formed that occlude the liquid acids and make the separation extremely difficult. This disadvantage is also accompanied as well by an inability to fractionate the solid acids from one another. The exact nature of the crystal promotion mechanism is unknown, but it is believed that the neutral fat furnishes foci at which the acid crystals are formed. If the feed stock contains some neutral fat, no further addition is required (*10*).

Refrigeration for the crystallizer and the filtering room is furnished by a two-stage ammonia machine, driven by a steam turbine, the exhaust of which is used in the solvent recovery operation. Cooling is accomplished by pumping cold methanol countercurrently through the jackets of the stainless steel crystallizer tubes to reduce the temperature of the feed to about 10° F. and absorb the heat of crystallization. Recovery of 75% of refrigeration is achieved by cycling this fluid through an economizer with the cold oleic acid–methanol filtrate from the next operation. Simplicity of design results from the use of a cooling agent of the same composition as the solvent and a single motor to drive all of the scraper blades in the tubes of the crystallizer. This unit (Figure 2) is the heart of the process; control of the cooling temperature here makes possible the single-stage separation of the liquid and solid acids or, upon recycling, the multistage fractionation of the fatty acids into the desired cuts.

After crystallization, the slurry from the crystallizer is delivered to an enclosed, rotary, vacuum filter (shown in the photographs on page 126) situated in a refrigerated room so designed as to keep the crystalline component solid. The filter is equipped with a multistring discharge, instead of the usual blade, to handle the bulky cake. During the rotation cycle the solid components on the filter are continuously washed with fresh solvent, whose temperature and flow are automatically controlled, to remove any residual mother liquor containing liquid acids.

After filtration, the solid cake which now contains 30–60% of solvent is melted and led to the so-called stearic still where recovery is effected. The oleic acid–methanol solution, before being fed to its respective still, is passed through the economizer where it serves to cool the alcohol entering the process; at the same time the solution is preheated prior to its own distillation.

Table II. Average Percentages in Which Common Fatty Acids Appear in Natural Substances

Acid	Chain Length	Double Bonds	Brown Grease	Coconut Oil	Cottonseed Oil	Garbage Grease	White Grease (Lard)	Palm Oil	Soybean Oil	Tallow	Yellow Grease Stearin
Lauric	12	0	[a]	48.0	..	[b]	..	..	..	..	[c]
Myristic	14	0	[a]	17.5	0.5	[b]	1.0	1.0	..	2.0	[c]
Palmitic	16	0	[a]	8.8	21.0	[b]	26.0	42.5	6.5	30.0	[c]
Stearic	18	0	[a]	2.0	2.0	[b]	11.5	4.0	4.5	21.0	[c]
Oleic	18	1	56.0	6.0	33.0	46.0	58.0	43.0	33.5	45.0	49.0
Linoleic	18	2	8.0	2.5	43.5	15.0	3.5	9.5	52.5	2.0	5.0

[a] Variable (total solid acids, about 36%). [b] Variable (total solid acids, about 39%). [c] Variable (total solid acids, about 46%).

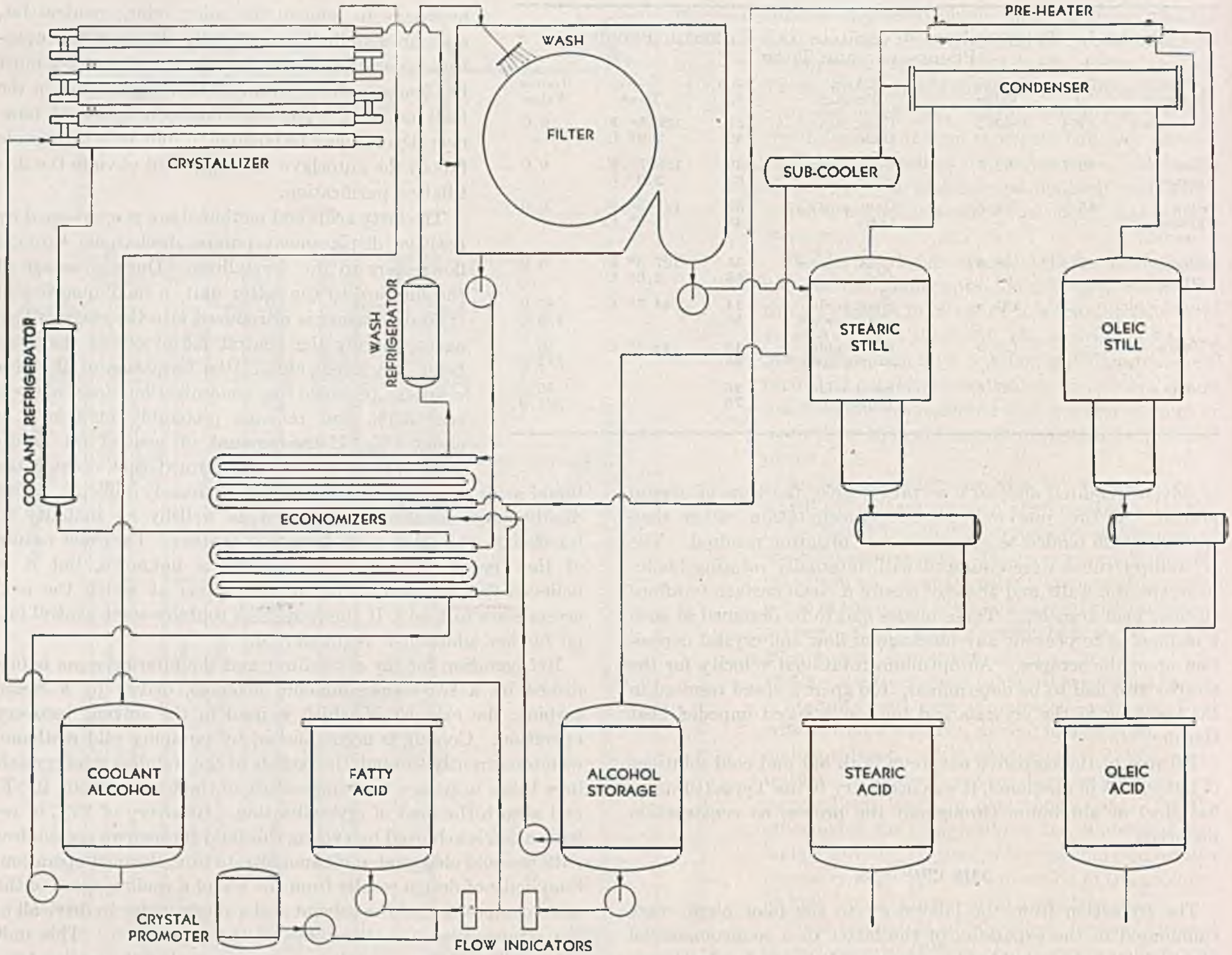


Figure 3. Flow Sheet of Emersol Process

The stills are of special design to prevent any esterification reactions between the methanol and the acids involved during the course of solvent removal. Of stainless steel construction, they consist essentially of a vertical stripping column comprised of a series of trays in staggered cascade fashion, a steam-heated preliminary evaporator, and a decanting section for the separation of the fatty acid from the water at the bottom.

In operation, the solvent–fatty acid solution, after partial evaporation, is introduced at the top of the stripping column and allowed to trickle downward over the trays to the boiler. During this course its solvent component becomes successively vaporized by the upward countercurrent flow of water vapor which becomes condensed as a result of the heat loss. By the time the fatty acid reaches the boiler, its solvent concentration is too low for esterification to take place, and at the same time its water content is high enough to permit separation from the water.

The latter is accomplished in a decanting tank which is really a section of the boiler, separated by a perforated baffle plate through which the mixture passes. Here it assumes a quiescent state in which an upper layer of fatty acids, which is continuously decanted off, separates from the lower aqueous portion that flows back to the main part of the boiler for revaporization and use in the stripping operation.

The boiler temperature is maintained a few degrees above the boiling point of water by a thermostatically operated steam valve, and a steam bleeder provides a means to replace water losses due to the entrainment in the fatty acid phase in the decanter (*4*).

The recovered solvent, about 90% methanol, is cooled and recycled to be mixed with the fatty acids entering the process, or may be used if necessary as the wash solvent during filtration. The fatty acid products, delivered from the distillation at about 218° F., are passed through coolers which reduce the temperature to about 170° F. in order to prevent a detrimental effect of heat, especially upon exposure to air

Table III. Comparative Cost Data on Production of Fatty Acids by Mechanical Pressing and Emersol Methods

	Cost per 1000 Lb. for Separating Single-Pressed Stearic Acid and 4-Titer Red Oil		Cost per 1000 Lb. for Separating Double-Pressed Stearic Acid and 4-Titer Red Oil	
	Pressing method	Emersol method	Pressing method	Emersol method
Labor	$2.82	$0.67	$3.47	$0.80
Supervision	0.15	0.14	0.17	0.17
Maintenance	1.30	0.42	1.30	0.50
Sulfuric acid	0.04	...	0.04	...
Press cloth replacement	1.11	...	1.21	...
Hair mat replacement	0.75	...	0.90	...
Miscellaneous supplies	0.06	0.11	0.06	0.11
Steam	0.60	1.20	0.64	1.40
Power and light	0.51	0.23	0.55	0.23
Water	0.04	0.04	0.04	0.04
Acid boiling and filtering red oil	1.26	...	1.33	...
Methanol	...	0.23	...	0.27
Total	$8.64	$3.04	$9.71	$3.52

After the products are collected in storage tanks, the milling and packaging steps that follow are substantially the same as those used in conjunction with other methods of fatty acid manufacture.

Since the Emersol process involves the use of a flammable solvent, certain safety factors must be considered. The narrow explosive range of methanol, however, coupled with the fact that all of the operating units are enclosed, precludes the possibility of a combustible level being reached in the atmosphere. In addition, safety valves and alarms are dispersed throughout the plant to nullify any excess pressure rises and indicate any operational irregularities. The plants are designed for 24-hour-a-day operation, except for scheduled shutdowns for routine maintenance.

Comparison of the operating costs (Table III) with those for mechanical pressing indicates that Emersol's are about 65% less (*8*). This difference is due mainly to the higher labor figure for the batch method as well as its additional expense of liquid acid recycling and purification, operations not required in the continuous method of separation.

ACKNOWLEDGMENT

The author wishes to acknowledge the helpful cooperation of V. J. Muckerheide and L. D. Myers of Emery Industries in the preparation of this article.

LITERATURE CITED

(1) Bailey, A. E., "Industrial Oils and Fat Products", pp. 434–5, New York, Interscience Publishers, 1945.
(2) *Ibid.*, pp. 650–3.
(3) *Ibid.*, pp. 666–7.
(4) Brown, A. C., U. S. Patent 2,352,160 (1944).
(5) Hilditch, T. P., "Industrial Chemistry of Fats and Waxes", 2nd ed., p. 7, London, Baillière, Tindall and Cox, 1941.
(6) *Ibid.*, pp. 275–6.
(7) Kistler, R. E., Muckerheide, V. J., and Myers, L. D., *Oil & Soap*, 23, 146–9 (1946).
(8) *Ibid.*, 23, 150 (1946).
(9) Myers, L. D., and Muckerheide, V. J., U. S. Patent 2,293,676 (1942).
(10) *Ibid.*, 2,298,501 (1942).
(11) U. S. Dept. of Commerce, Repts. of Industry Div., Fats and Oils Unit, Bur. of Census, 1945.

Lime Treatment of Waste Pickle Liquor

Richard D. Hoak, Clifford J. Lewis[1]*, Charles J. Sindlinger, and Bernice Klein*

MELLON INSTITUTE, PITTSBURGH, PA.

The current scarcity of high-calcium lime suggested the studies reported in this paper, which describes methods for attaining equivalent results with the less reactive, but more readily available, dolomitic lime where this material must be used for waste pickle liquor treatment.

THE first paper in this series described rapid analytical methods for determining the available alkalinity of limes and limestones and the total sulfate ion in waste pickle liquor (*1*). The second article discussed certain factors having economic importance where high-calcium limes and limestones are used to treat such waste liquors (*2*).

Dolomitic limes were not studied in detail in the previous work. The demand for high-calcium lime is now so great that new uses which would require substantial quantities will be forced to await augmented production. This situation results in part from the fact that high-calcium limes have long enjoyed the select chemical and metallurgical markets which, expanded during the war, continue to tax the productive capacity of the industry. On the other hand, circumstances during the war years curtailed certain choice markets for dolomitic lime; this condition, coupled with competitive factors, has resulted in a moderate surplus of dolomitic lime at present. It appeared reasonable to assume that, if the over-all expansion and recovery of lime markets in general permit any surplus of lime to accumulate in the next several years, such a surplus will be of the dolomitic material.

Stream pollution increased during the war through the establishment of new industries, enlarged production by old ones, lack of materials for constructing adequate treatment works, and depletion of the engineering staffs of public health agencies. In all industrial sections of the country health authorities have now embarked on aggressive campaigns to reduce stream pollution by requiring satisfactory treatment of municipal and industrial wastes. Where treatment of acidic wastes is involved, lime normally provides by far the cheapest source of basic agent. Dolomitic limestone occurs abundantly and is calcined to lime of chemical quality near all major centers of steel production. In most cases, especially where its higher basicity is the principal factor, dolomitic lime can be delivered to consumers at lower cost than similar high-calcium products. A consideration of these factors emphasized the desirability of studying the reaction between dolomitic limes and acidic wastes, particularly spent pickling liquors, with the object of demonstrating the means whereby this low-cost basic agent can be employed most effectively.

EXPERIMENTAL WORK

Nine types of lime, two high-calcium and seven dolomitic, supplied by an Eastern Pennsylvania manufacturer, were investigated. The samples were characterized as follows:

3. High-calcium lime
4. Shaft-kiln dolomitic lime
5. Rotary-kiln dolomitic lime
6. 60-40 blend of shaft- and rotary-kiln dolomitic lime
7. High-calcium lime hydrated at atmospheric pressure
8. Dolomitic lime hydrated at atmospheric pressure
9. Dolomitic lime hydrated at 30 lb./sq. in.
10. Dolomitic lime hydrated at 30 lb./sq. in. and air-floated
11. Dolomitic lime hydrated at atmospheric pressure and air-floated

Samples 4, 5, 10, and 11 were used in most of the experimental work because they represent the usual types generally available. The samples were analyzed, and then basicity factors were calculated from the analyses and determined experimentally with sulfuric and hydrochloric acids. The resulting data are given in Table I.

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[1] Present address, Warner Company, Philadelphia, Pa.

Table I. Analyses and Basicity Factors of Nine Limes

	Sample Number								
	3	4	5	6	7	8	9	10	11
Analysis, %									
SiO_2	1.51	2.69	3.15	4.13	1.12	2.72	2.18	1.02	1.55
R_2O_3	0.88	0.70	0.70	0.53	0.95	0.48	0.57	0.60	1.02
CaO	94.17	55.03	54.95	53.99	71.40	45.04	41.77	42.01	45.90
MgO	0.65	40.70	40.10	40.52	0.59	33.02	29.73	29.69	32.75
Moisture + CO_2	2.58	0.68	1.05	0.96	25.90	18.93	25.15	26.54	18.67
Total	99.79	99.99	99.95	100.13	99.96	100.19	99.40	99.86	99.89
Basicity factor[a]									
Calcd.	0.9508	1.1202	1.1109	1.1071	0.7222	0.9126	0.8339	0.8357	0.9275
H_2SO_4	0.9515	1.0837	1.0855	1.0594	0.7045	0.8611	0.8302	0.8410	0.8876
HCl	0.9517	1.1189	1.1351	1.1027	0.7225	0.8952	0.8364	0.8389	0.9115

[a] Basicity factor = gram equivalent CaO/gram sample. HCl factors and H_2SO_4 factor for sample 3 determined by boiling 15 minutes; others, 30 minutes.

It is desirable to point out that, although the experimental data to be reported apply equally well to all dolomitic limes, Eastern Pennsylvania dolomites are somewhat less pure than those from other sources. A dolomitic quicklime from Ohio, for example, may contain approximately 0.8% silica and 0.2% R_2O_3; in consequence, this lime would contain a slightly higher proportion of calcium and magnesium oxides. This difference will be reflected in the corresponding hydrate, depending upon the extent to which air separation removes the impurities.

Determination of basicity by calculation from chemical analysis may be misleading because analyses do not reveal the manner in which the silica and R_2O_3 are combined in the product. The availability of the calcium and magnesium oxides is reduced in proportion to the degree to which these impurities have fluxed during calcination. Other minor factors, such as slaking quality and distribution of the impurities between the calcium oxide and magnesium oxide components, cause uncertainties where basicity factors are calculated.

The rate of development of basicity in sulfuric acid is shown graphically in Figure 1. A basicity factor determined by boiling a sample in an excess of hydrochloric acid for 15 minutes may be regarded as an ultimately available basicity; these values for each sample are shown on the right-hand margin of the figure.

For practical purposes the full neutralizing value of these limes is available in about 15 minutes with sulfuric acid under the conditions given; but where sufficient time is allowed, it may approach the hydrochloric acid ultimate. These curves are of particular significance where the relative delivered cost of the limes is considered.

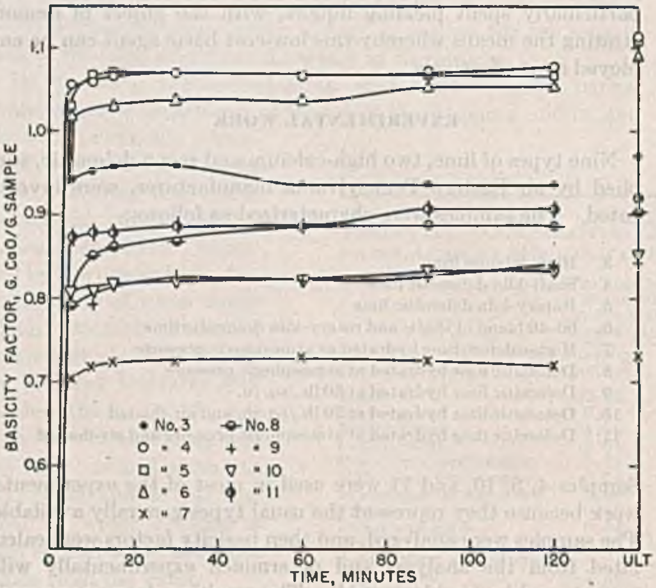

Figure 1. Basicity Factors of Limes

REACTION RATE

Where waste pickle liquor is to be treated with lime, the basicity factor is a guide to the quantity required, but reaction rate is a factor which may be of first importance in some cases. Dolomitic lime is available as quicklime, atmospheric hydrate, and pressure hydrate. The magnesia in pressure-hydrated dolomitic limes is almost completely converted to the hydroxide, in contrast with atmospheric hydrates where little, if any, of the magnesia is hydrated; this product has been developed within the past six to eight years. Each of these types of lime reacts with pickle liquor at a different rate. If the full basicity of quicklime is to be realized, it must be properly slaked in water before use; likewise, the hydrates must be thoroughly wetted and added as an aqueous slurry.

The rate of precipitation of ferrous iron is a function of the rate at which hydroxyl ions can be supplied at a pH of about 8.5. In illustration of the rate at which dolomitic limes react with an acid solution, compared with high-calcium lime, a 0.1 *N* solution of sulfuric acid was treated with a 2% excess of several limes at room temperature. The results (Figure 2) show clearly the differences in reaction rates. Similarly, a dilute pickle liquor (10.96 grams Fe^{++} and 35.68 grams SO_4^{--} per liter) was treated with slurries of the same agents (Figure 3).

The rate of removal of iron from a pickle liquor by these agents was traced by treating a pickle liquor (56 grams Fe^{++}, 180 grams SO_4^{--} per liter) at room temperature with a 5% excess of the limes slurries. The suspensions were stirred constantly (except where allowed to stand overnight) with electric mixers,

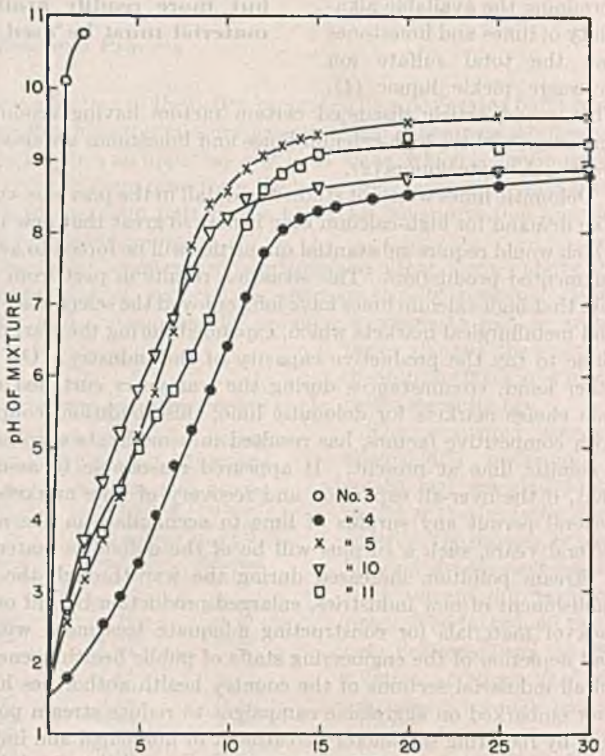

Figure 2. Reaction of Limes with 0.1 *N* Sulfuric Acid at 25° C.

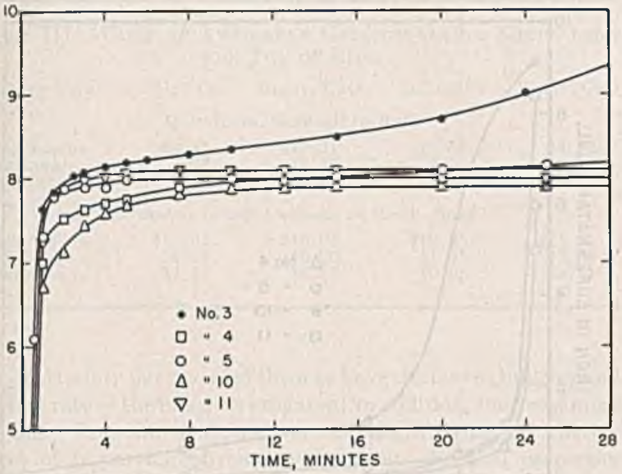

Figure 3. Reaction of Limes with Pickle Liquor at 25° C. (pH *vs.* Time)

samples were withdrawn at intervals and filtered, and the filtrates analyzed for iron. The reaction rate was negligible when the suspensions stood quiescent for 16 hours. The data are shown graphically in Figure 4.

RELATIVE REACTIVITY OF CaO AND MgO

As a partial explanation for these differences in reactivity it was assumed that the calcium oxide component of dolomitic lime reacted much more rapidly than its magnesium oxide fraction, and that the least soluble and least basic portion of the lime would, in consequence, be required to precipitate iron at a pH value where the solubility of magnesium oxide is very low indeed. In other words, since the reaction is ionic, the driving force for the production of hydroxyl ions becomes almost vanishingly small as the reaction approaches completion.

The relative rate of reaction of calcium and magnesium oxides was determined as follows: A solution of hydrochloric acid in a beaker partly submerged in iced water was treated with an excess of dolomitic lime slurry. Just at the point where the pH of the mixture began to rise, a sample was withdrawn by inserting a 2-cm. tube closed at one end with a piece of filter paper between two layers of filter cloth and applying vacuum to the open end. Analysis of the clear filtrates yielded the results presented in Table II.

Table II. Relative Rate of Reaction between Calcium and Magnesium Oxides and Hydrochloric Acid

Excess Lime, %	Grams per Liter Ca^{++}	Grams per Liter Mg^{++}	Molal Ratio, Ca/Mg	pH of Filtrate
10	1.36	0.495	1.66	9.4
20	1.42	0.356	2.42	7.6
30	1.47	0.35	2.54	9.3
40	1.31	0.435	1.82	8.5
50	1.61	0.193	5.05	8.1
60	1.54	0.314	2.98	9.0

These findings indicate the correctness of the assumption that the calcium oxide component of dolomitic lime reacts more rapidly than its magnesia. It would be expected that the ratio of calcium to magnesium would increase more or less uniformly with increasing excesses of lime. The accurate determination of the ratio, however, is a matter of some difficulty because a measurable time is required to withdraw a sample, and the rate of reaction in hydrochloric acid, even at 0° C., is so rapid that to obtain a sample while the difference in reactivity persists is indeed arduous. For this reason these data must be regarded merely as a qualitative indication that a difference in reaction rate does exist. In this light it may properly be assumed that this condition is even more significant where sulfates are involved because the removal of calcium ions, by precipitation as a sulfate, increases the driving force for solution of calcium oxide, whereas the reverse is true for magnesia.

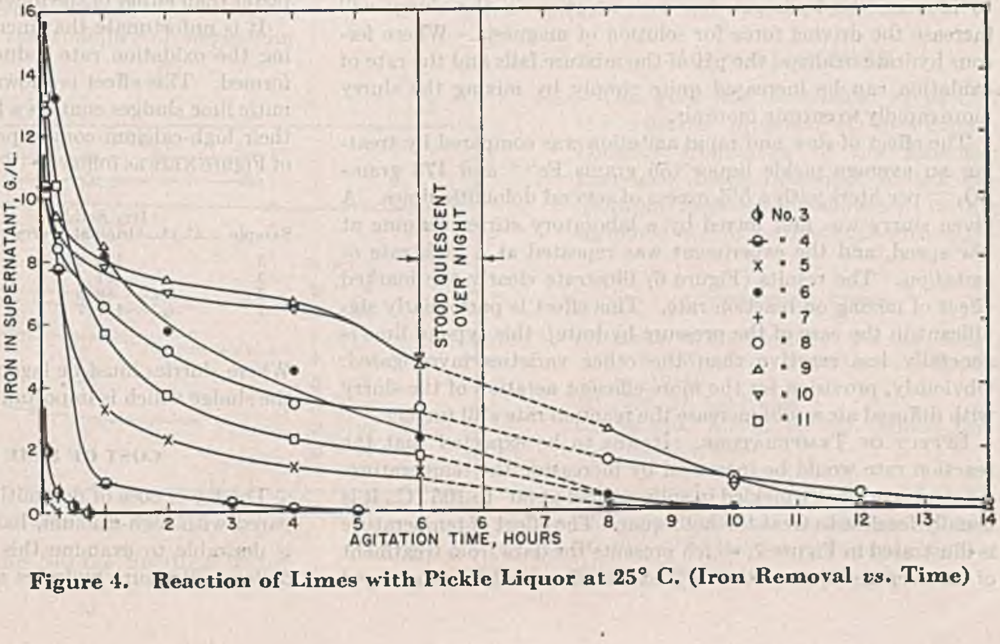

Figure 4. Reaction of Limes with Pickle Liquor at 25° C. (Iron Removal *vs.* Time)

In addition to the driving force for the solution of magnesia decreasing as the reaction proceeds to completion, the magnesia which remains at any time is less reactive than that which reacted previously. The explanation is that it is difficult to calcine dolomite without overburning the magnesia. The double carbonate of true dolomite begins to decompose at about 725° C. into calcite and magnesite (*3*). This point is higher than the decomposition temperature of magnesite (620° C.), which immediately decomposes into magnesium oxide and carbon dioxide. Calcite does not decompose below about 900° C.; owing to the intimacy of contact between the magnesia and the lime, attainment of complete decomposition of calcium carbonate usually results in moderate to severe overcalcination of the magnesia and thereby diminishes its reactivity.

These considerations make clear the low rate at which dolomitic limes react, as compared with the high calcium material, and suggest the means whereby the reaction rate can be increased. Several practices, and combinations of them, are proposed to permit the treatment plant operator to take advantage of the lower neutralization cost of dolomitic limes and their greater availability—namely, use of excess lime, increasing the rate of oxidation of the ferrous hydrate, and raising the temperature.

Use of Excess Lime. The decrease in reactivity of the magnesia component of dolomitic lime as less and less of it remains brings out the fact that the reaction rate could be increased by employing an excess of the alkaline agent. A moderate excess can be used at the same cost as a stoichiometric quantity of high-calcium lime because of the lower cost of dolomitic lime per unit of basicity.

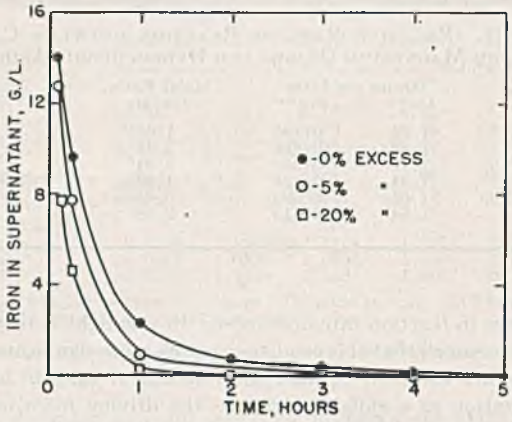

Figure 5. Effect of Excess Lime in Pickle Liquor Treatment at 25° C.

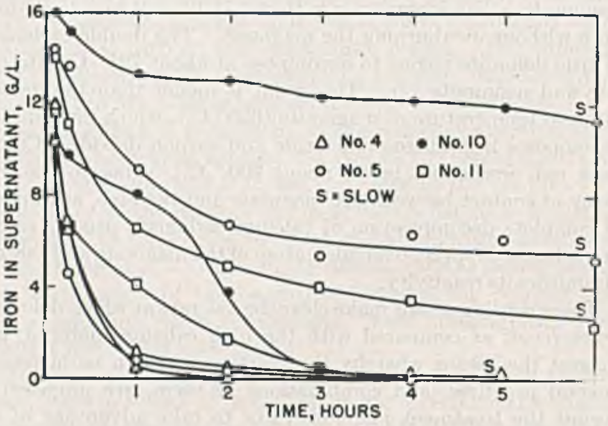

Figure 6. Effect of Agitation Rate in Pickle Liquor Treatment at 25° C.

An average pickle liquor was treated with 0, 5, and 20% excesses of several dolomitic limes at room temperature with moderate agitation. The results were plotted in terms of iron precipitation *vs.* stirring time. A typical set of curves is shown in Figure 5. Similar families of curves were obtained for other samples which indicate roughly that for every 5% excess lime completion of the reaction occurs about an hour sooner.

Increasing Rate of Oxidation. Any means which will tend to increase the hydrogen ion concentration in the slurry will increase the driving force for solution of magnesia. Where ferrous hydrate oxidizes, the pH of the mixture falls and the rate of oxidation can be increased quite simply by mixing the slurry more rapidly to entrain more air.

The effect of slow and rapid agitation was compared by treating an average pickle liquor (56 grams Fe^{++} and 178 grams SO_4^{--} per liter) with a 5% excess of several dolomitic limes. A given slurry was first mixed by a laboratory stirrer running at low speed, and the experiment was repeated at a high rate of agitation. The results (Figure 6) illustrate clearly the marked effect of mixing on reaction rate. This effect is particularly significant in the case of the pressure hydrate; this type of lime is generally less reactive than the other varieties investigated. Obviously, provision for the more efficient aeration of the slurry with diffused air would increase the reaction rate still further.

Effect of Temperature. It was to be expected that the reaction rate would be increased by increasing the temperature. As steel is normally pickled in sulfuric acid at 80° to 105° C., it is usually feasible to treat the hot liquor. The effect of temperature is illustrated in Figure 7, which presents the data from treatment of an average liquor with a 5% excess of several limes at rapid agitation. This figure combines the effect of the three variables (excess lime, agitation, temperature) which are important in the efficient use of dolomitic lime for treating pickle liquor. Comparison of Figures 7 and 4 illustrates the improvement in reaction rate which can be attained where proper attention is given these variables.

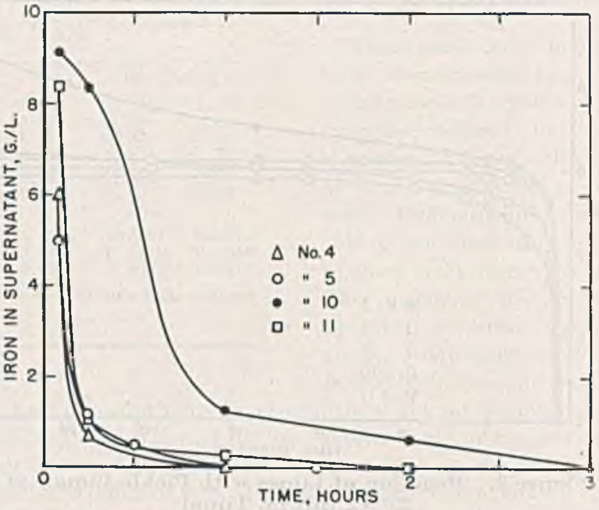

Figure 7. Effect of Increased Temperature, Excess Lime, and Rapid Agitation in Treatment of Pickle Liquor

SLUDGE SETTLING RATES

Where there is a limited area for lagooning the slurry from lime treatment of pickle liquor, the sludge settling rate is quite important. The fact that a large fraction of dolomitic lime does not form an insoluble sludge in pickle liquor treatment has frequently been cited as an advantage for the material. Figure 8 shows the settling rates of the sludge from the samples whose reaction rates were presented in Figure 4.

These curves demonstrate the wide variation in the settling rates of the sludges produced by the types of lime studied. In general, sludges produced by quicklimes settle faster than those from hydrates, and high calcium sludges faster than dolomitic. It was shown previously (*1*) that the settling rate of sludges will be approximately the same as the settling rate of the lime suspended in water. There is no explanation for the curious behavior of the sludge from sample 6, which settled considerably faster than either of the limes from which it was compounded.

It is unfortunate that increasing the reaction rate by increasing the oxidation rate reduces the settling rate of the sludges formed. This effect is shown in Figure 9. It is true that dolomitic lime sludges contain a lower total weight of dry solids than their high-calcium counterparts. The dry solids in the sludges of Figure 8 are as follows:

Sample	Dry Solids, G./L. Original Slurry	Sample	Dry Solids, G./L. Original Slurry
3	120.0	8	88.5
4	91.1	9	87.5
5	89.5	10	99.0
7	117.7	11	107.4

Where slurries must be lagooned, however, it is the final bulk of the sludge which is important, not its dry solids content.

COST OF LIME PER BASICITY UNIT

The lower cost of dolomitic limes per unit of basicity, as compared with high-calcium, has been mentioned several times. It is desirable to examine this statement in terms of actual cost dollars. Pressure hydrates are not included in the analysis be-

Table III. Cost of Available Calcium Oxide Equivalent per Ton of Lime

Delivery Point	High-Ca	Equiv. CaO	Dolomitic	Equiv. CaO
	Quicklimes, Carloads in Bulk			
Philadelphia	$9.81	$10.31	$9.55	$8.80
Pittsburgh	9.92	10.42	9.95	9.17
Cleveland	9.90	10.40	9.45	8.71
	Hydrated Limes, Carloads in 50-Lb. Bags			
Philadelphia	$11.31	$16.04	$10.05	$11.71
Pittsburgh	11.42	16.20	11.45	13.09
Cleveland	11.65	16.52	10.95	12.51

cause this study has revealed them to have the lowest basicity and reaction rate of the limes investigated; in addition, they cost more per ton. Pressure hydrates were developed with the specific object of improving physical rather than chemical properties of the hydrate—e.g., plasticity.

Table III gives typical quotations, as of February 1946, for four limes, delivered in carlots to the destinations indicated. Such quotations include both the base price of the lime and the freight charges. The prices have been divided by the corresponding sulfuric acid basicity factors of the materials to show the cost of available calcium oxide equivalent per ton.

Table III makes it plain that basicity purchased as dolomitic lime is cheaper than high-calcium lime basicity by an average of about 14% for quicklimes and 24% for hydrates. The cost advantage of dolomitic lime should, in most cases, overcome its disadvantage of lower reaction rate and place it on a more or less equal footing with high-calcium lime through the use of excess agent and more rapid agitation for a slightly longer reaction time.

SUMMARY

The increasingly aggressive attitude of state and federal agencies in demanding reduction of stream pollution through waste treatment, the cheapness of lime as a neutralizing agent for acidic wastes, and the continuing shortage of high-calcium lime led to an investigation of means whereby dolomitic lime could be substituted economically for its more reactive counterpart.

The lower rate of reaction of dolomitic limes as compared with high-calcium limes under the same conditions is illustrated graphically. Two related factors are largely responsible for the lower reactivity of dolomitic limes: low solubility of magnesium oxide and decreased reactivity of this component through overcalcination. Experimental data indicate that the calcium oxide reacts at a substantially greater rate than the magnesium oxide in dolomitic lime; in the treatment of an acid solution of ferrous sulfate this necessitates completing the reaction with the least reactive portion of the lime at a pH where the solubility of magnesium oxide is very low indeed. In addition, the magnesium oxide remaining at any time is less reactive than that previously consumed by the reaction.

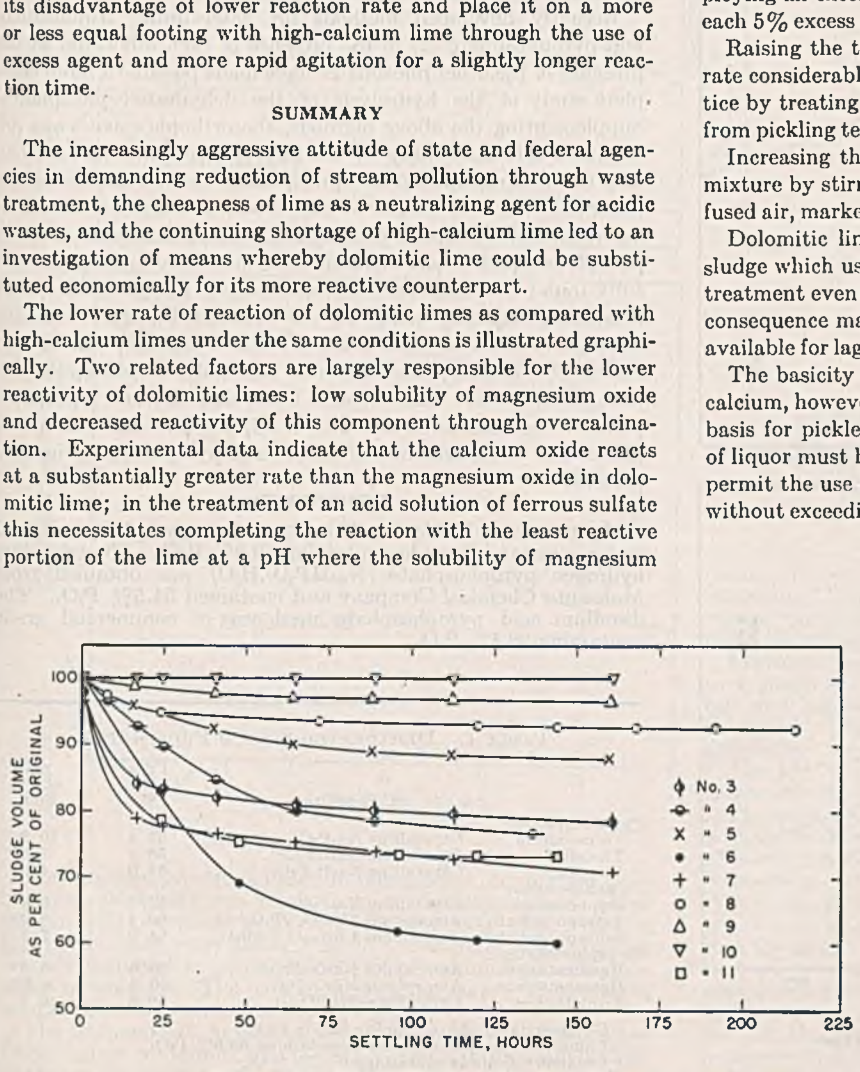

Figure 8. Lime Sludge Settling Rates

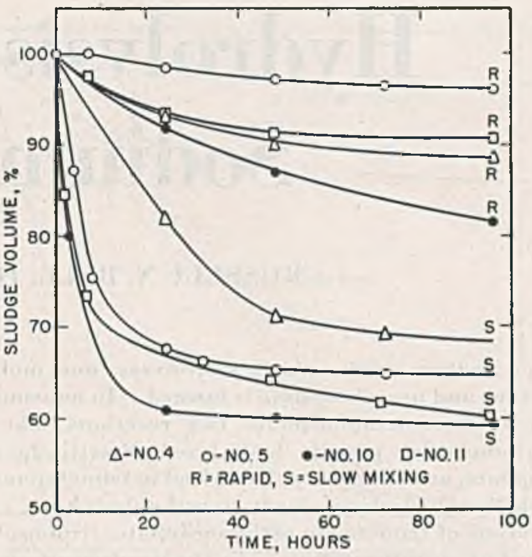

Figure 9. Effect of Mixing Rate on Sludge Settleability

The reaction rate of dolomitic lime can be increased by employing an excess of the agent. Very roughly, and within limits, each 5% excess reduces the reaction time about an hour.

Raising the temperature of the mixture increases the reaction rate considerably. Advantage can be taken of this factor in practice by treating pickle liquor before it has an opportunity to cool from pickling temperature.

Increasing the rate of oxidation of the ferrous hydrate in the mixture by stirring it more rapidly, or by the introduction of diffused air, markedly increases the reaction rate.

Dolomitic lime treatment of waste pickle liquor results in a sludge which usually is bulkier than that from high-calcium lime treatment even though it has a lower content of dry solids. This consequence may be a disadvantage where only a limited area is available for lagooning.

The basicity advantage which dolomitic lime holds over high-calcium, however, places the two agents on a relatively equivalent basis for pickle liquor treatment. Where considerable volumes of liquor must be treated, the saving in cost of alkaline agent will permit the use of several expedients to increase the reaction rate without exceeding the cost of the more reactive high-calcium lime.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Hoak, R. D., Lewis, C. J., and Hodge, W. W., Ind. Eng. Chem., 36, 274 (1944).
(2) *Ibid.*, 37, 553 (1945).
(3) Schallis, A., U. S. Bur. Mines, *Circ* 7247 (1943).

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Hydrolysis of Dehydrated Sodium Phosphates

RUSSELL N. BELL, *Victor Chemical Works, Chicago Heights, Ill.*

When sodium triphosphate hydrolyzes, one mole each of ortho- and pyrophosphate is formed. In aqueous solutions of hexametaphosphate two reactions take place simultaneously; part is hydrolyzed directly to orthophosphate, and part is depolymerized to trimetaphosphate which then hydrolyzes slowly to orthophosphate. In the hydrolysis of trimeta- to orthophosphate, triphosphate is formed as an intermediate. In the presence of an excess of alkali, trimetaphosphate is converted entirely to triphosphate. Pyrophosphates hydrolyze directly to ortho phosphates. Hydrolysis data confirm the fact that tetra- and septaphosphates are mixtures.

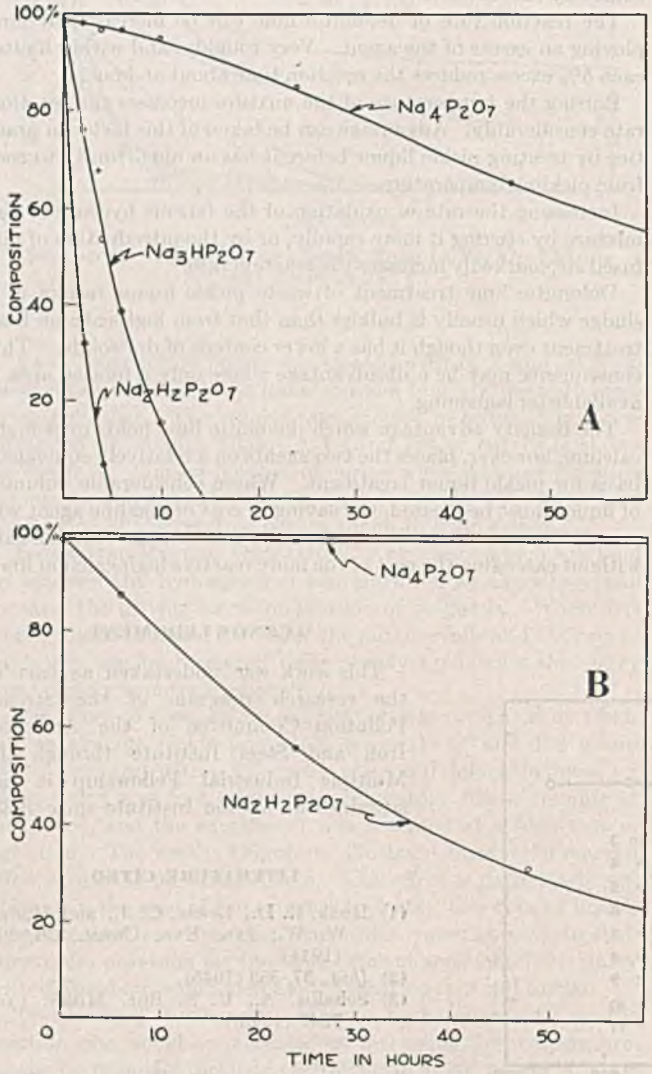

Figure 1. Sodium Pyrophosphates

A. **1% solution in water at 100° C.**
B. **1% solution in water at 70° C.**

REFERENCES in the literature to the use of molecularly dehydrated phosphates, in the treatment of water for various purposes, are too numerous to be tabulated here. The useful life of these compounds is dependent on their ability to withstand hydrolysis in aqueous solutions. Many attempts have been made to measure the rate at which these compounds rehydrate (hydrolyze), but the analytical methods used were inadequate to establish either the nature or the exact amount of the products formed. Morgen and Swoope (*8*) used the titration methods of Gerber and Miles (*4*), which do not determine polyphosphate as such. Germain (*5*) determined the hexametaphosphate by precipitating as barium hexametaphosphate and the pyro- and orthophosphate by acidimetric titrations using a series of indicators. Watzel (*10*) also used titration methods. None of these methods gave sufficient information on the products formed or the mechanics of the rehydration.

Recently developed methods for determining triphosphate and pyrophosphate (*2*) in the presence of each other and in the presence of the other phosphates have made possible a more complete study of the hydrolysis of the dehydrated phosphates. Supplementing the above methods, the orthophosphate was determined colorimetrically by the molybdenum blue method (*3*), and the hexametaphosphate precipitated as barium hexametaphosphate (*7*). No satisfactory method was found for determining trimetaphosphate in the presence of large amounts of other phosphates, and it was therefore determined by difference. Results found by analysis of pyrophosphate, polyphosphate, and hexametaphosphate, using the above methods, agree with the findings of Andress and Wüst (*1*) and Partridge, Hicks, and Smith (*9*)—namely, that only one true polyphosphate, the triphosphate, exists. The so-called tetraphosphate and septaphosphate were found to be mixtures of triphosphate and metaphosphate with small amounts of ortho- and pyrophosphate usually present.

HYDROLYSIS

MATERIALS. (Table I) The tetrasodium pyrophosphate used was a commercial grade containing 53.2% P_2O_5. The trisodium hydrogen pyrophosphate ($Na_3HP_2O_7.H_2O$) was obtained from Monsanto Chemical Company and contained 54.5% P_2O_5. The disodium acid pyrophosphate used was a commercial grade containing 63.1% P_2O_5.

TABLE I. DEHYDRATED SODIUM PHOSPHATES

	Composition	P_2O_5 Calcd., %	pH of 1% Soln.
Pyrophosphates			
Tetrasodium	Crystalline $Na_4P_2O_7$	53.4	10.2
Trisodium	Crystalline $Na_3HP_2O_7$	58.2	7.3
Disodium	Crystalline $Na_2H_2P_2O_7$	64.0	4.6
Polyphosphates			
Triphosphate	Crystalline $Na_5P_3O_{10}$	57.9	9.4
Tetraphosphate	Amorphous $3Na_2O-2P_2O_5$	60.4	8.0[a]
Septaphosphate	Amorphous $4.5Na_2O-3.5P_2O_5$	64.0	7.3
Metaphosphates			
Hexametaphos	Amorphous $Na_2O-P_2O_5$	69.6	6.2[b]
Hexametaphos	Amorphous $Na_2O-P_2O_5$	69.6	6.8[c]
Trimetaphos	Crystalline $(NaPO_3)_3$	69.6	6.7

[a] Commercial grade containing 62.5% P_2O_5.
[b] Laboratory-prepared product containing 69.6% P_2O_5.
[c] Commercial grade containing 67.2% P_2O_5.

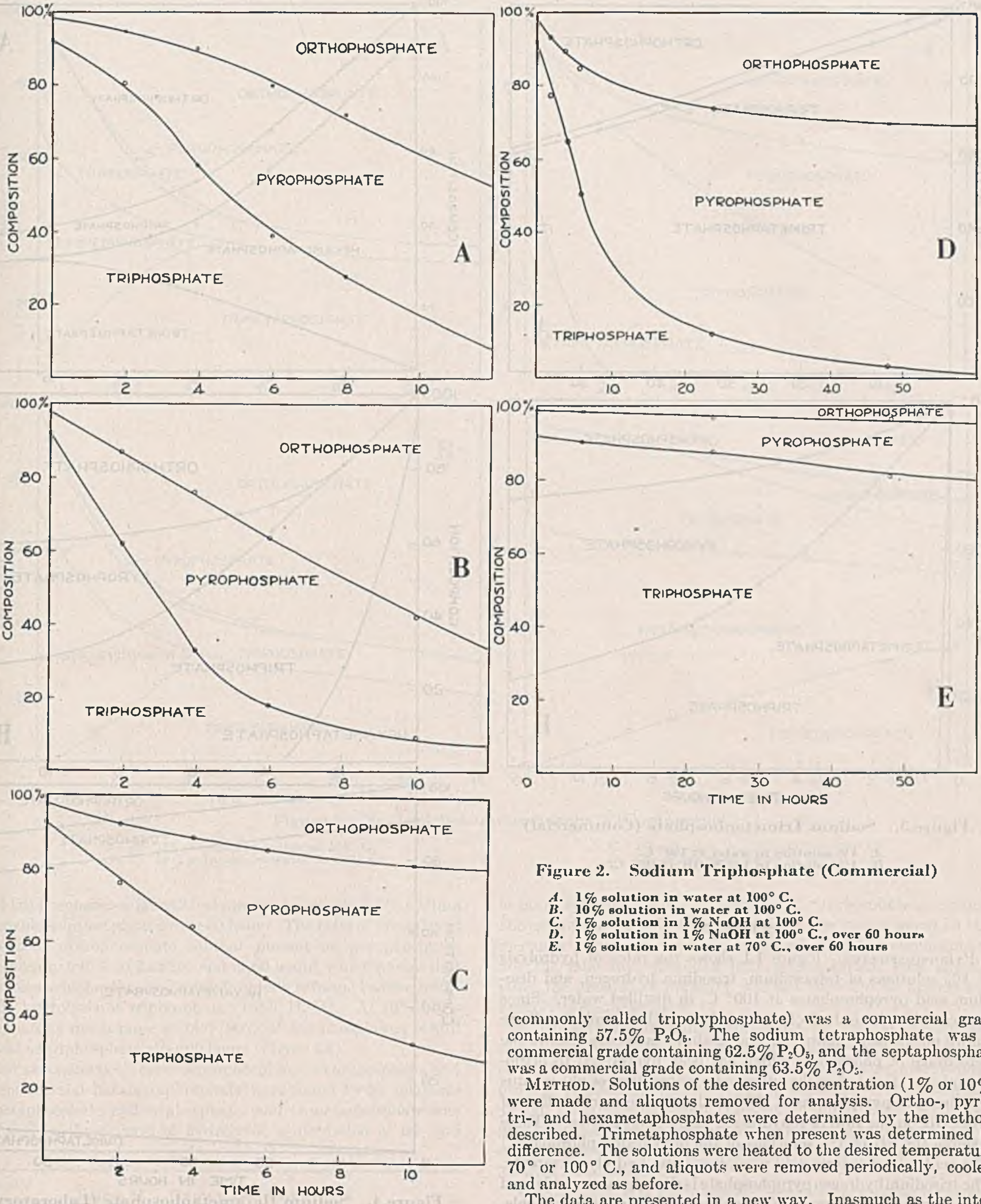

Figure 2. Sodium Triphosphate (Commercial)

A. 1% solution in water at 100° C.
B. 10% solution in water at 100° C.
C. 1% solution in 1% NaOH at 100° C.
D. 1% solution in 1% NaOH at 100° C., over 60 hours
E. 1% solution in water at 70° C., over 60 hours

The laboratory-prepared sodium metaphosphate referred to as hexametaphosphate was made from twice-recrystallized monosodium orthophosphate by heating to 800° to 900° C. and cooling rapidly between steel plates. All of the samples made in this manner contained between 90 and 93% of sodium hexametaphosphate by analysis. The balance was triphosphate. The material used in these tests contained 69.6% P_2O_5.

The commercial hexametaphosphate used was unadjusted Calgon glass containing 67.2% P_2O_5. The sodium trimetaphosphate was a commercial grade of the water-soluble crystalline polymer containing 69.6% P_2O_5. The sodium triphosphate (commonly called tripolyphosphate) was a commercial grade containing 57.5% P_2O_5. The sodium tetraphosphate was a commercial grade containing 62.5% P_2O_5, and the septaphosphate was a commercial grade containing 63.5% P_2O_5.

METHOD. Solutions of the desired concentration (1% or 10%) were made and aliquots removed for analysis. Ortho-, pyro-, tri-, and hexametaphosphates were determined by the methods described. Trimetaphosphate when present was determined by difference. The solutions were heated to the desired temperature, 70° or 100° C., and aliquots were removed periodically, cooled, and analyzed as before.

The data are presented in a new way. Inasmuch as the intermediate products of the rehydration were determined, and their presence materially affected the evaluation of the product, these products are shown in the hydrolysis curves. In the curves shown, the percentage of phosphorus present as ortho-, pyro-, tri-, hexameta-, and trimetaphosphate is plotted against time, so that the composition of the solute can be calculated at any given time. The area between the curves represents the percentage of phosphorus present as ortho-, pyro-, etc., as indicated. Thus the figures picture not only the disappearance of the starting material but also the formation of intermediates, a knowledge of which is necessary in determining the useful life of the product. The initial composition of each of the products, expressed in per cent of phosphorus, is shown at zero time.

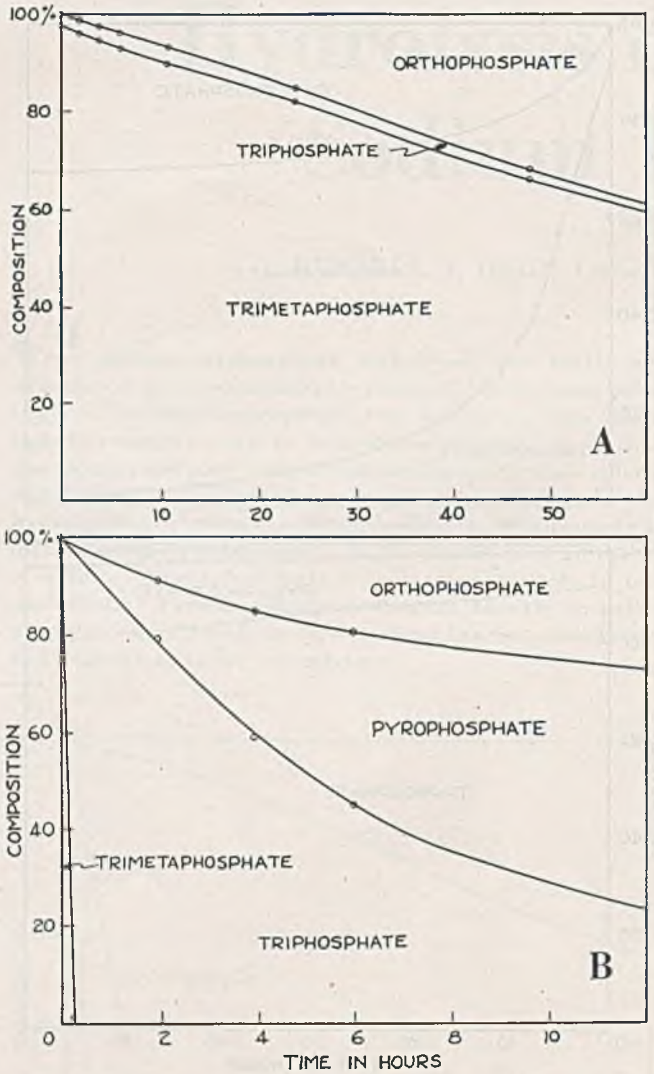

Figure 3. Sodium Trimetaphosphate (Commercial)

A. 1% solution in water at 100° C.
B. 1% solution in 1% NaOH at 100° C.

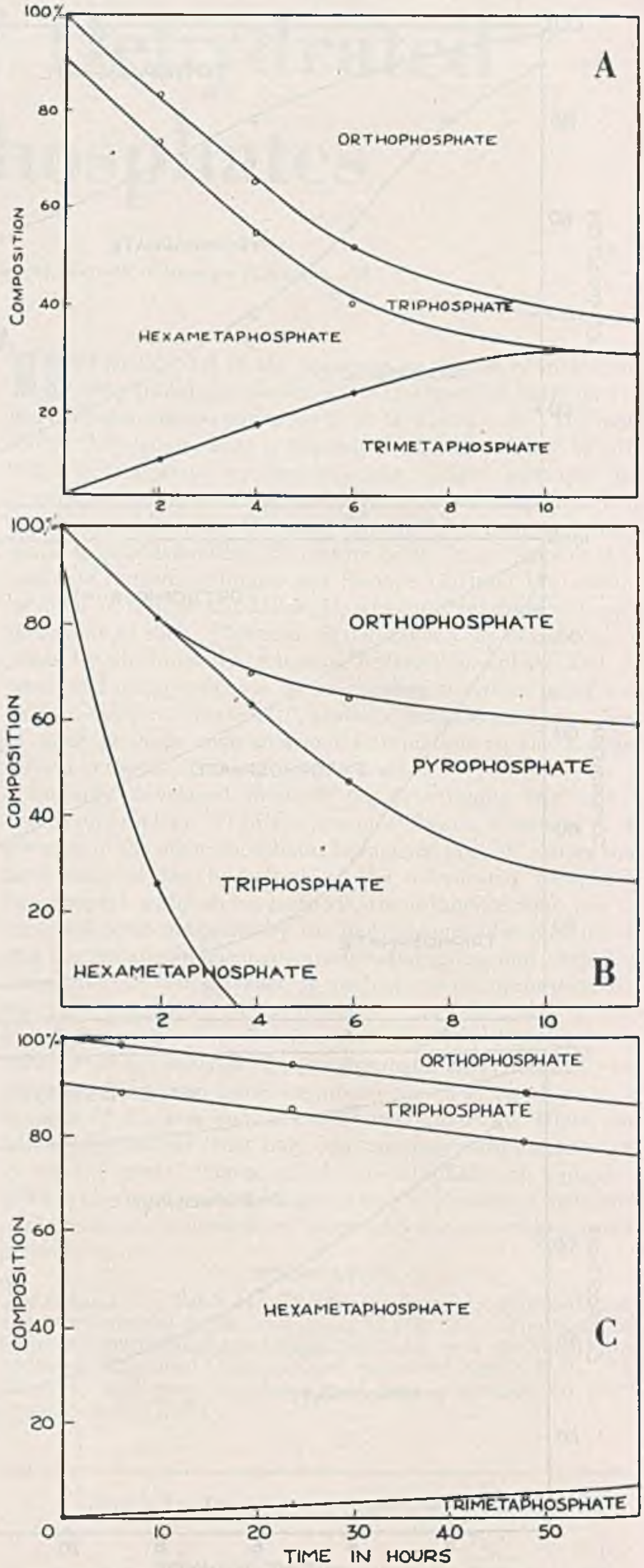

Figure 4. Sodium Hexametaphosphate (Laboratory)

A. 1% solution in water at 100° C.
B. 1% solution in 1% NaOH at 100° C.
C. 1% solution in water at 70° C.

DISCUSSION

PYROPHOSPHATES. Figure 1*A* shows the rates of hydrolysis of 1% solutions of tetrasodium, trisodium hydrogen, and disodium acid pyrophosphates at 100° C. in distilled water. Since the pyrophosphates hydrolyze directly to orthophosphate, all are shown on the same figure. The area above each curve shows the percentage of phosphorus which has been hydrolyzed to orthophosphate; that below the curve is the percentage of phosphorus remaining as pyrophosphate. This indicates the marked effect of lower pH on the rate of rehydration of pyrophosphates. (Table I shows the pH of 1% solutions of the dehydrated phosphates.) The acid salt, disodium acid pyrophosphate, hydrolyzes rapidly. The trisodium hydrogen pyrophosphate is slightly more stable, and the normal salt, tetrasodium pyrophosphate, is relatively stable. In 1% sodium hydroxide solution no hydrolysis is detectable in 96 hours at 100° C. Temperature also greatly affects the rate of hydrolysis of the dehydrated phosphates. At 70° C. the disodium acid pyrophosphate rehydrates much more slowly than at 100° C., and the tetrasodium pyrophosphate is unchanged for 60 hours (Figure 1*B*).

TRIPHOSPHATES. Figure 2 shows the rate of hydrolysis of a commercial grade of sodium triphosphate at 70° C. and 100° C. When sodium triphosphate hydrolyzes, both ortho- and pyrophosphates are formed. Increasing the concentration from 1 to 10% decreases the stability slightly (Figure 2*B*) but does not materially change the shape of the curves. In 1% sodium hydroxide solution sodium triphosphate is slightly more stable than in water (Figure 2*C*). Since pyrophosphate is found to be entirely stable in 1% sodium hydroxide solution at 100° C., extending the curve in Figure 2*C* should indicate the mechanism of the hydroly-

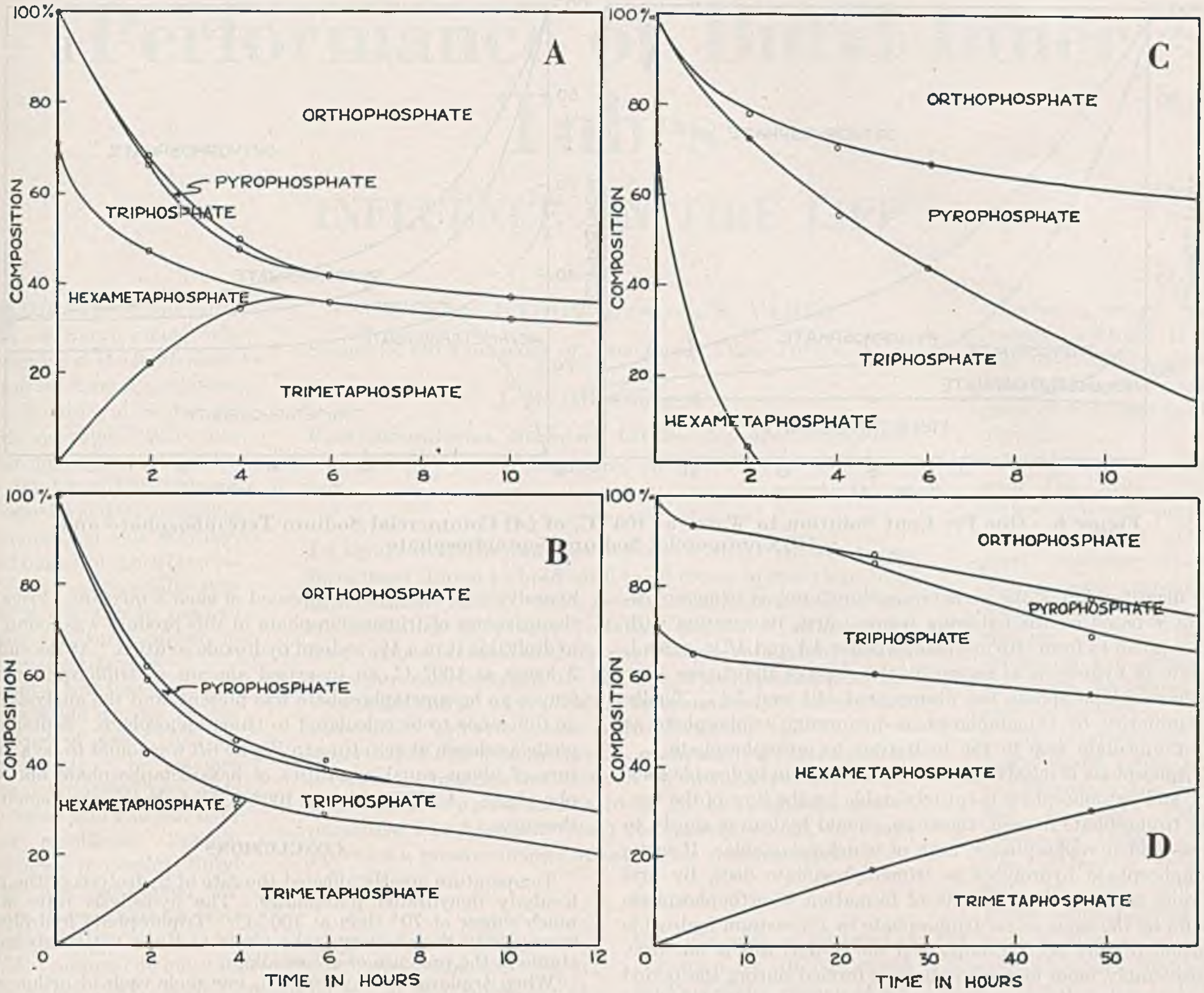

Figure 5. Sodium Hexametaphosphate (Commercial)

A. 1% solution in water at 100° C.
B. 10% solution in water at 100° C.
C. 1% solution in 1% NaOH at 100° C.
D. 1% solution in water at 70° C.

sis of triphosphate. Figure 2*D* shows triphosphate in 1% sodium hydroxide solution plotted over 60 hours. The ratio of phosphorus present as orthophosphate to that present as pyrophosphate is approximately 1 to 2 at the end of 60 hours, which means that one mole each of ortho- and pyrophosphate is formed as the result of the hydrolysis of triphosphate (Table II, D). At 70° C. triphosphate is much more stable; 80% of the phosphorus is still present as triphosphate after 60 hours (Figure 2*E*).

METAPHOSPHATES. Since septaphosphate, tetraphosphate, and the commercial hexametaphosphate were found to be mixtures of metaphosphate and triphosphate, and trimetaphosphate was produced in the process of hydrolysis, a discussion of tri- and hexametaphosphates will supplement the triphosphate discussion above and provide a basis for evaluating the results found on the mixtures. Although neither the commercial trimetaphosphate nor the laboratory-prepared hexametaphosphate were strictly pure, the amount of impurity was not sufficient to mask their hydrolysis characteristics.

TABLE II. HYDROLYSIS EQUATIONS

IN WATER

Hexametaphosphate: $3(NaPO_3)_6 + 12H_2O \rightarrow 2(NaPO_3)_3 + 12NaH_2PO_4$ (A)
Trimetaphosphate: $(NaPO_3)_3 + H_2O \rightarrow Na_3H_2P_3O_{10}$ (B)
$Na_3H_2P_3O_{10} + 2H_2O \rightarrow 3NaH_2PO_4$ (C)
Triphosphate: $Na_5P_3O_{10} + H_2O \rightarrow Na_3HP_2O_7 + Na_2HPO_4$ (D)
Pyrophosphates: $Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4$ (E)
$Na_3HP_2O_7 + H_2O \rightarrow Na_2HPO_4 + NaH_2PO_4$ (F)
$Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4$ (G)

IN 1% NaOH SOLUTION

Trimetaphosphate: $(NaPO_3)_3 + 2NaOH \rightarrow Na_5P_3O_{10} + H_2O$ (H)

A 1% solution of trimetaphosphate at 100° C. hydrolyzes slowly to orthophosphate (Figure 3*A*). However, the hydrolysis is not direct but appears to form triphosphate as an intermediate product (Table II, B and C). In 1% sodium hydroxide solution at 100° C. trimetaphosphate is converted immediately to triphosphate (*6*) and then hydrolyzes at the rate of triphosphate in 1% sodium hydroxide solution (Table II, H). Comparison of Figures 3*B* with 2*C* shows this.

When a solution of the laboratory-prepared hexametaphosphate is heated at 100° C., two reactions take place. Part of the hexametaphosphate is hydrolyzed to orthophosphate and part is depolymerized to trimetaphosphate. Figures 4*A* and 4*C* show that approximately twice as much phosphorus is hydrolyzed as is depolymerized. The trimetaphosphate is determined by difference. Evidence that this difference is trimetaphosphate is found by comparing Figures 4*A* and 4*B*. Trimetaphosphate in 1% sodium hydroxide was found to convert immediately to triphosphate. When hexametaphosphate is hydrolyzed in a 1% sodium hydroxide solution at 100° C., a large amount of triphosphate is found; this leaves no difference to be calculated to trimetaphosphate.

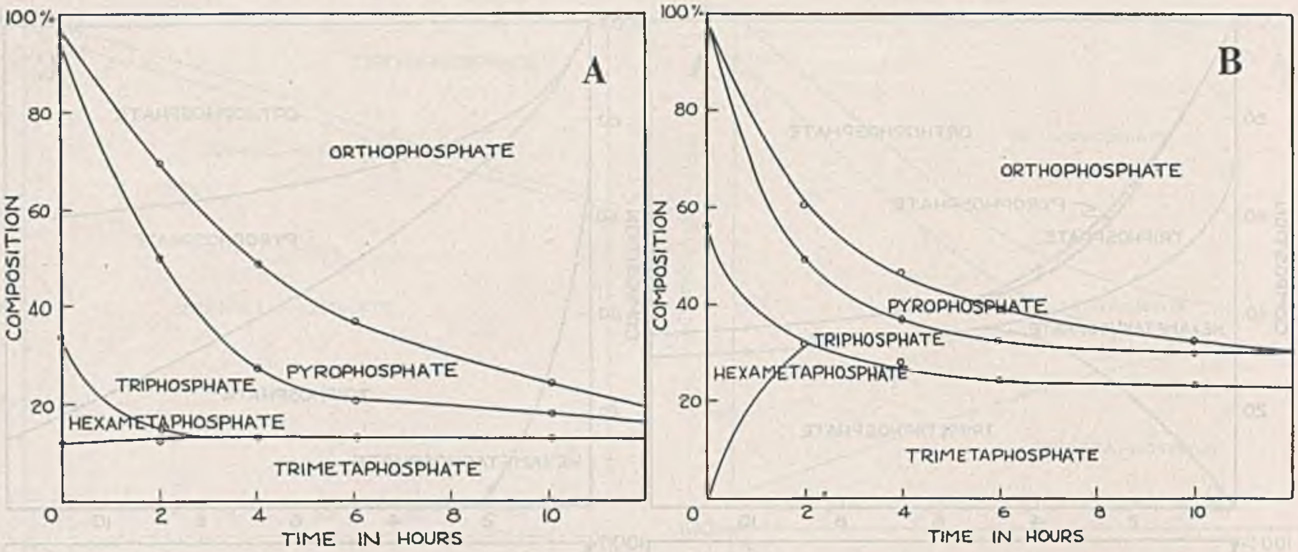

Figure 6. One Per Cent Solution in Water at 100° C. of (*A*) Commercial Sodium Tetraphosphate and (*B*) Commercial Sodium Septaphosphate

The identification of the undetermined material as trimetaphosphate is based on the following points: first, its reaction with excess alkali to form triphosphate (Figures 4*A* and 4*B*); second, its rate of hydrolysis as shown by the slope of the curves after the hexametaphosphate has disappeared (4*A* and 5*A*); finally its similarity to trimetaphosphate in forming triphosphate as an intermediate step in the hydrolysis to orthophosphate.

Triphosphate is relatively stable in 1% sodium hydroxide solution, and pyrophosphate is entirely stable for the time of the test. Any triphosphate formed, therefore, should hydrolyze slowly to ortho- and pyrophosphates, both of which are stable. If hexametaphosphate hydrolyzes as trimetaphosphate does, by first forming triphosphate, the rate of formation of orthophosphate should be the same as for triphosphate in 1% sodium hydroxide solution (Figure 2*C*). Comparison shows that this is not true. Considerably more orthophosphate is formed during the period while hexametaphosphate is present (approximately 4 hours); then the curve levels off to a slope corresponding to the hydrolysis rate for triphosphate. No pyrophosphate is found at the end of 2 hours, and only a small amount is present after 4 hours. This latter is formed as the result of the hydrolysis of the triphosphate. From these observations it is evident that the portion of hexametaphosphate which hydrolyzes goes directly to orthophosphate. The triphosphate is formed from that part which depolymerizes to trimetaphosphate; in the presence of excess alkali the latter converts to triphosphate. From the ratio of depolymerized to hydrolyzed phosphorus Equation A, Table II, is believed to represent the hydrolysis of hexametaphosphate in water.

Commercial sodium hexametaphosphate contains approximately 30% of triphosphate and 70% hexametaphosphate. The analysis is shown at zero time in Figure 5*A*, which indicates the rate of hydrolysis of a 1% solution of commercial hexametaphosphate in water at 100° C. Hexametaphosphate is slightly less stable in 10% than in 1% concentration (Figure 5*B*). Otherwise the curves are the same.

Figure 5*C* presents the hydrolysis of a 1% solution of hexametaphosphate in 1% sodium hydroxide solution at 100° C. As would be expected, a large amount of triphosphate is found, but no trimetaphosphate. The curves are similar to those found for the laboratory-prepared product in excess alkali. At 70° C. a 1% solution of commercial hexametaphosphate hydrolyzes as shown (Figure 5*D*). As was the case with the laboratory-prepared product, the commercial hexametaphosphate is much more stable at 70° than at 100° C.

Polyphosphates. Figure 6*A* shows the hydrolysis of a 1% solution of commercial tetraphosphate in water at 100° C. It hydrolyzes in the manner expected of such a mixture. Proof of the existence of trimetaphosphate in this product was found by hydrolyzing it in a 1% sodium hydroxide solution. At the end of 2 hours at 100° C. an increased amount of triphosphate was found, no hexametaphosphate was present, and the analysis left no difference to be calculated to trimetaphosphate. Septaphosphate as shown at zero time in Figure 6*B* was found to be a mixture of about equal quantities of hexametaphosphate and triphosphate. A 1% solution at 100° C. hydrolyzes as indicated on the curve.

CONCLUSIONS

Temperature greatly affected the rate of hydrolysis of the molecularly dehydrated phosphates. The hydrolysis rates were much slower at 70° than at 100° C. Triphosphate hydrolyzed more slowly than hexametaphosphate and was noticeably more stable in the presence of excess alkali.

When triphosphate hydrolyzed, one mole each of ortho- and pyrophosphate was formed. Hexametaphosphate hydrolyzed to orthophosphate and depolymerized to trimetaphosphate in aqueous solutions. The reactions were simultaneous. No pyro- or triphosphate was formed directly from the hydrolysis of the hexametaphosphate. Some triphosphate was found as a result of the hydrolysis of the trimetaphosphate formed. Trimetaphosphate hydrolyzed first to an acid triphosphate which then hydrolyzed to orthophosphate. If any pyrophosphate was formed it was hydrolyzed to orthophosphate and the amount present was not sufficient to be detected. In the presence of an excess of alkali, trimetaphosphate was converted to triphosphate, the reaction being very rapid at 100° C.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Andress, K. R., and Wüst, K. *Z., anorg. allgem. Chem.*, 237, 113–21 (1938).
(2) Bell, R. N., Ind. Eng. Chem., Anal. Ed., in press.
(3) Fiske, C. H., and Subbarow, Y., *J. Biol. Chem.*, 66, 375 (1925).
(4) Gerber, A. B., and Miles, F. T., Ind. Eng. Chem., Anal. Ed., 10, 519 (1938).
(5) Germain, Louis, *Chimie & industrie*, 35, 22–6 (1936).
(6) Hatch, G. B., U. S. Patent 2,365,190 (Dec. 19, 1944).
(7) Jones, L. T., Ind. Eng. Chem., Anal. Ed., 14, 536 (1942).
(8) Morgen, R. A., and Swoope, R. L., Ind. Eng. Chem., 35, 821–4 (1943).
(9) Partridge, E. P., Hicks, Victor, and Smith, G. W., *J. Am. Chem. Soc.*, 63, 454–66 (1941).
(10) Watzel, R., *Die Chemie*, 55, 356–9 (1942).

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Performance of Butyl Inner Tubes

INFLUENCE ON TIRE LIFE

I. E. LIGHTBOWN AND L. S. VERDE
Standard Oil Company of New Jersey, New York 4, N. Y.

J. R. BROWN, JR.[1]
Esso Laboratories, Standard Oil Development Company, Elizabeth, N. J.

In severe over-the-road service tests Butyl rubber tubes have been shown to hold air 8 to 10 times better than natural rubber tubes. Test results demonstrate that the maintenance of proper inflation pressure, afforded by Butyl tubes because of their superior air retention, results in an increase in tread life of 10 to 18%, depending on the test conditions. It is possible to make Butyl tubes which show less "growth" than natural rubber tubes. Butyl inner tubes age well in service, maintaining their original physical properties better than do natural rubber tubes. This superior aging results in an inner tube with better puncture and blowout (tear) resistance, which, in turn, provides a greater degree of safety for the motorist.

THE first scientific paper on Butyl rubber was presented at the 100th meeting of the AMERICAN CHEMICAL SOCIETY in September 1940 by Frolich. Since that time numerous publications (*1-12*) have described the properties and compounding technique of this polymer. Although Butyl has been referred to as a specialty rubber, it can also be used to replace natural rubber in many applications.

Butyl was found to be a remarkable barrier to the passage of gases (*10*), including air. The polymer also deteriorated very little on aging and had excellent tear resistance. Because of these properties Butyl was first considered for inner tubes, and in this application Butyl has found its largest commercial acceptance. Automobile inner tubes were first made experimentally in September 1940. With Butyl made in the Standard Oil pilot plant this experimental work continued until April 1943, when the first government plant began producing Butyl commercially. From that time until the present Butyl has been used successfully to manufacture all types and sizes of inner tubes ranging from bicycle tubes of $1\frac{1}{4}$-inch cross section to earth-mover tubes of 24-inch cross section.

Butyl tubes were first used by the United States Army for service in the European war theater in May 1944. The following month Butyl was used in essential civilian trucks; but not until September 1945 was sufficient Butyl available for civilian automobile tubes.

COMPOUNDING

Compounding studies carried out early in the development of Butyl tubes indicated that Butyl inner tube recipes could not be built around the recipes formerly used with natural rubber. Because of several unique fundamental characteristics, Butyl requires special compounding and handling techniques.

NERVE. "Pure gum" Butyl has a higher immediate elastic recovery than broken-down smoked sheets. Premastication was found to be ineffective in reducing this nerve; therefore, it was necessary to resort entirely to compounding techniques to obtain processability. Since softeners have a rather limited value, the present practice requires a rather high pigment loading and the use of pigments which exert considerable "deadening" effect.

Contrary to natural rubber and Buna S practices, the incorporation of carbon black in a Butyl inner tube recipe is primarily to improve processability. It is not employed as a means of developing increased tensile strength, although it does raise modulus and enhance tear resistance to a much greater extent than do other pigments.

RESISTANCE TO OXIDATION AND MILL BREAKDOWN. When properly stabilized, Butyl exhibits great resistance to oxidation and mechanical breakdown. Plasticity changes during milling operations are dependent only upon the temperature attained by milling.

This constancy of plasticity should prove to be an advantage and should lead to more uniform day-to-day factory operation. Moreover, as a result of this property, Butyl compounds for factory use may be designed on the basis of filler and softener changes alone without regard to processing changes, such as reworking cycles, periods of standing, etc., factors which had to be taken into account in the use of natural rubber.

COLD FLOW. In spite of its high nerve, Butyl will flow to a greater extent than natural rubber in a prolonged period of time. In inner tube manufacture this property results in fold marks or side-wall breakdown of tube sections if they are stored on trays for extended periods. The use of 20 parts of EPC black in a Butyl tube compound was found to minimize cold flow. The use of small quantities of Polyac at the beginning of the black master batching operation increases the viscosity of Butyl and thereby minimizes cold flow as well as improves bruise resistance. A consideration of these properties of Butyl led to the development of the basic recipe of Table I for use in the manufacture of Butyl tubes.

A mixture of EPC and SRF blacks is employed in order to minimize bruising and reduce cold flow. A total loading of 50 parts of black is used to reduce nerve and tend to overcome shortness. Paraffin and petrolatum are used as representative, fully saturated aliphatic softeners which exert a minimum effect on curing rate. High concentration of ultra-accelerator and an excess of sulfur are used to obtain a fast cure rate.

PERFORMANCE

As soon as the manufacture of Butyl tubes permitted, test fleet operations were begun for the Standard Oil Company of New Jersey in San Antonio, Tex., in order to allow a close study of the performance characteristics of Butyl inner tubes under carefully controlled conditions. Road tests had been going on elsewhere for some time. The individual rubber companies had tested Butyl tubes in their own test cars, as had the various government

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[1] Present address, Pro-phy-lac-tic Brush Company, Florence, Mass.

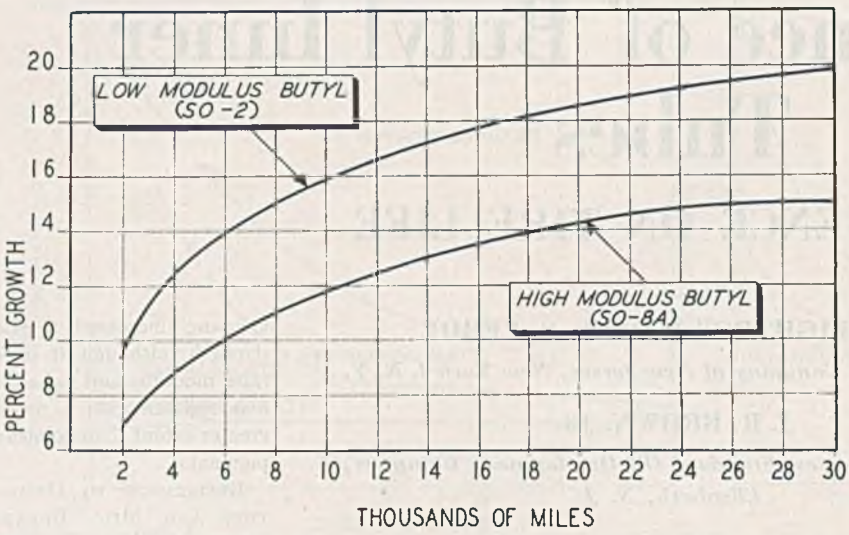

Figure 1. Comparison of Growth of Low Modulus Butyl and High Modulus Butyl Tubes

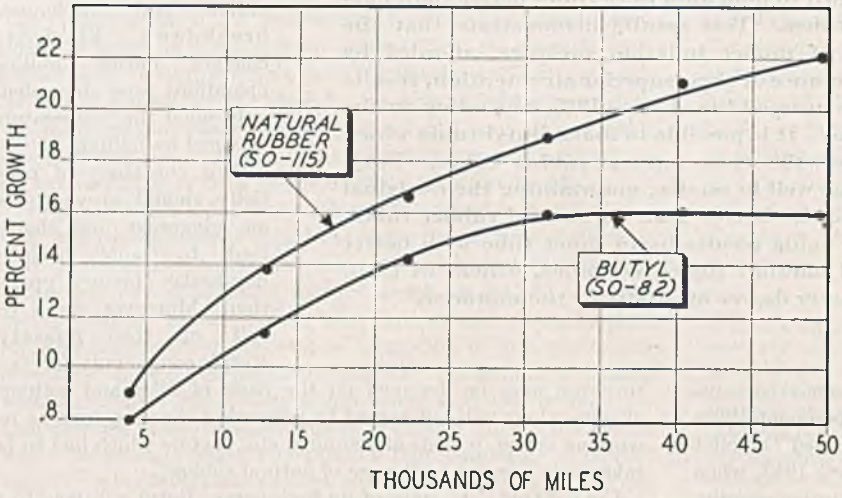

Figure 2. Comparison of Growth of Butyl and Natural Rubber Tubes

test fleets throughout the country. But the results presented in this paper are all gathered from data obtained on test cars operated for this company.

Test fleet operations were begun in January 1944, using Pontiac and Chrysler automobiles. These automobiles travel at the rate of 60 miles per hour, 24 hours per day, 6 days per week. In January 1945, fleet operations were expanded to include the testing of truck tubes.

GROWTH

When applied in a tire and inflated, an inner tube is expanded as much as 35% over its original dimensions. On deflation the tube does not return to its original size; it remains slightly larger, the increase depending on the permanent set of the rubber in service. This increase in the size of the tube is commonly referred to as its growth. Growth in service is one of the limiting factors in the life of an inner tube. The longer a tube remains in service the greater its growth. When this growth becomes great enough to make it difficult to remount the tube in a new tire without buckles or wrinkles, the tube must be discarded. For a tube to exhibit good growth characteristics it must not only possess balanced original physical properties but must maintain this proper balance after aging, particularly after aging in service.

Table I. Recipe for Manufacture of Butyl Tubes

Butyl	100	Petrolatum	2
Zinc oxide	5	Sulfur	2
EPC black	20	Thiuram-type accelerator[a]	1
SRF black	30	Thiazole-type accelerator[b]	0.5
Paraffin	1		

[a] Satisfactory thiuram accelerators include Ethyl Tuads, Methyl Tuads, Monex, Mono-Thiurad, Tetrone A, Thionex, Thiurad, Thiuram E, Thiuram M, and Tuex, Ethyl Tuex.

[b] Satisfactory thiazole accelerators include Captax, MBT, and Thiotax.

Compounding changes exert considerable influence on growth. Changes in type and amount of black and in type and amount of softener are of importance, as is the use of such materials as Polyac or Polybutene. Original tube dimensions, state of cure, type of service, and tube design also play an important part. Basically, however, growth depends on the type of Butyl used. The use of fast-curing (high modulus) Butyl results in a tube of correspondingly lower growth, when compared with low modulus Butyl, over the entire range of compounding changes. (In Rubber Reserve terminology, fast-curing Butyl is Y-15 or Y-25; this type is more highly unsaturated.)

Experimental work along this line was carried out by choosing two lots of Butyl; they were compounded (Table II) and cured 40 minutes at 307° F. according to the standard evaluation method. The moduli at 300% elongation were as follows: Butyl for tube SO-2, 400 pounds per square inch; Butyl for tube SO-8A, 650 pounds per square inch. The two different lots of polymer were then compounded in the same tube recipe and cured into inner tubes (column 3, Table II).

Tube SO-2 (low modulus Butyl) was compared with tube SO-8A (high modulus Butyl) in a road service test. The results of this test are given in Figure 1, which demonstrates the lower growth of the high modulus Butyl.

Figure 2 compares the progressive growth throughout 50,000 miles between a first-line black natural rubber tube and a well

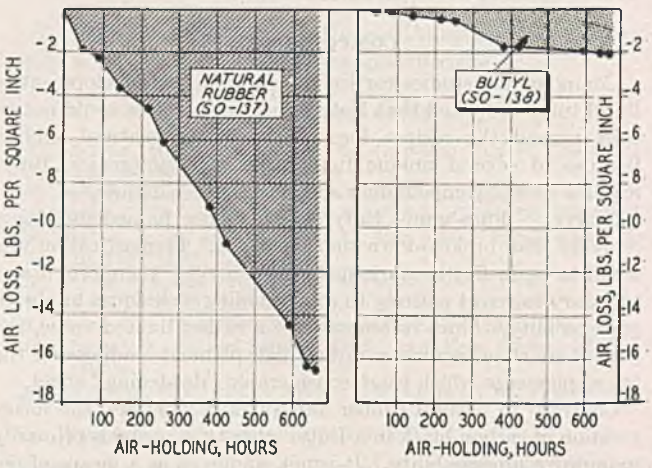

Figure 3. Comparison of Air Loss in Butyl and Natural Rubber Tubes after 20,176 Miles of Travel

Table II. Compounds Used for Growth Tests

	Standard Evaluation Compd.	Inner-Tube Compd.
Butyl	100	100
Zinc oxide	5	5
Stearic acid	3	1
EPC black	...	30
SRF black	50	20
Thiuram-type accelerator[a]	1	1
Thiazole-type accelerator[b]	0.5	0.5
Sulfur	2	2

[a] See footnote *a*, Table I.
[b] See footnote *b*, Table I.

Table III. Compounds Used in Progressive Growth Tests

Butyl Tube (SO-82)		Natural Rubber Tube (SO-115)	
Butyl	95	Smoked Sheets	100
Polybutene[a]	5	Zinc oxide	3
Zinc oxide	5	FT black	55
Petrolatum	2	Stearic acid	2.25
Thiuram-type accelerator[b]	1	Process oil	3.8
Thiazole-type accelerator[c]	0.5	Paraffin	0.5
Sulfur	2	Sulfur	1.5
MT black	35	Accelerators	1.58
HMF black	15	Age resister	1.15
Glycerol	1		
Polyac	0.1		

[a] Polybutene in this compound was used as a processing aid.
[b] See footnote *a*, Table I.
[c] See footnote *b*, Table I.

compounded, well cured Butyl tube made from high modulus polymer (Table III).

AIR HOLDING

The main function of an inner tube is to hold air. Before other polymers were available, natural rubber was considered to perform reasonably well as a gas barrier; it was used to make balloons, diaphragms, and gas masks as well as inner tubes. But inner tube manufacturers have long recognized that there is much room for improvement in the air-holding properties of natural rubber inner tubes. Before the war rubber companies conducted many experiments with materials which could be injected into natural rubber inner tubes to improve their air-holding qualities. Automobile owners, as well as tube manufacturers, are aware of the fact that air diffuses through natural rubber; and they are also aware that the rate of diffusion increases on aging.

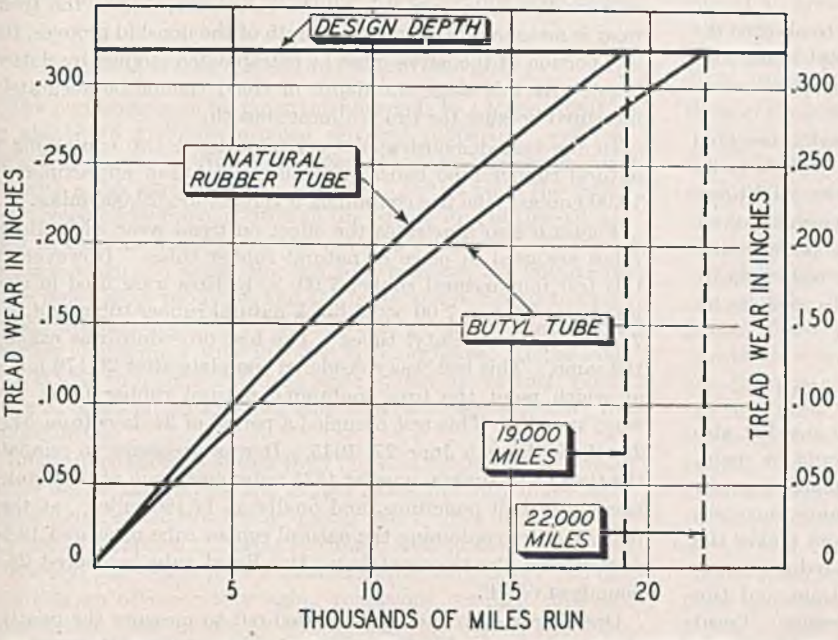

Figure 4. Comparison of Tread Wear of 6.00 × 16 GR-S(S-3) Tires, with Butyl and Natural Rubber Tubes, at 60 Miles per Hour

Figure 5. GR-S Tires with Natural Rubber Tubes (*left*) and Butyl Rubber Tubes (*right*) after 17,095 Miles

Controlled road tests were carried on at the test fleet to determine the actual air-holding properties of Butyl tubes in service and to compare Butyl with natural rubber tubes in this respect. In carrying out these air holding tests, precautions were taken to ensure a minimum loss of air from the valve. A special measuring device was used to prevent loss of air during measurement. The tubes were kept in the tires for the life of the tires. These same tubes were then remounted in new tires and the test continued. One test was continued until five sets of tires had been worn out. When a new set of tires was applied, a 5-day (5000 mile) "break-in" period was allowed before regular air-holding measurements were recorded, in order that errors caused by apparent loss of pressure due to tire growth would not be included in the data. At the end of the break-in period the tubes were reinflated to normal pressure. No air was added (except when tubes were remounted in a new set of tires) until one of the four tubes had fallen to 22 pounds pressure at room temperature. At this point all tubes were reinflated to the original pressure of 28 pounds at room temperature and the tests continued. Thus no tire ever fell below 22 pounds pressure. It was realized that many car drivers permit the pressure in their tires to fall below 22 pounds, but for these test car conditions of overload and continuous high speed driving it was considered dangerous to let the pressure get below that figure. The results that follow, then, are concerned with air losses only between an upper pressure of 28 pounds and a lower pressure of 22 pounds.

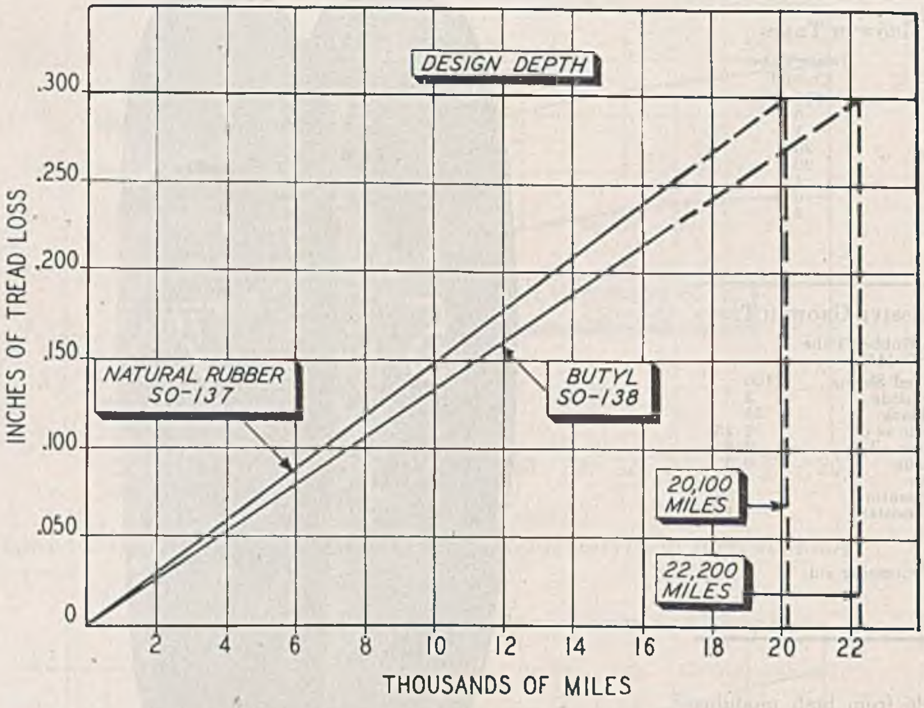

Figure 6. Comparison of Tread Wear of 7.00 × 15 Natural Rubber Tires with Butyl and Natural Rubber Tubes, at 60 Miles per Hour

Figure 3 illustrates the air-holding superiority of Butyl inner tubes over natural rubber tubes. Loss of air pressure in pounds per square inch is plotted against number of hours of air holding. This test was run on a Chrysler automobile operating at 60 miles per hour, 24 hours per day, $5\frac{1}{2}$ days per week. Air-holding measurements were continued over week-ends while the car was standing in the garage. The test was run using 7.00 × 15 natural rubber tires with two 7.00 × 15 black natural rubber and two 7.00 × 15 black Butyl tubes.

Both the natural rubber and the Butyl tubes were of the best quality and were of recent manufacture. The test was considered complete when the set of tires had worn smooth. This occurred after 20,176 miles, which included 664 consecutive air-holding hours (approximately 28 days).

Other air-holding tests were run at the test fleet to observe the effect of various compounding changes in the Butyl inner tube recipe. None of the changes studied so far had any influence on air-holding performance.

Air-holding tests run to date indicate that Butyl tubes hold air 8 to 10 times better than natural rubber tubes. These ratios of 8 to 1 or 10 to 1 were established under severe test conditions. Informal tests, under conditions of driving and standing more nearly approaching normal practice, indicated a permeability ratio even more favorable to Butyl. These latter tests indicate that it will be necessary for the average motorist to reinflate his tires only two or three times a year.

INFLUENCE OF BUTYL TUBES ON TIRE WEAR

Automobile manufacturers specify not only tire size but also optimum inflation pressure at which the tires should be maintained for safe and economical operation. Overinflation is undesirable. It reduces puncture and blowout resistance, increases tire strain, causes rapid and uneven tread wear, and makes the car less comfortable to ride in. Underinflation also reduces puncture and blowout resistance. It increases tire strain and tire operating temperature because of increased flexing. Tread wear, driving safety, and ease of steering are also reduced by underinflation.

Since the superior air-holding properties of Butyl tubes make it a relatively simple matter to maintain proper inflation pressures, it was suggested that an over-all increase in tread wear would result from the use of Butyl tubes. To test the validity of this proposition, tread wear was measured during the course of the air-holding tests.

Figure 4 illustrates the effect on tread wear when Butyl tubes are used in place of natural rubber tubes. In this test two 6.00 × 16 black natural rubber and two 6.00 × 16 black Butyl tubes were mounted in four GR-S (S-3) 6.00 × 16 tires. The test was run on a Chrysler automobile traveling at 60 miles per hour, 24 hours per day, 5 days per week. All tires were reinflated to the original pressure of 28 pounds whenever any one of the tires fell below 22 pounds pressure at room temperature. The tires were rotated every 24 hours (approximately every 1000 miles) and tread wear measurements made every 48 hours (approximately every 2000 miles). This test occupied a period of 25 days from January 2, 1945, through January 27, 1945. It was necessary to reinflate the tires once during the test. This occurred at 9825 miles, at which point the tire containing the natural rubber tube measured 20.5 pounds and the tire containing the Butyl tube measured 27.5 pounds at 65° F. The test was discontinued after 17,095 miles in order that photographs could be obtained. At this mileage the tires containing natural rubber tubes were practically smooth. The actual condition of the tires at the completion of this test is shown by the photograph in Figure 5.

Figures 4, 6, and 7 are drawn by plotting the number of miles that the tires have been tested on the road against tread wear in inches. At any point on the curve the tread wear, commonly expressed as miles per mil, can be calculated. Since the tread wear is measured by gaging the depth of the nonskid grooves, the last portion of the curve must be extrapolated (shown by dotted lines). At this stage the depth of tread cannot be accurately measured because the tire is almost smooth.

In the test demonstrated by Figure 4 the tire containing a natural rubber tube had a nonskid tread life of approximately 19,000 miles; the tire containing a Butyl tube, 22,000 miles.

Figure 6 also illustrates the effect on tread wear when Butyl tubes are used in place of natural rubber tubes. However, in this test four natural rubber 7.00 × 15 tires were used in conjunction with two 7.00 × 15 black natural rubber tubes and two 7.00 × 15 black Butyl tubes. The test procedure was exactly the same. This test was considered complete after 20,176 miles, at which point the tires containing natural rubber tubes had worn smooth. This test occupied a period of 34 days from May 25, 1945, through June 27, 1945. It was necessary to reinflate the tires three times: once at 4835 miles and again at 6840 miles because of nail punctures, and finally at 14,180 miles; at that point the tire containing the natural rubber tube measured 19.55 pounds and the tire containing the Butyl tube measured 25.2 pounds at 65° F.

One more control test was carried out to measure the relative tread wear when Butyl and natural rubber tubes are compared. The conditions of this test were somewhat different from the previous two tests. Figure 7 shows tread wear results when the test car was run at 40 miles per hour rather than at 60 miles per hour. Furthermore the tires were not reinflated until any one of them had fallen below 20 pounds pressure when measured at room temperature. The conditions of this test were adjusted so as to duplicate more closely the driving conditions used by the ordinary motorist. Other conditions of the test, such as tire rotation, etc., were followed as in previous tests. Under these conditions the tire containing the natural rubber tube had a nonskid tread life of approximately 36,000 miles, whereas the tire containing the Butyl tube had a nonskid tread life of approximately 43,000 miles. This difference—approximately 18%—is greater than was the case when the test cars were traveling at 60 miles per hour. This is to be expected, since the tread life of a tire is much higher at slower speeds; therefore, under the conditions of this test, the tires containing the natural rubber tubes were run for a longer increment of time at pressures lower than 28 pounds.

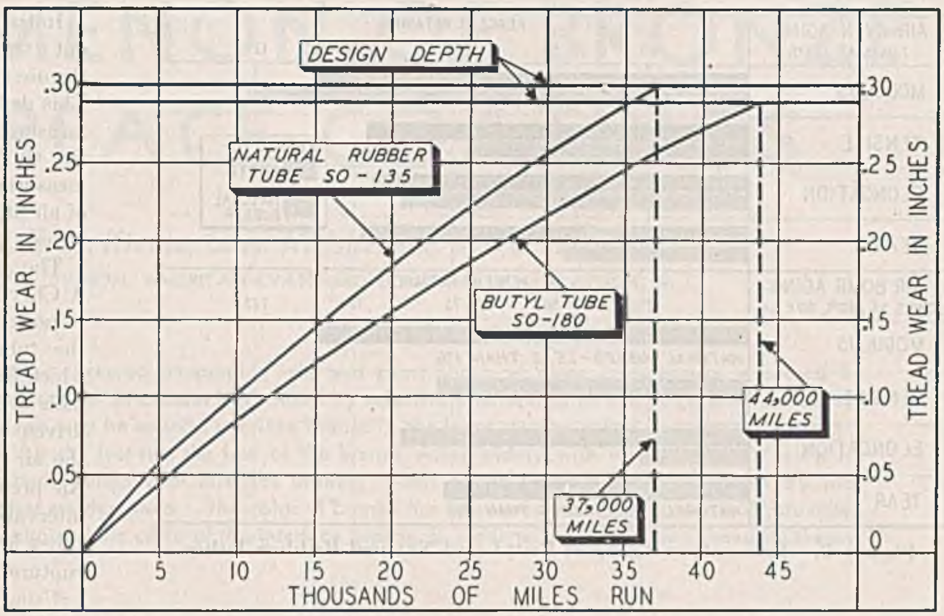

Figure 7. Comparison of Tread Wear of 7.00 × 15 Natural Rubber Tires with Butyl and Natural Rubber Tubes, at 40 Miles per Hour

In interpreting these results one must bear in mind the speed at which the cars were traveling, the mileage run at underinflation and the minimum pressure allowed prior to reinflation, as these factors greatly influence the results obtained. It will be recognized that all these objective conditions depend on a subjective function—namely, the diligence of the car operator.

Aside from increased tread wear, there are indications that other advantages in tire performance are to be gained by the use of Butyl tubes. Rapid tire aging, caused by seepage of air from the tube through the tire, will result in ply separation, side-wall blisters, and reduced blowout resistance. This is particularly true when the tire casing makes an airtight seal against the wheel rim and so prevents air, which has permeated outward through the tube, from escaping by any route other than the body of the tire.

MAINTENANCE OF AGING PROPERTIES

The performance of an inner tube depends to a large extent on its ability to maintain original physical properties over long periods of time in service. The average automobile owner starts out with a new inner tube in a new tire. At this point the tube is well protected by the new tire and the possibilities of tire failures, such as punctures and blowouts, are at a minimum. However, as the mileage and age of tire and tube increase, tire failures become much more probable, and the protection afforded the tube by the tire decreases. Now the physical properties and characteristics of the inner tube increase in importance. If the inner tube is able to maintain its resistance to tearing, cutting, pinching, etc., it will afford a much greater margin of safety to the automobile driver.

Butyl inner tubes maintain their physical properties to a much higher degree than do natural rubber tubes, not only under laboratory aging conditions but also after many miles of service.

Figure 8 compares the aging resistance (retention of properties) of a Butyl inner tube with a natural rubber tube under two different types of laboratory aging conditions. Actual tube sections taken from a factory production run were used. The Butyl tube was of standard quality. The natural rubber tube was of the best quality and was specifically compounded to withstand heat aging. (The tube compounds are the same as those of Table II.) The physical properties studied were modulus at 300% elongation, tensile strength, ultimate elongation, and tear resistance. The retention of these physical properties after aging is compared. In the first aging test the Butyl and natural rubber tube sections were suspended in a circulating air oven (Geer oven) for 7 days at 158° F. In the second aging test the tube sections were placed in an air bomb for 20 hours at 260° F. The superiority of the Butyl tube over the natural rubber tube is evident.

In service aging, that portion of the tube under the shoulder and crown of the tire is subject to the greatest heat and the greatest flexing. A deterioration in physical properties must therefore be sought in the shoulder and crown area. Just as a chain is no stronger than its weakest link, so an inner tube is no more serviceable than its weakest part. It makes little difference if an inner tube has maintained all its tensile strength and tear resistance at the base or rim side if it has lost most of its tensile strength and tear resistance under the shoulders of the tire. Under these conditions, for practical purposes, it is as if all portions of the inner tube had deteriorated to a like degree.

Figure 9 shows the deterioration in tensile strength of a Butyl tube compared with a natural rubber tube after 50,000 miles of road testing at 40 miles per hour. The compounds used in each of these tubes are again the same as those of Table II and the same as those used in the laboratory aging study.

To plot this curve, dumbbell specimens were cut from a new, unused tube at various cross-sectional positions—for example, crown, shoulders, base, etc. The tensile strength values of these dumbbells were determined. These values were plotted on polar coordinate paper at locations corresponding to their positions on the tube itself. With new tubes, either Butyl or natural rubber, the result is a circle, since a new tube is equally strong at all points. Companion tubes made from the same batch of rubber, given the same cure, etc., were placed on cars for road service. At the end of 50,000 miles dumbbell specimens were cut from shoulders, crown, base, etc., as had been done on the new tubes. The values determined on these specimens were plotted on the same polar coordinate paper. They are shown by the broken lines. Figure 9 gives a visual comparison in terms of tensile strength throughout the cross-sectional area, between Butyl and natural rubber tubes after service testing.

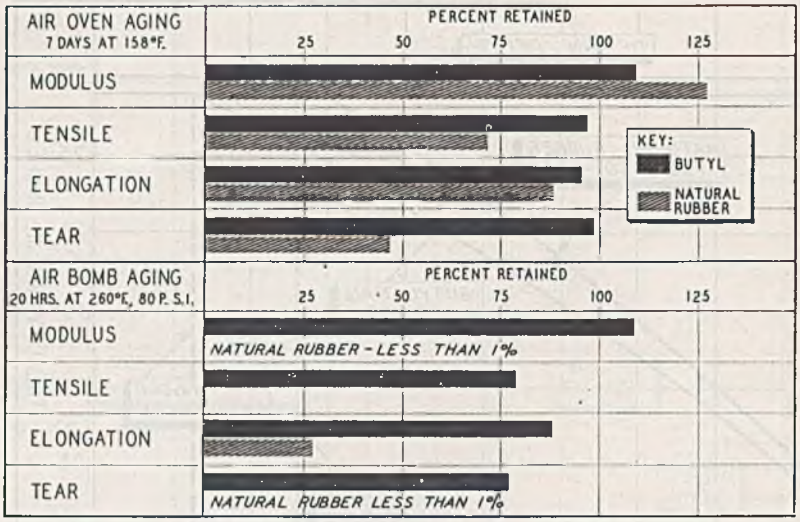

Figure 8. Laboratory Aging of Butyl and Natural Rubber Tubes

Even with this heavy-duty natural rubber tube the deterioration of tensile strength under the shoulders of the tire is marked; although the Butyl tube also deteriorated in tensile strength through the crown and shoulder area, it deteriorated to a much lower degree than did a natural rubber tube.

PUNCTURE AND BLOWOUT RESISTANCE

When a nail or other similar object penetrates a tire and punctures the inner tube, the ability of the tube to resist tearing at the point of rupture is of great importance as an economical consideration and from the viewpoints of safety and convenience. Tearing at the point of rupture will result in rapid deflation similar in results to a blowout of the casing. Tearing to even a slight degree will result in deflation sufficiently rapid to prevent the driver from reaching a service station, where he can obtain assistance in changing the tire. The final size of the rupture determines whether the tube is repairable or if it must be discarded in favor of a new tube.

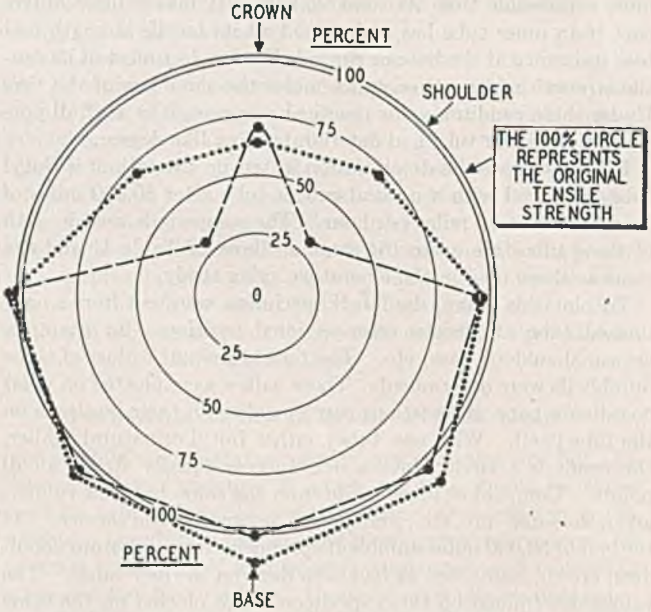

Figure 9. Tensile Retention of Road-Tested Inner Tubes in 6.00 × 16 GR-S Tires after 50,000 Miles at 40 Miles per Hour

- - - - Natural rubber tube (SO-116)
. . . . Butyl tube (SO-82)

Initial tests to study the puncture and blowout (tear) resistance of Butyl tubes involved the use of a special air pressure measuring device. This device can be attached to a tire and will measure continuously the air pressure as the tire travels over the road. By means of this measuring device it was possible to compare loss of air after puncturing Butyl and natural rubber tubes.

The procedure in these tests is as follows: A Chrysler automobile equipped with the continuous air pressure measuring device is used, the tubes to be tested are mounted in tires which have been worn smooth in previous tests, nails are driven into the tires, and the car is driven at a speed of 60 miles per hour until the air pressure in any tire measures 10 pounds. Air pressure readings are recorded at 2-minute intervals. At the completion of the test the tubes are dismounted and the condition of the ruptures are examined.

Using new natural rubber and new Butyl tubes, tests were run using (*a*) a tenpenny nail driven in at the crown and removed, (*b*) a tenpenny nail driven in the shoulder and removed, (*c*) a tenpenny nail driven in half way at the crown and allowed to remain, and (*d*) a large staple (same gage as tenpenny nail) driven into crown and allowed to remain. From these tests it was concluded that new Butyl tubes offer the same puncture and blowout (tear) resistance as new natural rubber tubes.

The next series of tests compared Butyl and natural rubber tubes that had already been in service. Butyl tubes which had been run 35,000 miles under normal conditions before being tested behaved fully as well as new Butyl tubes. No reduction in puncture or tear resistance could be noted. All ruptures in the Butyl tubes, either new or used, were small enough to be repairable. All of the used Butyl tubes were run at least 15 miles before the minimum pressure of 10 pounds was reached, and many of them could have been driven over 100 miles. There was no indication that any puncture would have caused a blowout type of tear.

Tests on used natural rubber tubes were made by using rubber tubes that had completed 25,000 miles of normal service. The same method of testing was employed as had been used on the Butyl tubes; that is, nails were driven into the tires while the car was stationary, and then the car was set in motion and accelerated to 60 miles per hour. In this case all tires containing used natural rubber tubes went flat in less than 5 miles. Examination revealed tears in the tube at the punctured area. The dimensions of some of these tears were such that it would have been impossible to repair them. The conclusion was reached that if the test car had been traveling at a high rate of speed when the puncture occurred, the tire would have gone flat almost instantaneously.

LITERATURE CITED

(1) Baldwin, Turner, and Zapp, Ind. Eng. Chem., 36, 791 (1944).
(2) Cohan, Sohn, and Steinberg, Ind. Eng. Chem., Anal. Ed., 16, 562 (1944).
(3) Cunningham and Turner, *Product Eng.*, Nov. 1945.
(4) Drogin, *Rubber Age* (N. Y.), 51, 483 (1942).
(5) Haworth and Baldwin, Ind. Eng. Chem., 34, 1301 (1942).
(6) Lightbown, *Rubber Age* (N. Y.), 51, 377 (1942).
(7) Rehner, Ind. Eng. Chem., 36, 46 (1944).
(8) Sturgis and Trepagnier, *Rubber Age* (N. Y.), 54, 325 (1944).
(9) Thomas, Lightbown, Sparks, Frolich, and Murphree, Ind. Eng. Chem., 32, 1283 (1940).
(10) Turner, Haworth, Smith, and Zapp, *Ibid.*, 35, 958 (1943).
(11) Zapp, *Ibid.*, 36, 128 (1944).
(12) Zapp and Gessler, *Ibid.*, 36, 656 (1944).

Presented before the Division of Rubber Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

PHENOMENON OF BRONZE IN SURFACE COATINGS

G. L. Buc, R. H. Kienle, L. A. Melsheimer, and E. I. Stearns

CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY, BOUND BROOK, N. J.

Bronze is a phenomenon frequently observed on printing inks and paint films. In some cases bronze is caused by selective reflectance at a single interface; in other cases it is caused by selective interference of light reflected from closely adjacent structures. The former type may be called "interface bronze"; the latter may be called "interference bronze". The two cases are differentiated by the fact that the hue of the bronze varies widely with varying angle of view for interference bronze but remains fairly constant for interface bronze. Some of the unusual colors exhibited by protective coatings in contact with glass are described. The color of bronze has been measured with a spectrophotometer. The general shape of the spectrophotometric curve of the interface bronze is predicted by calculation based on theory.

WHEN an ink which contains a large proportion of pigment is printed on a piece of paper and the printed area is viewed as shown in Figure 1, position *A*, the apparent color is sometimes different from the apparent color when the area is viewed as shown in Figure 1, position *B*. An example may be found on the back cover of the January 1946 issue of INDUSTRIAL AND ENGINEERING CHEMISTRY[1]. The three red dots in the center of the page appear orange in color when viewed from position *A*, and red from position *B*. The red color apparent in position *B* may be called "body" color. The orange color apparent from *A* is formed by a combination of red body color and a yellow color arising in specular reflection of light from the surface. The yellow may be called "surface" color. The yellow surface color is most easily observed when the body color is not present. The body color may be largely removed by printing the ink over a black background. The three red dots slightly overlap the black background, and, where they do, the yellow surface color is readily apparent when viewed in position *A*. This yellow surface color is an example of what the printing ink or paint technologist calls "bronze".

If a paint film formulated with a high proportion of iron blue is exposed to weathering for a time, it is likely to develop surface alteration such that the apparent color will vary, depending on the angle of view. Thus one panel of a dark blue automotive enamel weathered for 1000 hours in an artificial weathering machine was observed to change its apparent color from red through all the colors of the spectrum and back to red again as the angle of view was changed. A weathered paint film such as this is also said by the paint technologist to exhibit bronze.

The object of this paper is to present a physical explanation of bronze as exemplified by the two illustrations described. A separate physical explanation is required for each of the two examples. Together the two physical explanations account satisfactorily for nearly all cases of bronze which have come to our attention. One of these physical theories involves the reflection of light at the interface between two materials. The red dots furnish an example of bronze which is explainable by this theory. Air and red ink are the two materials forming the interface. The other physical theory involves the interference of light reflected from two closely adjacent structures. The weathered iron blue sample furnishes an example which is largely explainable by the second theory. In weathering, a "chalk" film is formed on the surface. This chalk film has a structure which gives rise to interference effects. The first type of bronze will be called "interface bronze" and the second type, "interference bronze".

It is not intended to imply that both kinds of bronze never occur simultaneously. The weathering of iron blue panels appears to be, first, an eroding of vehicle to expose iron blue particles to an air interface which gives rise to interface bronze while subsequent weathering introduces a chalk film having a structure capable of producing interference bronze. Further weathering produces such a thick chalk film that specularity is lost and the film becomes matte.

The colors of metallic oxide on metal surfaces are an example of interference bronze, and the phenomenon has been used to measure the thickness of the oxide film and, hence, the temperature inside a turbine has been inferred (*1*). The familiar colors of oil films on a wet asphalt road are also a form of interference bronze, as are the colors observed when acetone spreads over a mulling slab in the process of cleaning. Many bird and insect colors are examples of interference bronze (*7*). Examples of interface bronze may be seen in the surface colors of crystals of pure dye such as methyl violet. Interface bronze is the commonest type of bronze observed on unweathered films of high pigment formulation.

In describing illuminating conditions, it is customary to define the angle at which the light strikes the surface by measuring the angle between the light path and an imaginary line perpendicular to the surface. The viewing angle is similarly defined as the angle between the line of sight and the imaginary perpendicular to the surface. Throughout this discussion when it is necessary to refer to viewing and illuminating conditions, these standard definitions will be used. A complete description of the illuminating and viewing conditions requires that the angle between the plane of incidence and the plane of viewing be specified. The plane of incidence is the plane containing the light path and the perpendicular to the surface. The plane of viewing contains the line of sight and the perpendicular. The angle between these two planes will be called the "azimuth angle". For example, the conditions of Figure 1*A* would be described as 60° illumination, 60° viewing, and 180° azimuth.

In the presentation of the physical explanation, account must be taken of the state of polarization of the incident light. This is done by specifying the angle which the electric vector of the incident light makes with the plane of incidence. In general, only two possible orientations, perpendicular and parallel to the plane of incidence, need be considered since intermediate orientations may be dealt with in terms of the two mentioned.

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[1] In the event that a particular copy does not show bronze, it may be possible to make a bronzy area of this type by placing a drop of red writing ink on a piece of well-sized black paper and letting it dry unblotted.

MEASUREMENT OF BRONZE

Bronze may be measured by determining the relative reflectance of light of various wave lengths, using the geometry illustrated by Figure 1*A* instead of the geometrical conditions used in standard reflectance spectrophotometry. The plot of the resultant data is known as a spectrophotometric curve and differs from ordinary spectrophotometric reflectance data only in the illuminating and viewing conditions employed. Two samples of printing ink were prepared for measurement. One was alkali blue (CI 705) and the other bronze orange (CI 165). Each was made up as a commercial ink and printed on white paper with a commercial press.

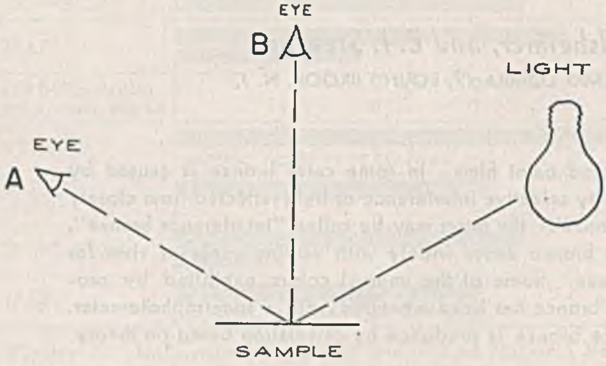


Figure 1. Method of Viewing Bronze

Figure 2 shows data on alkali blue. All reflectances were measured relative to the white paper. Curve *A* is the usual type of spectrophotometric reflectance measurement—that is, 0° illumination, diffuse viewing. This curve is highest around 450 millimicrons which means that the ink appears blue. Curve *B* is the reflectance of perpendicularly polarized light of 60° incidence, 60° viewing, 180° azimuth. This shows greater reflectance at both the blue (400 mμ) and red (700 mμ) ends of the spectrum and, accordingly, is purple. It is well known that applying grease or wax to a surface will eliminate interface bronze. Accordingly, after curves *A* and *B* were obtained, a thin layer of grease was applied to the sample and it was remeasured in the same position as for curve *B*. This gave curve *C*, which represents a very light blue color and lacks the characteristic purple color of the bronze shown in curve *B*.

Figure 3 shows the data on bronze orange. Again all measurements are relative to white paper. Curve *A* is 0° illumination, diffuse viewing, and represents a reddish shade of orange. Curve *B* is 60° illumination, 60° viewing, 180° azimuth, perpendicular polarization, and represents a yellowish orange color. Curve *C* is 60° illumination, 60° viewing, 180° azimuth, perpendicular polarization, but the sample was covered with a thin layer of grease. This is a light orange color and lacks the characteristic yellow color of the bronze shown in curve *B*.

To obtain a curve of alkali blue bronze free of background color, some alkali blue was made up with 50 parts pigment and 50 parts 00 lithographic varnish, and a mass-tone laboratory pulldown was made. This was considerably darker than the commercial ink print of Figure 2. The 0° illumination, diffuse viewing, measured against magnesium oxide showed less than 0.5% reflectance at all wave lengths. The curve of Figure 4 is made with angular conditions of 45° illumination, diffuse viewing, perpendicular polarization, and the reflectance is relative to a perfect mirror.

OPTICAL EXPLANATION OF INTERFACE BRONZE

Most textbooks on physical optics do not specifically explain bronze. Surface color is discussed at some length, but the authors generally review the subject of surface reflectance without specifically considering bronze. Consequently, simplifications are introduced into the reflection laws developed which make them inapplicable to bronze. For instance, many textbooks deal with the specular reflectance from a material with no color, such as a piece of plate glass; this has no application in the present analysis because pigmented films have considerable color. It is also common practice to deal with a metal, but this again is of no interest. Textbooks seem to avoid the intermediate case where a material has considerable color but is not a metal. Another difficulty is that they usually assume perpendicular incidence. A practical paint or ink man never looks for bronze in this viewing condition; rather, he looks for bronze at a glancing angle greater than 45°. Because of these simplifications in which types of samples and viewing conditions that are of no interest in the present connection are assumed, the elementary books do not present directly the equations which enable one to predict the color of bronze.

Nevertheless, the theory necessary to explain interface bronze has been developed. The first contribution toward an optical explanation of bronze was made by Fresnel (*5*). He derived an equation, relating the amount of energy reflected from the interface between two discontinuous media, which depends on the elastic constants:

$$R = \frac{1}{2}\left(\frac{\sqrt{K'}\cos\phi - \sqrt{K}\cos\theta}{\sqrt{K'}\cos\phi + \sqrt{K}\cos\theta}\right)^2 + \frac{1}{2}\left(\frac{\sqrt{K}\cos\phi - \sqrt{K'}\cos\theta}{\sqrt{K}\cos\phi + \sqrt{K'}\cos\theta}\right)^2 \quad (1)$$

where K = elastic constant of air
K' = elastic constant of ink
ϕ = angle of incidence
θ = angle of refraction
R = fraction of energy reflected

Equation 1 is a basic relation which applies not only to reflection of light but also to such reflections as sound echoes from a cliff and radar waves from a warship.

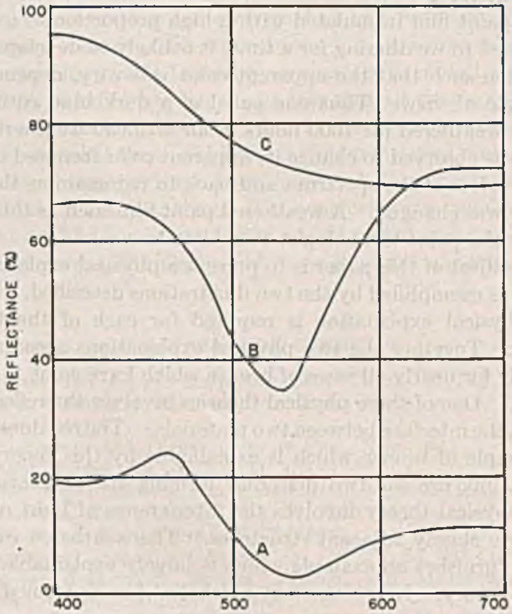


Figure 2. Spectrophotometric Measurement of Bronze on a Print of Alkali Blue Ink Relative to White Paper

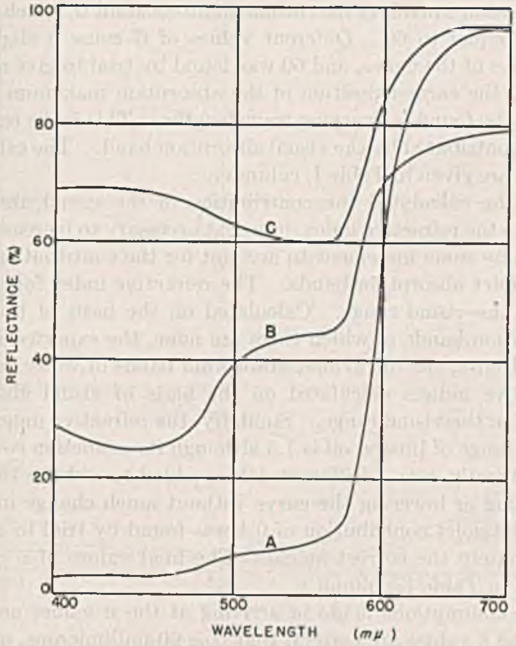


Figure 3. Spectrophotometric Measurement of Bronze on a Print of Bronze Orange Ink Relative to White Paper

A second contribution toward the explanation was made by Maxwell (*5*). According to his electromagnetic theory, if the energy of the Fresnel equation is light, then the elastic constants are specific inductive capacities. The latter are related to the refractive index and extinction coefficient in accordance with the following equations:

$$K = (n - ik)^2 \tag{2A}$$

$$K' = (n' - ik')^2 \tag{2B}$$

where n = refractive index of air
n' = refractive index of pigmented film
k = extinction coefficient of air
k' = extinction coefficient of pigmented film
$i = \sqrt{-1}$

Limiting the elastic constants of Equation 1 to specific inductive capacities means that Equation 1 no longer applies to all kinds of reflection but only to reflection of electromagnetic waves such as light and radar.

If Maxwell's Equations 2 are substituted in Fresnel's Equation 1, and i is eliminated, the resulting relation may be used to calculate bronze. This equation is not presented in textbooks because it is so involved.

A third contribution was made by Helmholtz (*5*). According to his theory of dispersion, the refractive index and the extinction coefficient may be calculated from the characteristics of those atoms in the pigment molecule which are responsible for the color and are hence known to chemists as the chromophore groups. The refractive index and extinction coefficient may both be calculated from the following equations:

$$n^2 - k^2 = 1 + \frac{M\lambda^2(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + G^2\lambda^2} \tag{3A}$$

$$2nk = \frac{MG\lambda^3}{(\lambda^2 - \lambda_0^2)^2 + G^2\lambda^2} \tag{3B}$$

$$M = \frac{Ne^2\lambda_0^2}{m\pi c^2} \tag{3C}$$

$$G = \frac{r\lambda_0^2}{2\pi mc} \tag{3D}$$

where λ = wave length of calculation
λ_0 = wave length of absorption maximum
N = number of chromophores per unit volume
e = electric charge involved in chromophore group
m = mass involved in chromophore group
π = 3.1416
c = speed of light = 3×10^{10} cm./sec.
r = damping resistance involved in chromophore group

Examination of these equations shows that reflectance R at wave length λ and angle ϕ depends on certain characteristics of the chromophore group and the number of chromophores per unit volume. For a particular pigment, which fixes the chromophore group, a way of altering the interface bronze is to vary the number of chromophore groups per unit volume.

CALCULATION OF INTERFACE BRONZE

A prediction was made of the bronze of alkali blue to determine if the theory agreed with the facts. For simplification both the measurement and the calculated prediction were limited to light with perpendicular vector of polarization. Figure 4 presents the measured bronze of an alkali blue ink, consisting of one part alkali blue and one part 00 lithographic varnish pulled down as a mass-tone on white paper. The points of Figure 4 show the predicted reflectance, and it may be concluded that the theory predicts the general shape of the observed curve quite satisfactorily.

The details of the exact calculation of interface bronze depend on such pigment characteristics as particle size. If the particles are large compared to the wave length of light, the individual particles may be considered as reflecting areas enbedded in a vehicle of optical characteristics different from the pigment. If the particle size is small compared to the wave length of light, the film may be considered as homogeneous as a true solution. For purposes of calculation, a homogeneous film was assumed.

To apply Equations 1 and 2 to the calculation of bronze, considering the two media forming the interface to be air and ink, it is necessary to know the extinction coefficients and the refractive indices as a function of wave length. These values are known for air, and it is necessary to determine them only for the ink surface. It is not easy to measure them for the ink surface without assuming the validity of Equations 1 and 2 (*9*), and this

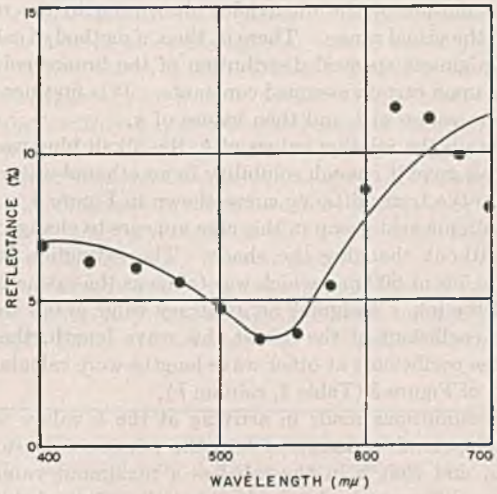


Figure 4. Calculation of Bronze

The solid line is a spectrophotometric measurement of bronze of alkali blue ink, consisting of one part pigment and one part vehicle pulled down on a piece of white paper. It was illuminated with light polarized with its electric vector perpendicular to the plane of incidence and incident at 45°. The measured light was the integrated light reflected in all directions. The points are the expected reflectance of the sample predicted by the Fresnel law of reflectance with the assumptions explained in the section on Calculation of Bronze.

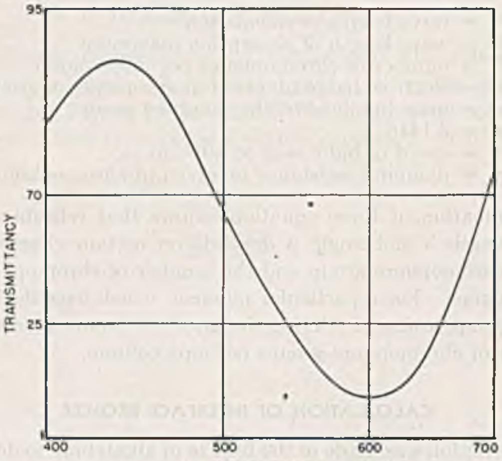


Figure 5. Transmittancy Curve, in 60% Ethanol–40% water, of an Alkali Blue Made Soluble by Sulfonation.

would defeat the purpose of the present paper which is to demonstrate the validity of Equations 1 and 2.

The values of k for the ink can be approximated by diluting the ink and making a transmittance measurement. This will not give the absolute values of k at the ink surface because the concentration of alkali blue relative to the vehicle exactly at the surface is unknown, but it will give relative values of k and the position of the absorption maximum. There is also the possibility of failure of Beer's law.

The values of n for the ink can be approximated by calculation using Equation 3. To calculate n exactly, all the absorption maxima and extinction coefficients over the entire visual and ultraviolet range must be known. In addition, the chromophore constant G of Equation 3 must be known for each absorption band, and these data are not available.

An approximate calculation can be made, however, by assuming a value of G for the visual absorption band (the band primarily responsible for determining the shape of the refractive index–wave length curve) and adding an increment to account for the contribution of the ultraviolet absorption to the refractive index in the visual range. There is, then, a method of calculating the approximate spectral distribution of the bronze color which depends upon certain assumed constants. It is first necessary to determine values of k and then values of n.

To obtain the relative values of k, the alkali blue was sulfonated; this gave it enough solubility in an ethanol-water mixture to obtain the transmittancy curve shown in Figure 5. Addition of the sulfonic acid group in this case appears to change the solubility without changing the shade. The extinction maximum of Figure 5 is at 600 mμ, which was taken as the extinction maximum of the ink. Assigning an arbitrary value of 0.2 to the extinction coefficient of the ink at this wave length, the relative extinction coefficients at other wave lengths were calculated from the data of Figure 5 (Table I, column k).

The assumptions made in arriving at the k values are, thus, that the spectral variation of k in the ink is similar to that in solution, and that k in the ink has a maximum value of 0.2. Assigning different absolute values has the effect of shifting the calculated curve of Figure 4 to the left or right, but does not alter its shape significantly.

If the k values are accepted, the effect of this absorption band on the refractive index can be calculated by means of Equation 3. Simplification of Equation 3 for purposes of this calculation gives:

$$n^2 - \frac{2nk(\lambda^2 - \lambda_0^2)}{G\lambda} - (k^2 + 1) = 0 \qquad (4)$$

Equation 4 involves the chromophore constant G, which was assumed equal to 60. Different values of G cause a slight shift sideways of the curve, and 60 was found by trial to give approximately the correct position of the absorption maximum. Then n' may be found for varying wave lengths. This is the refractive index contributed by the visual absorption band. The calculated values are given in Table I, column n'.

Having calculated the contribution of the visual absorption band to the refractive index, it is next necessary to increase all the values by some increment to account for the contribution of the ultraviolet absorption bands. The refractive index for water is 1.3 in the visual range. Calculated on the basis of the visual absorption bands of which there are none, the expected index is 1.0. Hence, the ultraviolet absorption bands of water raise the refractive indices calculated on the basis of visual absorption by 0.3 in the visual range. Similarly, the refractive index in the visual range of linseed oil is 1.5 although its extinction coefficient is practically zero. Different values added to n' have the effect of raising or lowering the curve without much change in shape. An ultraviolet contribution of 0.4 was found by trial to give approximately the correct height. The final values of n are presented in Table I, column n.

The assumptions made in arriving at the n values are, thus, that the k values are correct, that G is 60 millimicrons, and that the ultraviolet contribution is 0.4. The two latter arbitrarily assigned values have the effect of shifting the curve laterally and vertically, respectively, but do not alter its shape.

TABLE I. RESULTS OF CALCULATIONS OF FIGURE 4

λ	k	n'	n	R
400	0.000	1.00	1.40	0.068
425	0.002	0.98	1.38	0.064
450	0.005	0.97	1.37	0.062
475	0.012	0.94	1.34	0.055
500	0.025	0.91	1.31	0.049
525	0.060	0.85	1.25	0.037
550	0.100	0.85	1.25	0.039
575	0.175	0.88	1.28	0.055
600	0.200	1.02	1.42	0.087
625	0.175	1.17	1.57	0.116
650	0.100	1.18	1.58	0.113
675	0.050	1.13	1.53	0.099
700	0.015	1.05	1.45	0.080

λ = wave length at which calculation was made, millimicrons
k = assumed extinction coefficient of ink
n' = refractive index contribution to alkali blue ink of visual absorption band calculated by Equation 4
n = calculated refractive index of ink
R = reflectance calculated from k and n by Equations 1 and 2

The measured and calculated reflectances are shown in Figure 4. The purpose of Figure 4 is not to measure or predict bronze extremely accurately but only to show that, in general, the shape of the bronze curve is to be expected from theoretical considerations.

OPTICAL EXPLANATION OF INTERFERENCE BRONZE

The kinds of structures capable of producing interference bronze are many and varied. Interference may be produced by two parallel interfaces. There may be considerable variation in the indices of refraction of the three media making up the two interfaces. Regularly arranged structures, such as parallel ridges, also give rise to surface colors which can be explained on the principle of interference.

No comprehensive analysis of interference color is undertaken here, and no attempt has been made to determine the exact nature of the chalk film, which forms on iron blue panels on weathering. One feature, however, is common to all cases of interference color; namely, the color varies with viewing conditions. To illustrate this color variation, a simple case of a vehicle film in air was chosen for calculation.

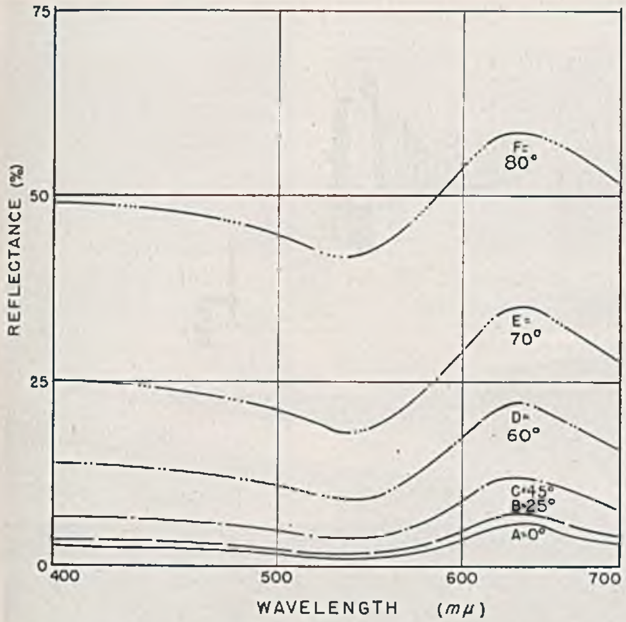


Figure 6. Calculated Bronze of Alkali Blue at Different Angles of Incidence

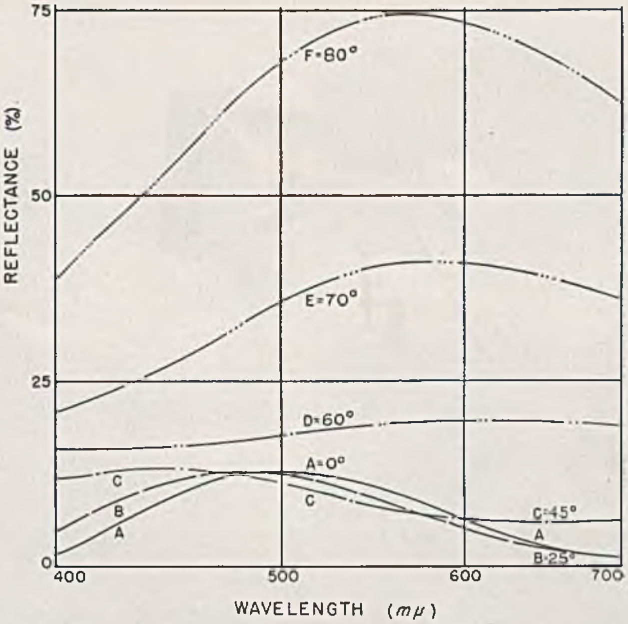


Figure 7. Calculated Bronze of a Vehicle Film in Air at Different Angles of Incidence

The reflectance of light from a thin film with parallel surfaces may be calculated by the equation giving the superposition of waves of the same frequency but different phase and amplitude:

$$R = A_1^2 + A_2^2 + 2A_1A_2 \cos \Delta \tag{5}$$

where R = intensity of reflected light
A_1 = amplitude of one wave
A_2 = amplitude of second wave
Δ = phase difference of waves

Considering a thin film, the amplitudes of the reflected waves may be calculated with the Fresnel equations in a slightly different form than Equation 1. The amplitude of the light wave reflected from the first surface, A_1, is:

$$A_1 = \frac{\sqrt{K} \cos \phi - \sqrt{K'} \cos \theta}{\sqrt{K} \cos \phi + \sqrt{K'} \cos \theta} \tag{6}$$

The amplitude of the light wave reflected from the second surface, A_2, is similar but must be multiplied by the fraction of light transmitted by the first surface. The complete equation is:

$$A_2 = \left(\frac{2\sqrt{K} \cos \phi}{\sqrt{K} \cos \phi + \sqrt{K'} \cos \theta}\right)\left(\frac{\sqrt{K''} \cos \theta - \sqrt{K'} \cos \psi}{\sqrt{K''} \cos \theta + \sqrt{K'} \cos \psi}\right) \tag{7}$$

where K'' = elastic constant of third medium
ψ = second angle of refraction

The retardation Δ depends upon the properties of the film:

$$\Delta = \frac{4nd\pi}{\lambda} \cos \theta - \alpha \tag{8}$$

where Δ = retardation angle
d = separation of two parallel interfaces
n = refractive index of medium
λ = wave length of light
α = difference between phase changes at two reflecting surfaces (may be calculated by known methods, *5*)

CALCULATION OF INTERFERENCE BRONZE

For calculation it is necessary to know K, K', K'', d, and ϕ. θ may be calculated from:

$$\sqrt{K} \sin \phi = \sqrt{K'} \sin \theta \tag{9}$$

ψ may be calculated from:

$$\sqrt{K'} \sin \theta = \sqrt{K''} \sin \psi \tag{10}$$

No attempt was made to predict the appearance of a particular sample. However, calculations were made with Equations 5 to 9 which would predict the color appearance of this kind of bronze for a hypothetical sample at different angles to compare it with the color appearance of interface bronze at different angles. For these calculations the case of vehicle film in air was assumed. This means that $K = 1$, $K' = 1.5$, $K'' = 1$, $\alpha = \pi$, and d was assumed equal to 2.5×10^{-5} cm. The results of the calculation are discussed later.

DIFFERENTIATION OF TWO KINDS OF BRONZE

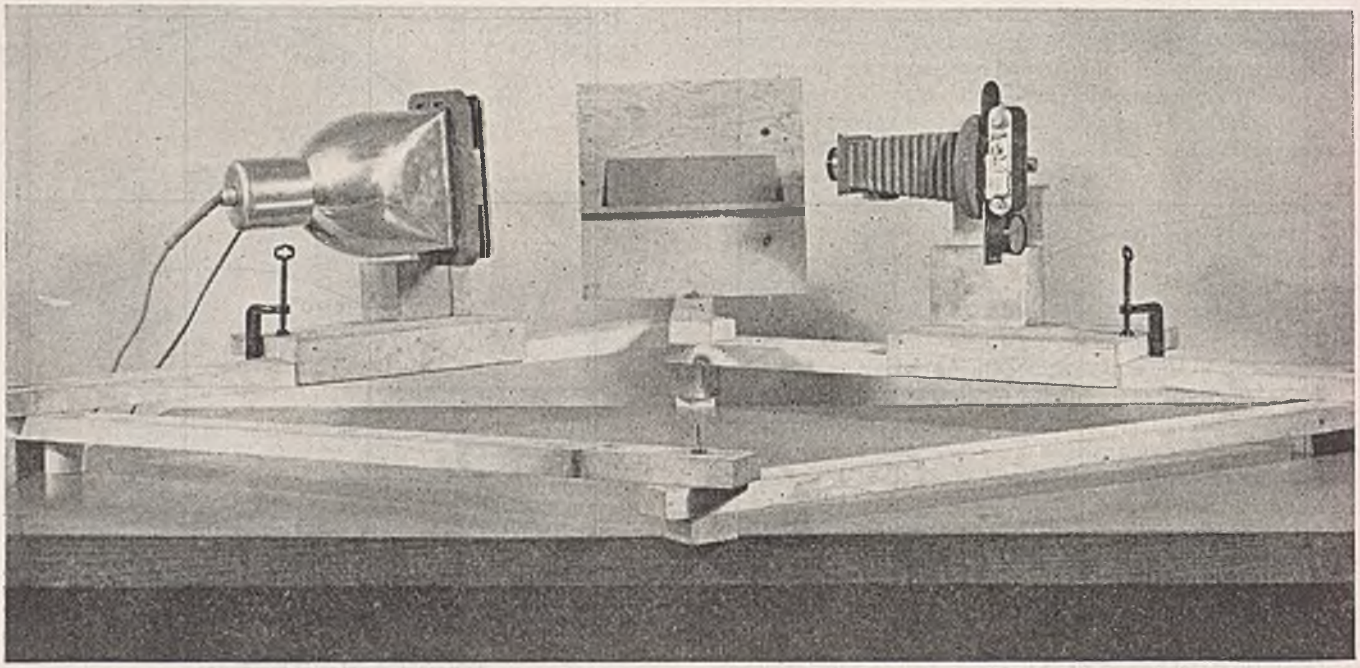
Interface and interference bronze may be distinguished by observing the color at different angles of view. Visual observation of alkali blue ink shows that the bronze is purple viewed by daylight at all angles of view from 0° to 85°. Visual observations on a particular weathered iron blue panel showed that, as the angle of view was varied from 0° to 85°, a complete change of bronze color occurred from red through yellow, green, blue, and back to red. This difference in behavior can be explained by assuming a different kind of bronze in these two cases and gives a method of distinguishing the two types.

Calculations made on interface bronze gave the curves of Figure 6. These curves vary in total light reflected, but the dominant wave length remains the same. (*Continued on page 153*)

Table II. Dominant Wave Lengths Calculated from Spectral Reflectance Curves of Bronze in Figures 6 and 7[a]

	Dominant Wave Length	
ϕ	Interface	Interference
0	−496	496
25	−496	487
45	−496	476
60	−496	573
70	−497	571
80	−498	569

[a] I.C.I. (International Commission on Illumination) standard observer, and illuminant C.



Apparatus to Photograph Bronze Effects

The light from the enlarger head of a Kodak precision enlarger is photographed with a Leica 35-mm. camera after reflecting from a bronzy sample. The angle of incidence can be varied from 10° to 80°, always maintaining the angular conditions of Figure 1*A*.

The color effects described in this article are shown by the color plate on the facing page. It is impossible to reproduce exactly all the effects because of the limits of color reproduction. The pictures were taken on Kodachrome film and were reproduced by the four-color method of printing. Despite its limitations, the plate illustrates the main points.

Photographs 1 to 5 show the constancy of hue of interface bronze as the angle of view is changed. These pictures, at about half natural size, were taken with the geometrical conditions of Figure 1*A* by means of the apparatus shown above. They demonstrate the prediction of column 2, Table II. The sample was a mass tone of alkali blue at a pigment-ink ratio of 1 to 1.5.

Photograph 1.	10° incidence
Photograph 2.	30° incidence
Photograph 3.	45° incidence
Photograph 4.	60° incidence
Photograph 5.	75° incidence

Photograph 6 shows mass tones of alkali blue at pigment-vehicle ratios of 1 to 1, 1 to 2, and 1 to 3. This change in color of bronze is predictable on the basis of a changing k in Equation 2.

Photographs 7 to 11 illustrate the change in hue of interference bronze as the angle of view is changed. These pictures were taken with the geometrical conditions of Figure 1*A*. They demonstrate the prediction of column 3, Table II. The sample was an enamel of iron blue sprayed on a steel panel. The left-hand half was exposed in a Weather-Ometer for 1000 hours; the right-hand half, 500 hours. The inevitable water spots are readily apparent. The depth of focus was not adequate to accommodate the sample at the extreme angles of incidence used in photographs 10 and 11.

Photograph 7.	10° incidence
Photograph 8.	30° incidence
Photograph 9.	45° incidence
Photograph 10.	60° incidence
Photograph 11.	75° incidence

Photograph 12 shows the contrasting bronze and body colors of a printing ink with the pigment bronze orange. Left-hand side of the composite sample is a tight pulldown over a black background viewed in position *A*, Figure 1. The right-hand side is a tight pulldown over a white paper background viewed in position *B*, Figure 1.

Photograph 13 shows a pile of methyl violet dye crystals. They appear yellowish green rather than violet because of interface bronze.

Photograph 14 is a bronzy car with normal photographic exposure. The high lights are overexposed and do not show the bronzy colors well.

Photograph 15 is the same car as 14, but photographed with a short exposure to show the color of the highlights.

Photograph 16 is a typical bronzy car.

Photograph 17 is a typical bronzy car.

Photograph 18 is a car with the weathered film so thick that the bronze color is optically scattered and not apparent. The car has a heavy "chalk".

Photograph 19 is an ornamental steel button viewed in position *B*, Figure 1.

Photograph 20 is the button of photograph 19 viewed in position *A*, Figure 1, and illustrates one of the cases where interference bronze is desired.

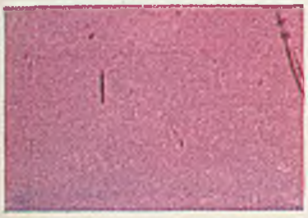
Photograph 21 is a thin film on the surface of water, similar to an oil film on a wet asphalt road; it corresponds optically to interference bronze.

Photograph 22 is a beetle with diffuse lighting, an example of interference bronze colors in nature.

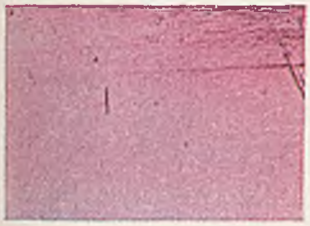
Photograph 23 is the same beetle as 22 but with different illumination. The different colors with varying viewing conditions are characteristic of interference bronze.

Photograph 24 shows museum skins of two birds, the bronze grackle and the purple grackle, both of which illustrate interference bronze in nature (from the collection of J. T. S. Hunn).

ILLUSTRATIONS FOR THE PHENOMENON OF BRONZE IN SURFACE COATINGS



No. 1. Alkali Blue,
10° Incidence



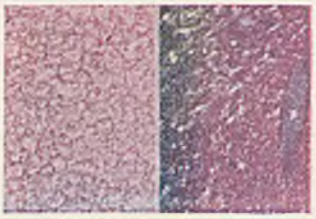
No. 2. Alkali Blue,
30° Incidence

No. 3. Alkali Blue,
45° Incidence

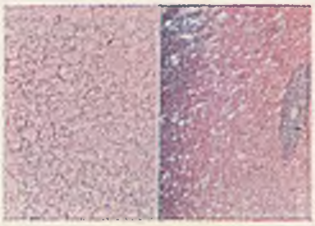
No. 4. Alkali Blue,
60° Incidence

No. 5. Alkali Blue,
75° Incidence

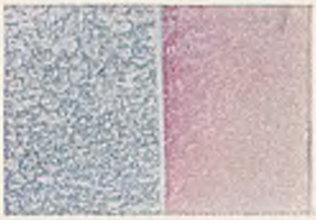
No. 6. Alkali Blue,
Concentration Effect



No. 7. Weathered Iron Blue,
10° Incidence



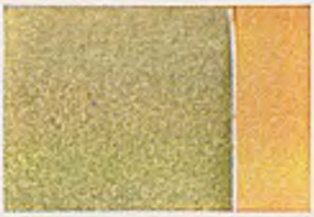
No. 8. Weathered Iron Blue,
30° Incidence



No. 9. Weathered Iron Blue,
45° Incidence

No. 10. Weathered Iron Blue,
60° Incidence

No. 11. Weathered Iron Blue,
75° Incidence



No. 12. Bronze Orange
Bronze and Body Colors

No. 13. Methyl Violet Crystals

No. 14. Bronzy Automobile A,
Normal Photographic Exposure

No. 15. Bronzy Automobile A,
Short Photographic Exposure

No. 16. Bronzy Automobile B

No. 17. Bronzy Automobile C

No. 18. Automobile D with
Heavy "Chalk"

No. 19. Steel Button
Body Color

No. 20. Steel Button
Bronze Color

No. 21. Thin Film on Surface
of Water

No. 22. Beetle Illuminated with
Diffuse Light

No. 23. Beetle Illuminated with
Spotlight

No. 24. Bronze Grackle (Top)
Purple Grackle (Bottom)

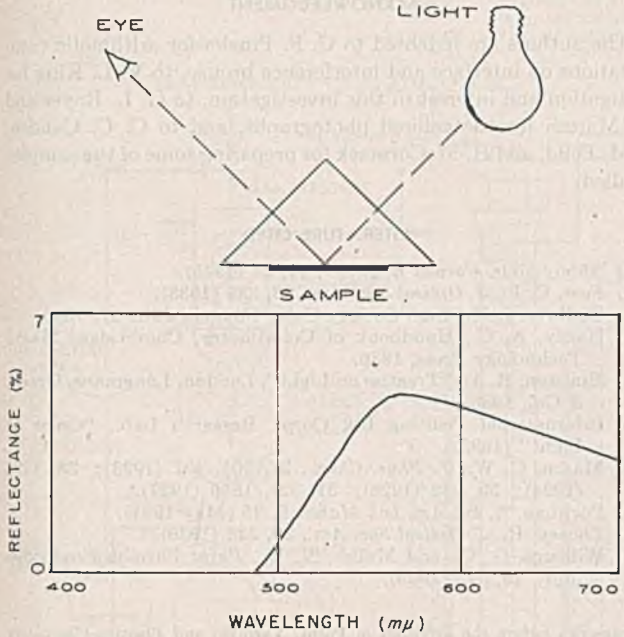


Figure 8. Method of Viewing Yellow Color of Alkali Blue Ink

Ink is placed on a right-angle glass prism as shown and viewed as indicated; spectrophotometric curve measured at 45° incidence with perpendicular polarization

The dominant wave lengths, calculated in the conventional manner (*4*) are given in Table II. Calculations made on interference bronze gave the curves of Figure 7. The dominant wave lengths of this series of curves are also listed in Table II.

The dominant wave lengths of interface bronze are practically constant, whereas those of interference bronze vary widely. This is a practical way to distinguish bronzes which are definitely one or the other. In cases where both occur together, intermediate effects are observed.

DEFINITION OF BRONZE

Bronze is apparently easier to observe than to define. A partial definition was given by Portman (*8*): "Some colors when converted into inks and printed have more bronze than others. This is a feature somewhat different from finish." Portman then gave various factors which alter the amount of bronze, but his definition is only that this is a feature somewhat different from finish. Foss (*2*) stated: "In certain printing inks an unusually selective reflection may be noticed which varies considerably with viewing conditions. This is designated as bronze." Williams and Muller (*10*) referred to a specific sample as follows: "Light reflected from the surface of the formulation with Prussian blue shows a reddish cast which is known as bronze." However, they do not limit bronze to a surface reflection for later on they say: "Examination of lacquer films by transmitted light indicates that a bronze may be developed in the interior of films as well as on either surface." The American Association of Textile Chemists and Colorists is not directly concerned with coating compositions or printing inks, but encounters a similar phenomenon on some textile dyeings at high concentrations. The definition of bronze given by this association is included in a comparative list of color terms compiled by member bodies of the Inter-Society Color Council in 1939: "Bronzy, having a metallic surface appearance that partly obscures the body color of the material. Bronziness is usually yellowish, reddish, or greenish, and complementary to the body color."

Godlove (*3*) discussed surface colors briefly, but did not attempt to define bronze or to evaluate it quantitatively. The International Printing Ink Corporation (*6*) published an excellent illustration of bronze and spoke of it as a metallic luster.

A review of the literature thus reveals that there has been no universally accepted definition of bronze. In view of the optical explanations given earlier, the following is suggested as a scientific definition of bronze: Bronze is the appearance of color which originates in selective reflectance at one interface or interference of white light reflected at closely adjacent structures. As a practical definition of bronze, we may say that bronze is the appearance of color of surfaces, illuminated and viewed specularly, that differs in hue from the color observed with normal viewing.

COMPARISON OF BRONZE AND GLOSS OR FINISH

The definition of bronze specifies a colored reflection. Bronze depends only on the spectral distribution of the reflected light. It is possible for a sample to scatter light geometrically and still have a high bronze—that is, have the reflected light highly colored.

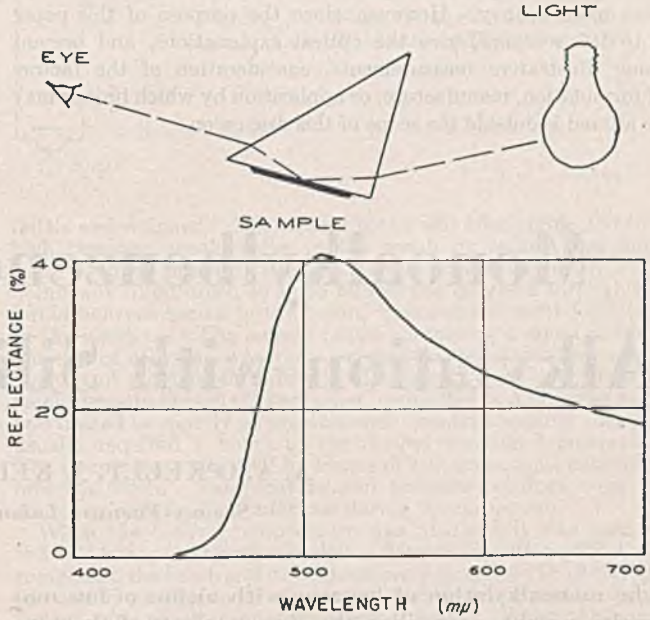


Figure 9. Method of Viewing Green Color of Alkali Blue Ink

Ink is placed on a right angle glass prism as shown and viewed as indicated; spectrophotometric curve measured at 72° incidence with perpendicular polarization

"Gloss" or "finish", which is also a surface reflectance phenomenon, depends on regularity of reflected light. A sample of high gloss or finish has light reflected quite regularly geometrically and may or may not be colored. Bronze is, therefore, a chromaticity of surface-reflected light. In comparing two samples for amount of bronze, the one which deviates more from white light or the body color should be called more bronzy. Specular conditions of viewing are necessary when observing either gloss or bronze to minimize the contribution of body color to the over-all appearance.

UNUSUAL METHODS OF VIEWING BRONZE

In observations of practical interest, light passes through air, then strikes the sample, and is reflected back through air. Under these usual conditions it is observed that an alkali blue ink pull-down on paper has a reddish purple reflection. It may be of academic interest, however, to examine the phenomenon of surface reflection further with the conditions imposed that the light must travel through glass before and after striking the surface. Under these conditions some interesting additional color effects can be observed. If a right-angle prism is available, some freshly prepared alkali blue ink may be placed upon the glass surface and viewed as illustrated in Figure 8; the spectrophotometric measurement of the observed yellow color is also shown. On the other hand, if the viewing conditions are changed to those of Figure 9, the observed color will be green. The spectrophotometric curve of this color is also given. The reason the color changes from yellow to green in the two cases is that the angle at which the light strikes the sample is changed. This experiment may not be of practical importance to the paint or ink man, but the various colors exhibited by alkali blue, which include blue, yellow, violet, and green, are all to be expected from a consideration of the Fresnel equation. This is evidence of the soundness of the optical explanation of the phemonenon of interface bronze.

CONTROL OF BRONZE

The appearance of bronze can be controlled to some extent by formulation. For instance, if alkali blue is made up with one part of varnish and compared with a second sample made up with three parts of varnish, the pulldown with lesser varnish will appear more bronzy. However, since the purpose of this paper is to define bronze, give the optical explanations, and present some illustrative measurements, consideration of the factors of formulation, manufacture, or application by which bronze may be altered is outside the scope of this discussion.

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The authors are indebted to C. F. Pinzka for arithmetic computations on interface and interference bronze, to V. L. King for instigation and interest in this investigation, to G. L. Royer and C. Maresh for the colored photographs, and to C. C. Candee, J. M. Feild, and H. McCormack for preparing some of the samples studied.

LITERATURE CITED

(1) Anonymous, *Cornell Engineer*, 11, 23 (1945).
(2) Foss, C. F., *J. Optical Soc. Am.*, 28, 389 (1938).
(3) Godlove, I. H., Inter-Society Color Council, June 27, 1940.
(4) Hardy, A. C., Handbook of Colorimetry, Cambridge, Mass., Technology Press, 1936.
(5) Houston, R. A., "Treatise on Light", London, Longmans, Green, & Co., 1938.
(6) International Printing Ink Corp., Research Lab., "Color as Light" (1935).
(7) Mason, C. W., *J. Phys. Chem.*, 27, 201, 401 (1923); 28, 1233 (1924); 30, 382 (1926); 31, 321, 1856 (1927).
(8) Portman, A. B., *Am. Ink Maker*, 9, 35 (May 1931).
(9) Tousey, R., *J. Optical Soc. Am.*, 29, 235 (1939).
(10) Williams, G. C., and Muller, N. W., *Paint Varnish Production Mgr.*, 19, 240 (1939).

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Monoalkylbenzenes by Vapor-Phase Alkylation with Silica-Alumina Catalyst

A. A. O'KELLY, J. KELLETT, AND J. PLUCKER
Socony-Vacuum Laboratories, Paulsboro, N. J.

The monoalkylation of benzene with olefins of low molecular weight, over silica-alumina catalysts of the type used in commercial catalytic cracking and at elevated temperatures, is accomplished with substantial yields of monoalkylbenzenes at relatively low pressures. The utilization of ethylene was found to be favored by increased reaction time, increased temperature, and increased molar ratio of benzene to ethylene. Small amounts of polyethylbenzenes produced may be recycled in the charge stream to give increased yields of monoethylbenzene based on ethylene and benzene consumed. The catalyst indicates long life and sustained activity under the conditions used. A cyclic operation such as is used in catalytic cracking is adaptable to the production of monoethylbenzene in which air regeneration of the catalyst is carried out at temperatures in the same range as the reaction temperatures.

THE low temperature alkylation of aromatic hydrocarbons with olefins in the presence of various catalysts has been liberally described. Ipatieff, Corson, and Pines (*5*) showed that sulfuric acid catalyzes the reaction between benzene and amylene to give good yields of mono-, di-, and triamylbenzenes. Propylene and butenes are also readily reacted with benzene in the presence of sulfuric acid (*5, 17*). Substantially the same results were obtained by the use of hydrogen fluoride (*15*). Ethylene, however, did not give appreciable yields of ethylbenzene in either case.

The standard method for effecting the reaction of ethylene with benzene at relatively low temperatures to give ethylbenzenes was described by Balsohn (*1*) and was the subject of numerous investigations (*2, 3; 4, 9, 11*). The catalyst for the reaction consists mainly of metal halides of the Friedel-Crafts type.

Ipatieff, Pines, and Komarewsky (*7*) used *o*-phosphoric acid at 300° C. to effect the reaction. Pardee and Dodge (*12*) described the use of sodium–aluminum chloride complexes supported on pumice, and extruded phosphoric acid–kieselguhr catalysts, in the formation of ethylbenzene from ethylene and benzene in the vapor phase at 230–270° C., with pressures in the order of 200 pounds per square inch. More recently extensive investigations of the use of an extruded phosphoric acid–kieselguhr catalyst in pellet form containing 62–63% by weight of P_2O_5 for the reaction were reported by Mattox (*10*) and Ipatieff (*8*). The temperature used was 270–300° C.; this indicated vapor phase operation. The maximum pressure used was 900 pounds per square inch. Results obtained indicated a high conversion of ethylene and benzene to ethylbenzene per pound of catalyst consumed over the catalyst life range. The ultimate life indicated under the conditions of the run was 48 days.

Schollkopf (*14*) disclosed the use of an activated hydrosilicate catalyst at elevated temperatures for effecting the addition of unsaturated hydrocarbons to compounds containing the benzene or naphthalene ring.

The removal and transfer of side chains from aromatics at elevated temperatures by the use of silica-alumina catalysts of the type used in commercial catalytic cracking operations was described by Thomas, Hoekstra, and Pinkston (*16*) and Hansford, Myers, and Sachanen (*4*). Sachanen and O'Kelly (*13*) described

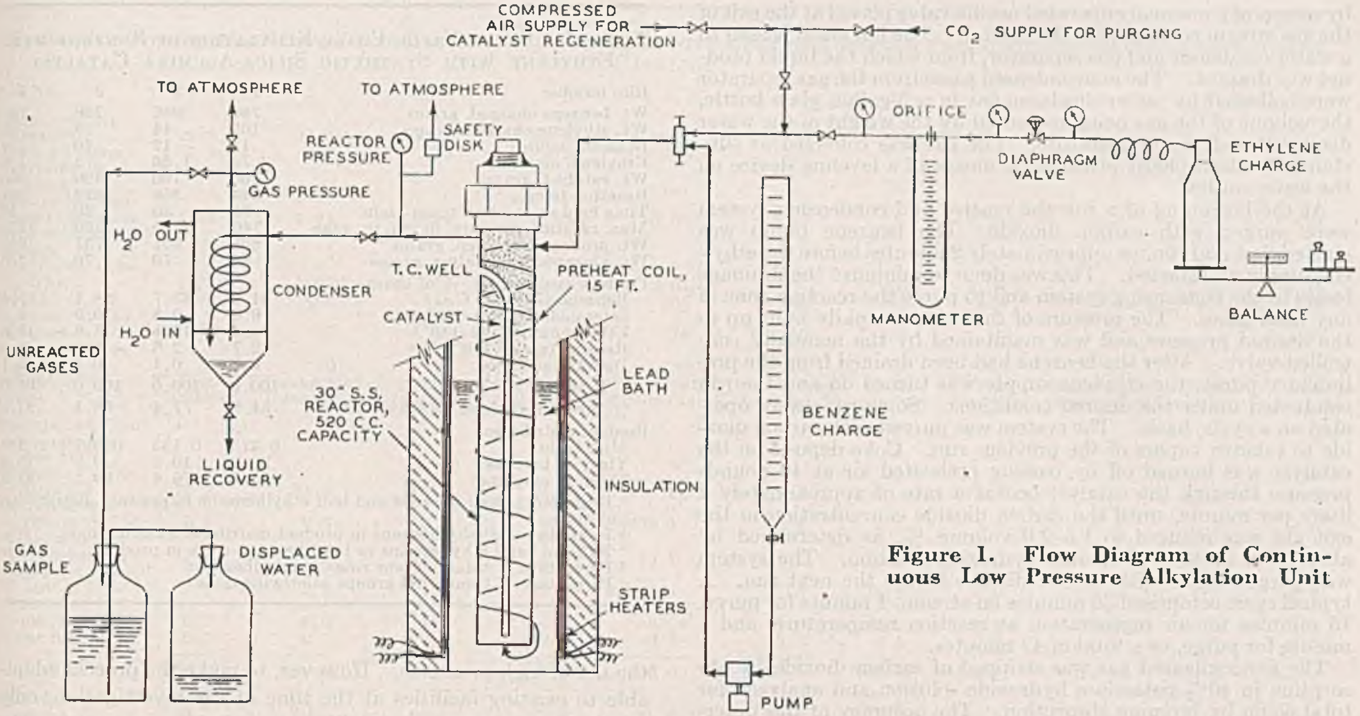

Figure 1. Flow Diagram of Continuous Low Pressure Alkylation Unit

the vapor-phase destructive alkylation of aromatics, benzene, and toluene with various olefins at elevated temperatures (400–480° C.) and at pressures as high as 3200 pounds per square inch. A clay catalyst in pellet form was employed. Under such drastic temperature conditions a series of alkyl aromatics was produced.

This article describes the direct alkylation of benzene with ethylene in the vapor phase over a silica-alumina catalyst for the production of monoethylbenzene. Both batch and continuous operations were conducted and are described. Several continuous runs with propylene and benzene for the formation of cumene were made with the same catalyst and are included in this paper.

MATERIALS FOR CATALYTIC RUNS

The benzene was the standard C.P. thiophene-free grade containing at least 99% benzene. The polyethylbenzene used in the dealkylation run was obtained from the Dow Chemical Company. Although it was not analyzed for the relative amounts of polyethylbenzenes, all the material boiled above monoethylbenzene. The ethylene used was Matheson's 98% grade, which indicated 94 volume % total olefin by bromine absorption and less than 1% olefin above ethylene by absorption in 92% sulfuric acid. The propylene used was supplied by Matheson and indicated 95 volume % olefin higher than ethylene by absorption in 92% sulfuric acid, and less than 1% isobutene by absorption in 70% sulfuric acid. The propylene-propane mixture used in the experiments was obtained from refinery gases by distillation under pressure and was analyzed by absorption in sulfuric acid.

The catalyst employed was a synthetic silica-alumina catalyst that is used in the commercial catalytic cracking process. It was prepared by the coprecipitation of the hydrous oxides in a weight ratio of about 9 to 1 of silica to alumina. This catalyst was similar to that described by Hansford, Myers, and Sachanen (*4*).

APPARATUS AND PROCEDURE

Batch Runs. The reactor for processing the materials consisted of a 2-liter stainless steel bomb made by the American Instrument Company. A small ethylene lecture bottle with attached valve was used to charge the ethylene under pressure. The bottle could be weighed to the nearest gram.

The cold bomb was charged with catalyst and benzene and sealed in the customary manner. The proper amount of ethylene was previously transferred from a large cylinder into the lecture bottle and weighed. The lecture bottle was then connected to a high pressure needle valve in the bomb by means of a short piece of high pressure tubing of small inside diameter. The bomb was tilted down so as to bubble the ethylene through the liquid benzene sealed in the bomb; this assured partial solution of the ethylene. The lecture bottle containing a small residual amount of ethylene was then weighed to determine the actual amount of ethylene introduced. The bomb was then placed in its electrically heated shaker jacket, connected to a pressure gage, and heated as rapidly as possible with constant rocking (heating usually required 1 hour) to the desired reaction temperature. The temperature was read by means of a thermocouple extending into the bomb. Temperature and pressure readings were recorded at definite time intervals during the entire run.

When the desired temperature was attained it was held at ±3° C. during the reaction period. After the reaction period was completed, the bomb and its contents were cooled as rapidly as was felt safe by passing an air stream between the bomb and enclosing jacket; this required approximately 2 hours. When the bomb was substantially at room temperature, it was vented and opened, and its contents were poured into a cooled flask. The catalyst was separated from the liquid product by filtration. Weights were recorded in each operation. The liquid product was then distilled through a Fenske distillation column having twenty-five plates and a total reflux-variable take-off head. The reflux ratio used during the plateau period of a compound was approximately 20 to 1. The specific gravities of the definite fractions agreed well with the values of the particular compounds in the literature, and the iodine number of all fractions was zero. The composite residues of several runs were distilled through the same column.

Continuous Runs. The continuous alkylation reaction was studied in a small laboratory unit illustrated in Figure 1. The reactor consisted of a length of 1-inch seamless steel tubing of 520-cc. capacity, with a high pressure union at one end for closure. The reactor and preheat line were immersed in an electrically heated molten lead bath to give accurate heat control. A thermowell was welded into the reactor so that temperatures could be read at any longitudinal position in the catalyst bed. It was found that the temperature did not vary more than 5° C. in the catalyst bed with the rates used. The charge was preheated by means of a 15-foot length of small diameter, high pressure tubing wrapped around the reactor and entering the bottom. The benzene was charged directly from a calibrated buret into the preheat line by means of a Manzel chemical feeder. The ethylene was charged from a lecture bottle placed on a balance and connected to a reducing valve by means of coiled copper tubing of small diameter. After passing through the reducing valve, the ethylene was metered by means of a calibrated flow meter and charged into the preheat line. The flow meter was used only to give instantaneous rates of flow; the weights on the balance were taken at definite time intervals and used in calculating the over-all charge. The reaction was maintained at the desired pressure ±1 pound by means of a manually operated needle valve placed at the exit of the gas stream coming from the reactor. The hot gases passed to a water condenser and gas separator, from which the liquid product was drained. The noncondensed gases from the gas separator were collected by water displacement in a 5-gallon glass bottle, the volume of the gas being measured by the weight of the water displaced and the temperature. The gas was collected at substantially atmospheric pressure by means of a leveling device on the water outlet.

At the beginning of a run the reactor and condensing system were purged with carbon dioxide. The benzene pump was started first and run for approximately 2 minutes before the ethylene supply was started. This was done to minimize the drainage losses in the condensing system and to purge the reaction zone of any fixed gases. The pressure of the reactor rapidly built up to the desired pressure and was maintained by the manually controlled valve. After the benzene had been drained from the preliminary purge, the ethylene supply was turned on and the run conducted under the desired conditions. Some runs were operated on a cyclic basis. The system was purged with carbon dioxide to remove vapors of the previous run. Coke deposit on the catalyst was burned off by passing preheated air at 40 pounds pressure through the catalyst bed at a rate of approximately 2 liters per minute, until the carbon dioxide concentration in the exit gas was reduced to 1.5–2.0 volume %, as determined by absorption in 40% potassium hydroxide solution. The system was purged again with carbon dioxide before the next run. A typical cycle comprised 30 minutes on-stream, 1 minute for purge, 15 minutes for air regeneration at reaction temperature, and 1 minute for purge, or a total of 47 minutes.

The noncondensed gas was stripped of carbon dioxide by absorption in 40% potassium hydroxide solution and analyzed for total olefin by bromine absorption. The accuracy of this determination might be open to question, since the bromine absorption would indicate all olefin present plus any benzene that was carried along in the gas stream. However, several low temperature Podbielniak distillation analyses showed that, within the limit of error of the distillation, all the unsaturated hydrocarbon present was ethylene. Hydrogen also was detected in the exit gas, but the weight percentage was so small that it was not included in the material balance calculations.

Coke deposition on the catalyst was determined after several runs by purging the system with nitrogen and by prolonged passage of controlled amounts of preheated air through the catalyst bed. The regeneration gases were passed through hot copper oxide to convert any carbon monoxide present to carbon dioxide. The gas was then passed through a weighed Ascarite bulb and the increase in weight calculated to percentage carbon based on the total charge of the previous run. The maximum amount of carbon based on the total charge was 0.5 weight % in the case of run at higher temperatures (496° C.). Since this is below the experimental error involved in charge and product determinations, it was used as a constant value throughout the material balance calculations.

The liquid products from the continuous runs were analyzed in the same manner as indicated in the batch runs.

EXPERIMENTAL DATA

Batch Runs. The batch runs were made to qualify the reaction for further study and positive results were obtained (Table I). The pressure drop due to reaction at constant temperature was approximately 50 pounds in all runs. In addition to conventional methods of estimation, the yields were also calculated by the method proposed by Francis and Reid (*2*), in which the selectivity of monoethylbenzene formation based on liquid product distribution is calculated with regard to competing secondary reactions—that is, polyethylbenzene formation—and the molar excess of benzene necessary to attain this distribution. Table I shows that the highest temperature (399° C.) and highest molar ratio of benzene to ethylene were most favorable to the yield of monoethylbenzene based on the total ethyl groups present.

Batch operations of this type are unsatisfactory because the reaction time, temperature, and pressure are indefinite as a result of the relatively long heating and cooling periods in the operation. For this reason attendant secondary reactions, such as cracking, polymerization, and polyethylation, could conceivably alter the reaction picture.

Continuous Runs. The continuous operation of the reaction on a small laboratory unit (Figure 1) eliminated the objections to the batch procedure. Increased yields are probably favored by the use of high pressures. However, to make the process adaptable to existing facilities at the time of the investigation, only relatively low pressures (50–75 pounds gage) were used. The effects of low pressure and short residence time were compensated by a much higher reaction temperature. Since monoethylbenzene was the desired product, a molar excess of benzene was used in all experimental runs.

Table I. Batch Vapor Phase Ethylation of Benzene with Ethylene with Synthetic Silica-Alumina Catalyst

Run number	1	2	3	4
Wt. benzene charged, grams	780	936	780	702
Wt. ethylene charged, grams	105	44	28	45
Benzene, moles	10	12	10	9
Ethylene, moles	3.74	1.56	1	1.6
Wt. catalyst, grams	100	100	100	100
Reaction temp., ° C.	344	366	322	399
Time held at reaction temp., min.	30	30	30	30
Max. reaction pressure, lb./sq. in. gage	1740	1770	1350	1470
Wt. product recovered, grams	808	901	731	662
Wt. absorbed on catalyst, grams	65	70	70	70
Product analysis, wt. % of charge				
Benzene (78–100° C.)	61.9	83.7	88.1	77.4
Intermediate (100–132° C.)[a]	0.4	0.8	0.9	1.3
Ethylbenzene (132–140°)	24.8	12.8	8.6	18.6
Residue (above 140° C.)[b]	12.7	2.6	1.6	2.6
Distillation losses	0.2	0.1	0.8	0.1
Total	100.0	100.0	100.0	100.0
% theoretical based on ethylbenzene	54.8	77.4	68.1	82.9
Product distribution				
Mole ratio[c]	0.378	0.133	0.087	0.183
Yield on benzene[d]	20.9	10.2	6.9	15.0
Yield on ethylene[e]	55.5	76.6	79.5	82.5

[a] Regarded as half benzene and half ethylbenzene in product distribution calculations.

[b] Regarded as diethylbenzene in product distribution calculations.

[c] Ratio of total ethyl groups to total benzene rings in product.

[d] Percentage of total benzene rings as ethylbenzene.

[e] Percentage of total ethyl groups as ethylbenzene.

Table II lists data from the low pressure experimental runs. The effect of temperature variation with constant molar ratio of benzene to ethylene and constant space rate can be seen from comparison of runs 1, 2, and 3. The highest temperature investigated (496° C.) produced the highest yield of ethylbenzene in the liquid product. Reduction in temperature resulted in lower percentages of ethylbenzene and larger amounts of unreacted ethylene. The effect of variation of molar ratio of benzene to ethylene at approximately constant temperature and space velocity can be seen by comparison of runs 3, 8, and 9. As would be expected from the law of mass action, the higher molar ratio favored more complete reaction of the ethylene charged. The effect of liquid space velocity or reaction time can be seen by comparison of runs 1 and 6. Although the reaction temperature of run 6 was 68° C. below that of run 1, approximately the same product distribution was obtained by using twice the reaction time in run 6 with the same molar ratio of benzene to ethylene.

The data based on product distribution calculations do not seem to give a definite trend with respect to the variables involved. This may be explained by the fact that these values are very sensitive to the per cent residue, assumed to be diethylbenzene, found in the product distillation. Since this value is small (1–3%) with respect to the total product, small errors in distillation analysis are amplified. Although this method of calculation is desirable theoretically, precise analysis is necessary to obtain concordant results.

Most of the runs performed failed to react all the ethylene charged. However, by using a molar ratio of benzene to ethylene of 10 to 1, substantially all the ethylene was reacted, as indicated in runs 5 and 9. The use of higher pressures would probably aid in reacting a higher percentage of ethylene.

The coke deposition on the catalyst was extremely small under the reaction conditions. This would be expected because of the high thermal stability of the reactants. Regeneration at a temperature approximately equal to that of the preceding run was easily accomplished. Successive runs were readily duplicated after catalyst regeneration. The decrease in catalyst activity in successive runs was not noticeable in the number of reaction

Table II. Continuous Vapor Phase Ethylation of Benzene with Ethylene (Single-Pass) with Synthetic Silica-Alumina Catalyst

Run No.	1	2	3	4	5	6	7	8	9	10	11
Charge, wt. %											
Benzene	92.8	93.2	93.2	95.8	96.5	92.8	70	94.4	96.5	93.4	93.2
94% ethylene	7.2	6.8	6.8	4.2	3.5	7.2	...	5.6	3.5	6.6	6.8
Polyethylbenzenes	...	...	...	...	...	...	30	...	...	...	...
Mole ratio, benzene to ethylene	4.64	4.91	4.91	7.85	10.55	4.64	...	6.06	10.5	5.09	4.9
Space velocity of liquid, cc. at 25° C./cc. catalyst/hr.	1.97	1.97	1.97	1.68	2.01	1.07	2.0	2.08	2.2	2.06	0.94
Temp., ° C.	496	468	448	468	468	428	463	468	471	469	468
Pressure, lb./sq. in. gage	50	50	50	75	75	50	50	50	50	50	50
On-stream time, min.	30	30	30	30	90	30	30	30	30	35	30
Catalyst treatment	Fresh catalyst	Regenerated from run 1	Regenerated from run 2	Regenerated from run 3	Regenerated from run 4	Regenerated from run 5	Fresh catalyst	Fresh catalyst	Regenerated from run 8	Aged catalyst	Aged catalyst
Products, wt. % of charge (no loss basis)											
Benzene (78–100° C.)	78.2	81.0	83.7	84.7	87.96	78.8	66.1	79.8	88.2	86.9	82.8
Intermediate 100–132° C.)[a]	0.7	0.5	0.2	0.5	0.3	0.4	0.4	1.3	0.2	0.2	0.5
Ethylbenzene (132–140° C.)	17.2	13.9	11.3	12.0	10.1	17.0	16.1	15.0	9.6	8.3	12.1
Residue (above 140° C.)[b]	2.7	2.2	2.3	2.2	1.1	2.3	16.7	2.9	1.5	1.1	2.2
Unreacted ethylene	0.7	1.9	2.0	0.1	0.04	1.0	0.2	0.5	Nil	3.0	1.9
Coke deposit	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ethylene reacted, %	89.7	70.2	68.7	97.5	98.8	85.2	...	90.5	100	51.6	70.3
Theoretical yield based on ethylene to monoethylbenzene, %	67.2	57.3	46.6	80.2	81.1	66.4	...	75.3	77.0	35.3	50.0
Product distribution											
Mole ratio[c]	0.173	0.141	0.117	0.122	0.091	0.165	...	0.161	0.094	0.079	0.115
Yield on benzene[d]	13.9	11.1	8.98	9.55	7.82	13.6	...	12.5	7.45	6.56	9.7
Yield on ethylene[e]	80.5	79.0	76.4	78.5	85.7	82.8	...	78.0	79.4	83.5	78.8

[a] Regarded as half benzene and half ethylbenzene in product distribution calculations.

[b] Regarded as diethylbenzene in product distribution calculations (except in run 8 where polyethylbenzenes were charged).

[c] Ratio of total ethyl groups to total benzene rings in product.

[d] Percentage of total benzene rings as ethylbenzene.

[e] Percentage of total ethyl groups as ethylbenzene.

and regeneration cycles performed. However, a representative sample of the same catalyst which had been through 3700 cycles (equivalent to 100 days of continuous operation) in a semicommercial catalytic cracking unit under somewhat more drastic thermal conditions was tested for the ethylation reaction. This catalyst is designated as aged in runs 10 and 11 (Table II). Although the percentage of unreacted ethylene at the same temperature and space rate increased (comparison of runs 2 and 10) with the aged catalyst, substantially the same yields were obtained by reducing the space rate (runs 2 and 11). This is a conservative indication of catalyst life, since coke deposition is much greater under cracking conditions; therefore the regeneration conditions are more severe. The residue of the reaction product in the single pass operation contained mainly diethylbenzene with small amounts of higher ethylbenzenes, as distillation analysis of combined residues indicated. This residue would not be lost to monoethylbenzene production, since it is possible to recycle these polyethylbenzenes with a molar excess of benzene and obtain increased yields of monoethylbenzene based on ethylene consumed. This procedure of alkyl group transfer has been reported (4, 16). Run 7 was made to verify these conclusions; polyethylbenzene was charged with benzene under the conditions used in the straight ethylation runs. There was a net loss of polyethylbenzenes in favor of monoethylbenzene formation under the conditions of the experiment.

The intermediate fraction between benzene and monoethylbenzene in the liquid product distillation (100–132° C.) suggested

Table III. Continuous Vapor Phase Propylation of Benzene (Single-Pass) with Synthetic Silica-Alumina Catalyst

Run No.	1	2	3[a]	4[a]	5[a]
Charge, wt. %					
Benzene	88.3	91.5	81.0	81.5	81.0
Propylene	11.7	8.5	7.6	7.4	7.6
Propane	...	...	11.4	11.1	11.4
Mole ratio, benzene to propylene	4.05	5.78	5.9	6.0	5.9
Space velocity liquid, cc. at 25° C./cc. catalyst/hr.	2	2	3	3	3
Temp., ° C.	382	382	422	462	377
Pressure, lb./sq. in. gage	75	75	500	500	500
On-stream time, min.	20	20	30	30	30
Catalyst treatment	Fresh catalyst	Regenerated from run 1	Fresh catalyst	Regenerated from run 3	Regenerated from run 4
Products, wt. % of charge (no loss basis)					
Benzene (80–100° C.)	76.8	81.8	75.0	76.2	71.1
Intermediate (100–145° C.)	0.9	1.0	1.3	2.1	0.9
Isopropylbenzene (145–155° C.)	18.0	13.2	11.9	7.9	14.5
Residue (above 155° C.)	3.1	3.5	3.2	3.4	2.5
Unreacted gas	0.7	Nil	8.2	9.6	10.4
Coke	0.5	0.5	0.5	0.8	0.6
Total	100.0	100.0	100.0	100.0	100.0
Yield monopropylbenzene, % of theoretical based on propylene	55.0	56.6	57.8	47.5	68.8

[a] Runs 3, 4, and 5 were conducted with apparatus similar to that described, adapted for use of higher pressures.

the presence of toluene. However, in reported results (*4, 16*) under similar conditions of catalyst and temperature, there was no indication of toluene formation from ethyl group decomposition in the ethyl group transfer between polyethylbenzene and benzene. In the product distribution calculation this small intermediate fraction was considered to be half benzene and half monoethylbenzene.

Several continuous experimental runs were made with propylene, propylene-propane mixtures, and benzene for the formation of cumene. Data for these runs appear in Table III. Temperature conditions for this reaction are less severe than those for the ethylation reaction, and the reaction proceeds with greater ease. Runs 3, 4, and 5 indicate that substantial selective reaction occurred in the presence of paraffin gases which were inert under the conditions of the experiment.

LITERATURE CITED

(1) Balsohn, M. M., *Bull. soc. chim.*, [2] 31, 539 (1879).
(2) Francis and Reid, Ind. Eng. Chem., 38, 1194 (1946).
(3) Grosse and Ipatieff, *J. Org. Chem.*, 1, 559 (1936).
(4) Hansford, Myers, and Sachanen, Ind. Eng. Chem., 37, 761 (1945).
(5) Ipatieff, Corson, and Pines, *J. Am. Chem. Soc.*, 58, 919 (1936).
(6) Ipatieff and Grosse, *Ibid.*, 58, 2339 (1936).
(7) Ipatieff, Pines, and Komarewsky, Ind. Eng. Chem., 28, 222 (1936).
(8) Ipatieff and Schmerling, U. S. Patent 2,374,600 (1945).
(9) Komarewsky, V. I., *J. Am. Chem. Soc.*, 59, 2715 (1937).
(10) Mattox, W. J., *Trans. Am. Inst. Chem. Engrs.*, 41, 463 (1945).
(11) Milligan and Reid, Ind. Eng. Chem., 15, 1048 (1923).
(12) Pardee and Dodge, *Ibid.*, 35, 273 (1943); U. S. Patent 2,388,007 (1945).
(13) Sachanen and O'Kelly, Ind. Eng. Chem., 33, 1540 (1941); U. S. Patent 2,242,960 (1941).
(14) Schollkopf, K., U. S. Patent 2,115,884 (1938).
(15) Simons and Archer, *J. Am. Chem. Soc.*, 60, 986, 2952 (1938).
(16) Thomas, Hoekstra, and Pinkston, *Ibid.*, 66, 1694 (1944).
(17) Wunderly, Sowa, and Nieuwland, *Ibid.*, 58, 1007 (1936).

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Phase Study of Commercial Soap-Alkaline Electrolyte Water-Systems

REYNOLD C. MERRILL
Philadelphia Quartz Company, Philadelphia, Pa.

A phase study of commercial mixed soap-water-electrolyte systems was made using sodium chloride and nine salts industrially important as soap builders. The data cover soap concentrations to 50%, electrolyte concentrations to 27%, and temperatures to 180° C. The salts used were sodium chloride, carbonate, and tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon (sodium hexametaphosphate), sodium metasilicate, sodium silicates of SiO_2/Na_2O ratios by weight of 2.46 and 3.93, and a potassium silicate of SiO_2/K_2O ratio by weight of 2.04. The solubility of the soap in solutions of these salts and their effect on the transition from crystalline to liquid crystalline soap varies widely both on weight and molecular bases. The order of increasing effect differs with concentration and temperature; however, sufficient regularities exist to enable predictions to be made of the phase diagrams for other soaps and at other concentrations.

THE value of adding alkaline electrolytes or builders, such as the soluble silicates, to soaps is attested by many years of experience and numerous publications (*1, 3, 5, 6, 25, 26*). In 1937, the last year for which accurate data on consumption are apparently available, 160,000 tons of 40° Baumé sodium silicates and 39,500 tons of sodium phosphates were consumed by the United States soap industry according to the Bureau of the Census (*23*). Since then the amounts of such builders used have substantially increased. Wartime shortages of fats, oils, and rosins for soapmaking re-emphasized the value of builders in soap. Attention has been focused on the amounts of various builders which can be added to different soaps under varying conditions and on the nature of such systems.

During the past twenty-five years the manufacture of soap, previously an industrial art, has been studied scientifically from the phase-rule point of view by McBain and collaborators (*13, 16, 18*), Ferguson and Richardson (*7*), and others. Phase diagrams of approximately a dozen ternary aqueous soap systems with sodium or potassium chloride have been published (*7, 13, 18*). Only incomplete data on the behavior of soaps with other salts are available. Probably the earliest work was done in 1888 by Hofmeister, who studied the salting out of sodium oleate from solution by several salts (*10*). Later workers (*2, 12, 21, 22, 24*) measured the amounts of sodium and potassium chloride, carbonate, and hydroxide required to salt out various single and mixed soaps. These data were summarized and interpreted by McBain and Walls (*20*). Qualitative observations on gelation of soaps in the presence of sodium carbonate, borate, and silicate were reported by Fischer (*9*). McBain and Pitter (*17*) measured the concentrations of eleven electrolytes required to salt out 0.25 weight normal (approximately 6.5%) sodium palmitate. McBain, Vold, and Gardiner (*18*) found that substituting for sodium chloride a sodium silicate, having a SiO_2/Na_2O weight ratio of 3.18 in concentrations of 3.6 and 5.6%, caused 10% sodium oleate to set to an elastic, transparent jelly instead of a liquid crystal.

If a determination is made of the relative efficiency of various salts in salting out soap at a single concentration and temperature, hypothetical phase diagrams can be outlined for aqueous systems of that soap with all of these salts. The diagram for one of them must be known; the assumption is then made that the relative efficiency is the same for different soap concentrations involving several crystalline and liquid-crystalline phases at different temperatures.

This paper reports a study of the phase behavior of a typical commercial mixed soap with one potassium and nine sodium salts. The salts used were sodium chloride, carbonate, and

Table I. Analyses of Silicates

Analysis, %	Metso Crystals, $Na_2SiO_3.5H_2O$	2.46-Ratio Silicate	S-Brand	Kasil No. 6
Na_2O[a]	28.89	12.98	6.60	12.70
SiO_2	28.13	31.99	25.78	25.99
H_2O	42.13	54.55	67.42	60.83
Fe_2O_3	0.002	0.017	0.0085	0.066
Al_2O_3	0.052	0.108	0.104	0.151
TiO_2	Trace	0.017	0.0058	0.004
CaO	Trace	0.007	0.018	0.02
MgO	0.005	0.04	0.024	0.06
SO_3	0.003	0.01	0.014	0.05
Cl	0.13	0.16	0.028	0.12
CO_2	0.51	0.07	0.030	0.10
Ratios				
SiO_2/Na_2O, wt. basis[a]	0.974	2.46	3.93	2.04
SiO_2/Na_2O, molecular basis[a]	1.00	2.54	4.05	3.21

[a] K_2O for Kasil.

tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon (sodium hexametaphosphate), sodium metasilicate, sodium silicates of SiO_2/Na_2O weight ratios of 2.46 and 3.93, and a potassium silicate of SiO_2/K_2O weight ratio of 2.04. Except for the chloride and carbonate, no previous work on these systems has appeared in the literature.

Soap concentrations up to 50%, salt concentrations as high as 27%, and temperatures to 180° C. were studied. The data outline phase boundaries between isotropic solution and the two phase regions, middle soap–nigre, neat soap–nigre, and nigre-lye (*13*). The observations on each of the ten soap-water-electrolyte systems cover the temperature range from the lowest temperature at which isotropic solution separates a second isotropic or liquid crystalline phase up to 180° C. The temperatures at which hydrated crystals or curd fibers change completely to liquid crystal or isotropic solution are also included.

The complete data provide a test of the hypothesis that the relative efficiencies of these salts, some of which are alkaline or colloidal, for salting out soap are approximately the same on a molecular basis at all concentrations and temperatures. Complete (although tentative and hypothetical) phase diagrams can also be outlined from the data by analogy with previous work.

MATERIALS AND METHOD

The commerical mixed soap had the composition of a typical fitted and settled household soap made from fatty acids of average molecular weight 273 and an iodine value of 48.4 (Hanus method). After drying at 105° C., the soap contained 88.44% fatty acids with less than 0.046% excess sodium oxide, 0.62% sodium chloride (Volhard method), and less then 0.2% of insoluble siliceous matter. It was furnished through the courtesy of Lever Brothers Company.

The silicates used were regular commercial products of the Philadelphia Quartz Company. Their analyses are given in Table I. The S-brand was clarified somewhat by heating at 90° C. for several days and filtering off the precipitated material. The Calgon was the regular, unadjusted, commercial product. All other salts used were C.P. Although some of the salts were hydrates, all data are given here on the anhydrous basis.

All data were obtained by the synthetic method. The calculated quantities of soap, salt, and freshly distilled water were weighed in the order named into narrow-neck tubes made from 13 × 100 mm. test tubes. The tubes were sealed to prevent changes in composition and then heated in an oil bath until their contents formed an isotropic, homogeneous solution. They were then allowed to cool slowly and a determination was made of the temperature, T_i, at which liquid crystal or a second isotropic liquid first formed. Observations were made with crossed polaroid disks 1.75 inches in diameter. After standing at room temperature at least overnight and usually several months, the tubes were slowly heated and a record was made of the temperature, T_c, at which all traces of the opaque white solid (formed at room temperature) just disappeared to complete the formation of a liquid or anisotropic liquid-crystalline phase, or mixture of both of these. T_i values are readily reproducible to within 2° C.; the T_c values are precise to 1° C. or less. Temperatures were measured with calibrated thermometers.

COMMERCIAL SOAP-WATER SYSTEMS

Data on the system commercial mixed soap–water are given in Table II. Such systems behave as two-component soap-water systems, except where salting out into curd fibers occurs (*7, 13*). The phase diagram of this soap up to 50% soap resembles that of the sodium soap *A* of McBain, Vold, and Porter (*19*), although its T_i boundary is 1% to the left—that is, more soluble; the maximum temperature at which middle soap exists is 10° C. lower and occurs at 43 instead of 46% soap, and the T_c curve is 1° C. lower. The T_c curve is only 1–2° C. higher than that for the soap used by Dedrick and Wills for which a fatty acid analysis is given (*6*) and within 2° C. of that for the framed soap of Vold and Lyon (*27*). Their results, therefore, can reasonably be used in deducing phase diagrams involving this soap.

From room temperature up to the T_c temperature aqueous systems of the commercial mixed soap containing from 5 to 50% soap consist in part of white opaque solids; those below about 5% are semisolid, somewhat translucent jellies. The white opaque solid material is commonly called curd. Under varying conditions it may consist of one or more of the multiplicity of phases which can exist in aqueous solid soap systems at room temperature (*4, 8*). At T_c the system melts completely to isotropic liquid, nigre, at soap concentrations below 27.5%. From 27.5 to about 52% soap T_c is the temperature of final disappearance of all solid phases to form (*a*) a two-phase equilibrium between middle soap and nigre, (*b*) a liquid crystalline middle soap, and (*c*) a two-phase equilibrium between middle soap and neat soap. Above about 52% soap the phase soap-boiler's neat soap is formed at T_c. The upper boundary of the middle soap phase is outlined by the T_i values. Experience has shown that undercooling does not occur when T_i determinations are made with reasonable care. According to McBain (*14*), the principle that supersaturation does not occur in regard to the appearance of a liquid phase is a direct deduction from kinetic theory. It apparently also applies to the liquid crystalline phases, neat and middle soap. If the system is sufficiently agitated and time is allowed for it to reach equilibrium, the temperature at which the last trace of middle soap, neat soap, or lye just dissolves on heating is within 1–2° C. of the T_i value. This is true for all the systems of this investigation, including the colloidal silicates. T_i, therefore, is the temperature of complete melting of middle or neat soap.

Table II. Two-Component System, Commercial Mixed Soap–Water[a]

% Soap	T_i, ° C.	T_c, ° C.	% Soap	T_i, ° C.	T_c, ° C.
4.77	..[a]	44	34.8	133	48
9.89	..[a]	44	40.8	157	49
14.2	..[a]	45	43.1	161	..
19.9	..[a]	46	44.6	160	50
27.4	..[a]	47	49.5	151	..
28.5	71	47	50.5	166	51
29.4	77	..	52.5	>175	..
30.1	91	..			

[a] Compositions for which no T_i value is given changed directly from isotropic solution to hydrated crystal. Up to 27.5% soap the system melts completely to isotropic liquid (nigre) at T_c. From 27.5 to 52%, hydrated crystal at T_c changes to a two-phase equilibria between middle soap and nigre, a liquid crystalline middle soap, and a two-phase equilibria between middle and neat soap. The T_i values give the upper boundary of the middle soap phase.

COMMERCIAL SOAP-ELECTROLYTE-WATER SYSTEMS

The influence of ten salts on the transition temperature, T_c, of hydrated, crystalline, commercial mixed soap is shown in Figure 1. The curves at definite temperature were deduced by linear interpolation from the T_c determinations (circles) made at intermediate temperatures. The data are given in Table III and are separated according to the number and probable nature of the phases formed above T_c, based on analogy with previous work (*7, 13, 15, 18*). Salt concentrations are given in this paper both in weight per cent and weight normality (gram moles per kg. of water) to enable comparison on both technical and molecular bases. The systems forming liquid crystal when heated are shown in Figure 1 as open circles, and those forming isotropic solutions only, as filled circles. Below 47° C. the isotherms shown are, with the exception of some systems containing potassium silicate, the isotropic solution boundaries. Above 47° C. equilibria with liquid crystalline phases are involved. Analogy with the sodium laurate system (*15*) suggests the possibilities that (*a*) between 47° and 53° C. the crystalline soap dissolves to form either middle soap or middle soap and isotropic solutions, and (*b*) above 53° C. the isotherms trace out the neat lye edge of the triangle hydrated crystal–neat soap–lye. The T_c values in this range determine the limiting concentrations of soap and salt at which the system exists as neat soap and lye, although the nature of the last trace of white "solid" which disappears is not known. In a system containing a mixed soap, fractionation occurs in this region.

Figure 1 shows that the effect of these ten electrolytes on the transition temperature of the soap varies considerably. The steepness of the isotherms or the T_c value at any arbitrary soap or electrolyte concentration may be taken as a measure of the salting-out power of the electrolyte. It is evident that Calgon raises the T_c value of the soap more than any salt tested. This is true on both weight and molecular bases, even if the formula weight of $NaPO_3$ is taken as the minimum molecular weight. This is especially true when Calgon is regarded as a colloidal electrolyte of high molecular weight, which ultracentrifuge determinations and other types of measurements indicate it to be (*11*). It is also evident that potassium silicate raises the T_c value of soap systems much less than any other salt. In fact, the addition of potassium silicate up to about 5% lowers the T_c value of soap-water systems, in part, at least, because of the formation of some potassium soap. As much as 25% of the 2.04 weight-ratio potassium silicate can be added to these aqueous soap systems without increasing their T_c value more than 3° C.

To facilitate quantitative comparison of the salts, Table IV gives maximum concentration of each which can be added to the commercial mixed soap at the arbitrarily chosen concentration of 24% before raising the T_c value to 50° C. The maximum concentrations under these conditions vary from 1.1 and 1.6% for Calgon and sodium chloride, respectively, to 26% for the 3.93-ratio silicate and much greater than 30% for the potassium silicate. On a weight basis the amount of the salt which can be added increases in the following order: Calgon, sodium chloride, carbonate, metasilicate, and borate, trisodium phosphate, 2.46-ratio sodium silicate, tetrasodium pyrophosphate, 3.93-ratio sodium silicate, and potassium silicate. On a molecular basis the concentration of the chloride and tetraborate required to raise the T_c to 50° C. is practically the same and that of the carbonate perhaps somewhat greater, whereas the amount of trisodium phosphate and metasilicate is about 60% greater than that of the chloride. About twice as much of the pyrophosphate and 2.46-ratio silicate is required under these conditions as is required of chloride or carbonate, and about four or five times as much of 3.93-ratio silicate. Calgon, on a minimum formula-weight basis, requires less than half as much as the chloride.

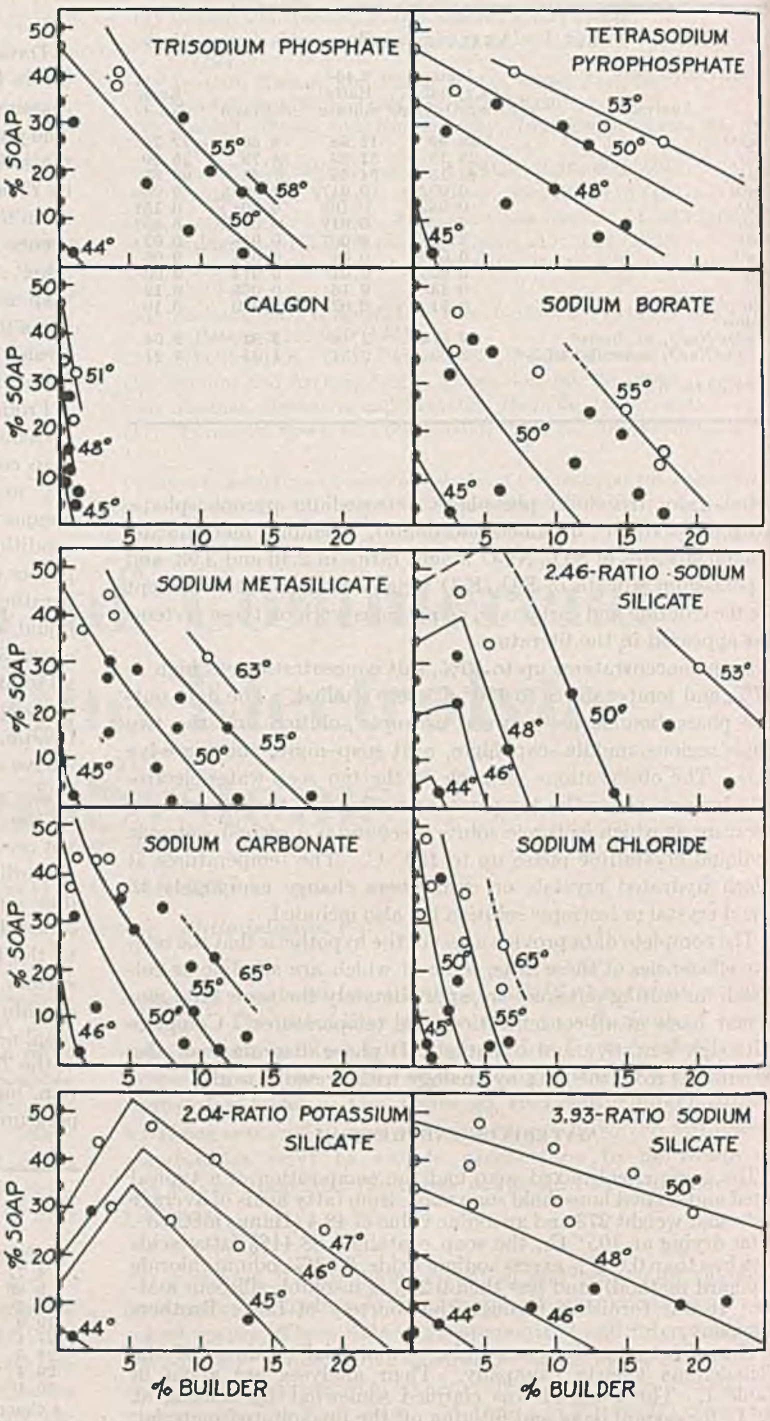

Figure 1. Solubility and Transition Temperature (T_c) Isotherms of Hydrated Crystalline Commercial Mixed Soap at Definite Temperatures (Curves) as Deduced from T_c Determinations (Circles) Made at Intermediate Temperatures

Open circles represent compositions forming liquid crystals on heating; filled circles, those forming isotropic solution. The solubility of the electrolytes in pure water should be given by the intercepts of the isotherms on the horizontal (0% soap) axes. The values for the solubility of the various electrolytes in pure water indicated in the figures are smaller than the true values.

Figure 2. Boundaries of the Field of Aqueous Isotropic Solutions at 70°, 120°, and 150° C. (Curves) as Deduced from T_i Determinations (Circles) Made at Intermediate Temperatures

Open circles represent compositions forming liquid crystals on cooling; filled circles, those forming two isotropic liquids (nigre and lye), isotropic solution, or jelly. The solubility of the electrolytes in pure water should be given by the intercepts of the isotherms on the horizontal (0% soap) axes. The values for the solubility of the various electrolytes in pure water indicated in the figures are smaller than the true values.

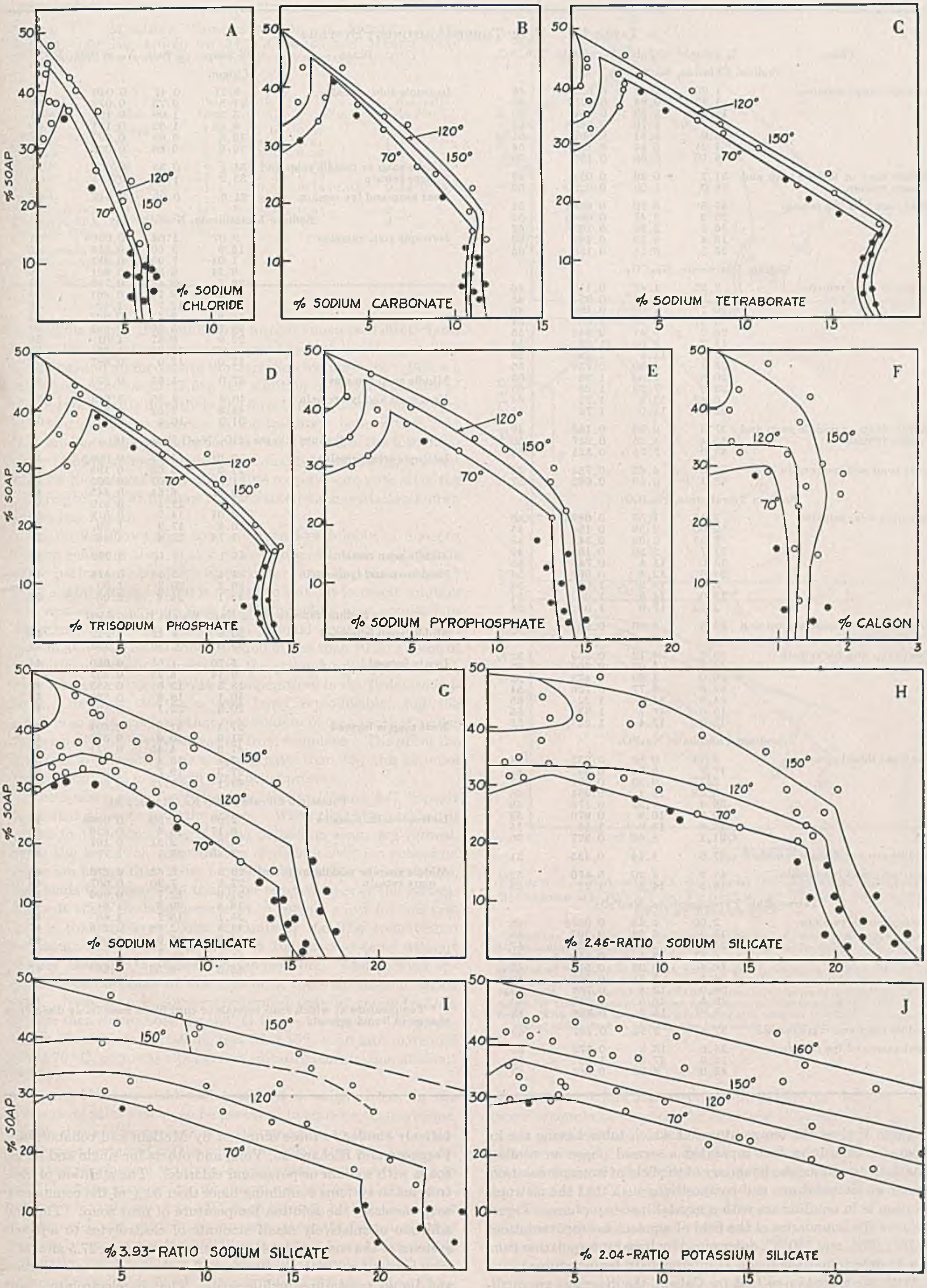
A
% SOAP
50
40
30
20
10
120°
150°
70°
% SODIUM CHLORIDE
5
10
B
120°
70°
150°
% SODIUM CARBONATE
5
10
15
C
120°
150°
70°
% SODIUM TETRABORATE
5
10
15
D
% SOAP
120°
70°
150°
% TRISODIUM PHOSPHATE
5
10
15
E
120°
150°
70°
% SODIUM PYROPHOSPHATE
5
10
15
20
F
150°
120°
70°
% CALGON
1
2
3
G
% SOAP
150°
120°
70°
% SODIUM METASILICATE
5
10
15
20
H
150°
120°
70°
% 2.46-RATIO SODIUM SILICATE
5
10
15
20
I
% SOAP
150°
150°
120°
70°
% 3.93-RATIO SODIUM SILICATE
5
10
15
20
J
160°
150°
120°
70°
% 2.04-RATIO POTASSIUM SILICATE
5
10
15
20

TABLE III. T_c OF THREE-COMPONENT SYSTEMS

Phase	% Soap	% Salt	N_w of Salt	T_c*, ° C.
Sodium Chloride, NaCl				
Isotropic soln. remains	1.95	1.24	0.0220	45
	4.82	0.84	0.0152	45
	11.8	2.59	0.0517	50
	38.7	1.70	0.0488	51
	18.0	3.11	0.0676	51
	4.21	5.44	0.103	54
	5.10	6.68	0.130	60
Middle soap or middle soap and nigre remain	31.7	0.46	0.011	49
	38.0	1.03	0.0290	50
Neat soap and lye remain	47.8	0.90	0.0302	51
	26.3	3.47	0.0845	53
	36.3	3.58	0.102	57
	16.4	6.39	0.141	63
	25.3	6.36	0.159	65
Sodium Carbonate, Na_2CO_3				
Isotropic soln. remains	2.27	1.47	0.159	46
	11.6	2.64	0.321	48
	30.7	1.09	0.194	48
	4.27	8.80	1.06	51
	28.2	5.41	0.848	55
	11.7	9.66	1.28	55
	3.07	11.3	1.38	55
	35.1	4.30	0.739	56
	20.8	9.33	1.20	63
	33.3	7.28	1.28	63
	6.42	13.3	1.72	64
	22.4	11.0	1.72	65
Middle soap or middle soap and nigre remain	37.3	0.96	0.162	49
	43.4	1.26	0.237	50
	43.0	2.71	0.521	56
Neat soap and lye remain	37.0	4.43	0.788	56
	43.1	3.49	0.682	57
Sodium Tetraborate, $Na_2B_4O_7$				
Isotropic soln. remains	2.16	1.53	0.0896	45
	2.60	2.58	0.134	45
	7.65	6.08	0.348	48
	31.7	2.50	0.188	49
	13.0	11.4	0.748	53
	23.9	12.4	0.967	54
	6.62	15.9	1.02	54
	19.0	14.5	1.08	54
	2.22	17.6	1.08	54
Middle soap or middle soap and nigre remain	36.6	2.83	0.231	50
Neat soap and lye remain	39.2	4.12	0.359	52
	44.9	3.05	0.290	53
	36.0	5.59	0.473	53
	32.3	8.77	0.736	54
	24.8	14.9	1.22	55
	16.0	17.7	1.33	55
	13.2	17.4	1.24	55
Trisodium Phosphate, Na_3PO_4				
Isotropic liquid remains	3.24	0.82	0.052	44
	17.7	6.14	0.492	47
	7.77	9.30	0.691	47
	3.28	13.1	0.954	48
	30.4	1.92	0.173	48
	20.2	10.9	0.970	53
	15.8	13.0	1.11	55
	31.1	8.66	0.877	56
Middle soap and nigre remain	37.9	4.14	0.435	51
Neat soap and lye remain	41.2	4.20	0.470	52
	16.5	14.3	1.27	58
Tetrasodium Pyrophosphate, $Na_4P_2O_7$				
Isotropic soln. remains	2.60	1.38	0.0538	45
	13.3	6.54	0.307	46
	28.4	2.37	0.128	47
	6.57	13.1	0.612	47
	16.4	9.99	0.511	48
	34.4	5.81	0.366	49
	26.0	12.4	0.761	50
	29.4	10.5	0.657	50
	8.91	14.9	0.734	48
Middle soap and nigre remain	37.4	2.98	0.187	49
Neat soap and lye remain	29.6	13.3	0.872	52
	26.6	17.6	1.18	53
	41.0	6.99	0.505	53
Calgon				
Isotropic soln. remains	9.21	0.47	0.046	45
	11.8	0.73	0.072	46
	5.32	1.09	0.108	46
	6.88	1.32	0.131	47
	15.8	0.98	0.097	47
	26.8	0.68	0.067	48
Middle soap or middle soap and nigre remain	34.1	0.33	0.033	48
	32.2	1.15	0.114	51
Neat soap and lye remain	21.6	0.99	0.048	49
Sodium Metasilicate, Na_2SiO_3				
Isotropic soln. remains	2.07	1.04	0.0696	45
	15.9	3.60	0.366	47
	1.01	7.96	0.881	48
	8.24	6.85	0.661	48
	26.8	3.48	0.796	49
	30.3	3.71	0.461	50
	1.37	12.7	1.42	51
	16.9	8.41	0.922	52
	28.7	5.59	0.697	52
	22.9	8.47	1.01	54
	2.53	17.8	1.83	55
	17.0	12.0	0.697	56
Middle soap remains	37.0	1.65	0.220	49
Neat soap and lye remain	40.3	3.95	0.613	53
	44.8	3.52	0.558	54
	31.2	10.4	1.46	63
Sodium Silicate (SiO_2/Na_2O Ratio, 2.46)				
Isotropic soln. remains	3.01	1.77	0.0863	44
	21.6	3.08	0.195	46
	31.9	3.07	0.225	47
	12.2	6.64	0.445	48
	24.1	11.1	0.819	50
	3.01	14.2	0.818	50
	16.8	17.9	1.30	51
	5.74	22.4	1.48	51
Middle soap remains	45.1	3.15	0.292	49
Neat soap and lye remain	34.4	5.16	0.418	49
	29.3	20.2	1.90	53
	18.1	24.9	2.08	53
Sodium Silicate (SiO_2/Na_2O Weight Ratio, 3.93)				
Middle soap is formed	30.5	4.12	0.212	48
	39.0	3.96	0.234	49
Lye is formed	5.70	1.65	0.060	44
	9.14	8.24	0.337	46
	13.3	12.8	0.583	47
	10.1	18.8	0.892	48
	10.3	22.1	1.10	49
Neat soap is formed	27.1	11.0	0.601	49
	31.6	10.0	0.581	49
	47.3	4.45	0.311	50
	37.4	15.4	1.10	50
	27.3	19.7	1.26	50
	42.1	9.72	0.681	50
Potassium Silicate (SiO_2/K_2O Ratio, 2.04)				
Isotropic soln. remains	2.89	1.89	0.0988	44
	6.17	13.4	0.829	45
	28.9	2.31	0.167	46
	3.85	25.1	1.77	47
Middle soap or middle soap and nigre remain	29.5	3.62	0.270	45
	27.3	7.90	0.607	45
	21.8	12.7	0.966	46
	16.8	20.3	1.61	46
	25.1	18.7	1.66	47
	43.5	2.78	0.258	47
	14.3	25.0	2.05	48
Neat soap and lye remain	40.6	10.9	1.12	47
	46.8	6.53	0.698	47

* Temperature at which soap crystals or curd fibers completely dissolve or change to liquid crystal.

Table V gives the temperatures at which tubes having the indicated composition first separated a second phase on cooling. The data determine the boundary of the field of isotropic solution, except at temperatures and compositions such that the isotropic solution is in equilibrium with a crystalline soap phase. Figure 2 shows the boundaries of the field of aqueous isotropic solutions at 70°, 120°, and 150° C. determined by linear interpolation from the T_i determinations made at intermediate temperatures.

With the exception of that for Calgon, the diagrams are qualitatively similar to those obtained by McBain and collaborators, Ferguson and Richardson, Vold, and others for single and mixed soaps with sodium or potassium chloride. The addition of electrolytes to systems containing more than 50% of the commercial soap increases the solution temperature of neat soap. The first addition of relatively small amounts of electrolytes to aqueous systems of the commercial soap containing between 27.5 and 50% soap lowers transition temperature T_i between isotropic solution and liquid crystalline middle soap. That is, electrolytes "salt

Table IV. Maximum Concentration of Various Salts Which Can Be Added to 24% Commercial Mixed Soap before Raising Transition Temperature to 50° C.

Salt	Mol. Wt.	Weight: Per cent	Weight: Ratio to NaCl	N_w	N_w Ratio to NaCl
NaCl	58.45	1.6	1.0	0.37	1.0
Na_2CO_3	106	3.2	2.0	0.41	1.1
$Na_2B_4O_7$	202	5.3	3.3	0.37	1.0
Na_3PO_4	164	6.7	4.2	0.59	1.6
$Na_4P_2O_7$	266	13.2	8.2	0.79	2.1
Calgon	102[a] (612)[b]	1.1	0.69	0.14 (0.02)[b]	0.39 (0.06)[b]
Na_2SiO_3	122	5.0	3.1	0.58	1.6
$Na_2O.2.46\ SiO_2$	210[a]	11	6.9	0.81	2.2
$Na_2O.3.93\ SiO_2$	298[a]	26	16	1.7	4.7
$K_2O.2.04\ SiO_2$	...	30	...	..	..

[a] Formula weights.
[b] Assuming $(NaPO_3)_6$.

in" middle soap. The addition of further amounts of electrolytes causes the formation of one or more types of liquid crystalline neat soap and an increase in the transition temperature. Below a soap concentration of 27.5% the addition of larger amounts of electrolytes results directly in the formation of one or more types of neat soap and an increase in the transition temperature. At still smaller soap concentrations electrolytes cause the formation of two isotropic liquid phases, nigre and lye. Although it is not clear on the scale of the graphs, dilute soap systems with all of the electrolytes appear to show the characteristic indentation known as the bay region.

Figure 2*F* shows that soap is much less soluble in aqueous Calgon solutions than in any other solutions tested. (The scale of the horizontal axis of this figure is four times that of the others.) Only slightly more Calgon is needed to salt out isotropic solution into neat soap and nigre than to salt in middle soap, contrary to experience with other electrolytes. Liquid crystals form in this system at a total solids concentration of less than 10%. Some of the Calgon probably reverted to the orthophosphate during the 3- or 4-hour heating at elevated temperatures in the T_i determinations. However, the data were fairly reproducible, and the curve is so different from that of trisodium phosphate that, under these conditions, reversion was far from complete. The pH of the solutions after heating was always greater than 8.5; this excludes the possibility of much acid soap being present.

The system with the potassium silicate (Figure 2*J*) appears somewhat different from the others. When the potassium salt is added to the sodium soaps, some potassium soaps are formed. Since the transition temperatures of middle soap for potassium soaps are higher than those for the corresponding sodium soaps, this tends to increase the transition temperatures of the system. The salt effect tends to decrease it. The net effect for this system is that relatively large amounts of the 2.04 weight-ratio potassium silicate can be added to the soap systems without greatly changing the transition temperature. Middle soap appears to predominate in this system at the soap concentrations used. Neat soap is apparently formed only at concentrations greater than those above the 160° C. line in the figure. The separation of solutions containing less than 13% soap into nigre and lye at 70° C. occurs at a potassium silicate concentration of about 25.5%.

Figure 2 shows wide variations, on a weight basis, in the amounts of salts which can be dissolved in aqueous soap systems. It also shows differences in their temperature coefficient of solubility, as determined by the amount of salt which raises the solution temperature of a given soap concentration from 70° to 150° C. As an example, the maximum weight per cent salt concentration which dissolves in 24% soap solution at 70° C. without salting out liquid crystalline soap increases in the following order: Calgon 1.0, sodium chloride 3.9, carbonate 8.5, metasilicate 8.5, 3.93-ratio sodium silicate 9.9, trisodium phosphate 10.7, 2.04-ratio potassium silicate 11.5, tetraborate 12.6, tetrasodium pyrophosphate 11.9, and 2.46-ratio sodium silicate 13. At 10% soap larger amounts of soap can be dissolved in solutions of the siliceous silicates than in solutions of the other salts. Comparison at other soap concentrations gives a somewhat different order. The order of the effect of salts on 24% soap at 50° is different from that at 70° C. No general order of the effectiveness of salts in salting out soap can be obtained which is completely valid for all concentrations and at all temperatures.

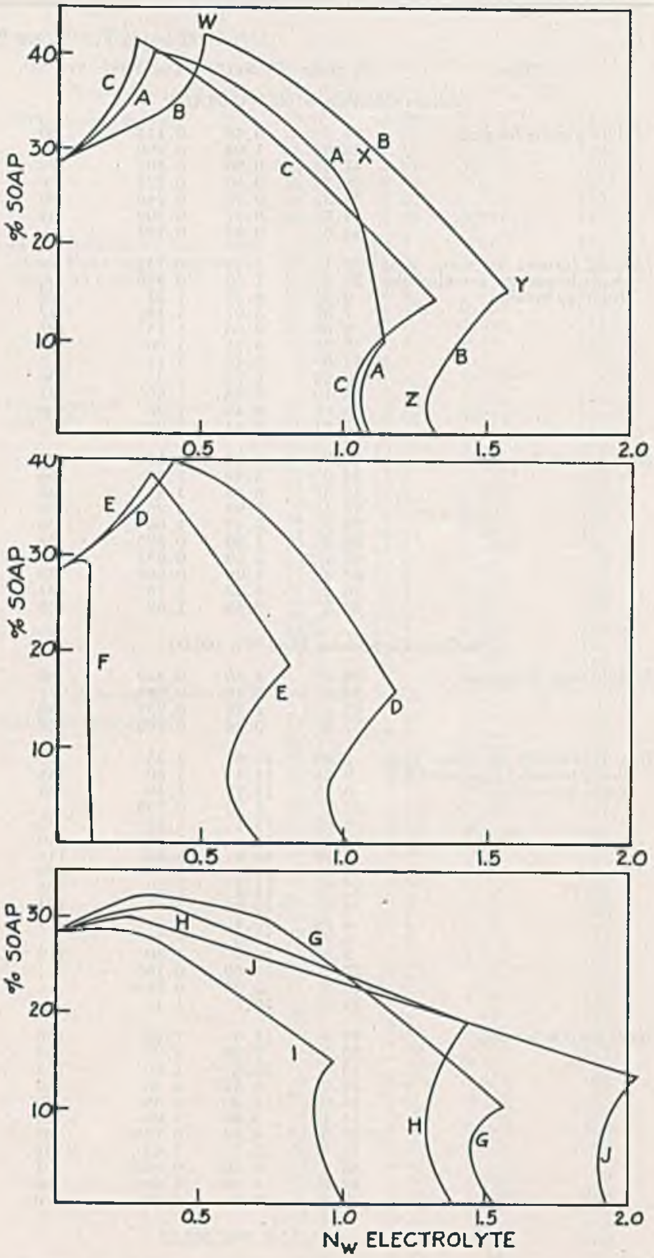

Figure 3. Boundaries of Field of Aqueous Isotropic Solutions at 70° C. as Function of Weight Normality (N_w) of Electrolyte

A, sodium chloride; *B*, sodium carbonate; *C*, sodium tetraborate; *D*, trisodium phosphate; *E*, tetrasodium pyrophosphate; *F*, Calgon (sodium hexametaphosphate); *G*, sodium metasilicate; *H*, sodium silicate of SiO_2/Na_2O weight ratio 2.46; *I*, sodium silicate of SiO_2/Na_2O weight ratio 3.93; *J*, potassium silicate of SiO_2/K_2O weight ratio 2.04. The solubility of the electrolytes in pure water should be given by the intercepts of the isotherms on the horizontal (0% soap) axes. The values for the solubility of the various electrolytes in pure water indicated in the figures are smaller than the true values.

As a measure of the temperature coefficient of solubility the author determined the weight per cent of salt required to raise the transition temperature of a 24% soap solution containing

TABLE V. T_i OF THREE-COMPONENT SYSTEMS

Phase	% Soap	% NaCl	N_w of Salt	T_i*, °C.
Sodium Chloride, Mol. Wt. 58.45				
Middle soap is formed	31.7	0.46	0.115	89
	38.0	1.03	0.290	90
	47.8	0.90	0.302	176
	38.1	0.80	0.225	88
	34.3	0.93	0.246	83
	44.6	0.67	0.209	134
	43.0	0.55	0.167	
Lye is formed or soln. near phase boundary remains isotropic on cooling	23.1	3.19	0.741	...
	35.5	1.60	0.436	...
	9.44	6.26	1.27	128
	7.59	5.97	1.18	117
	3.59	6.05	1.14	125
	7.70	5.11	1.00	...
	11.9	5.49	1.14	...
	7.83	6.73	1.35	169
	5.10	6.68	1.30	171
	8.77	6.43	1.30	159
	4.21	5.44	1.03	...
Neat soap is formed	20.7	4.93	1.13	122
	24.0	5.49	1.33	154
	16.3	6.39	1.41	153
	13.4	5.92	1.26	132
	26.3	3.47	1.08	69
	36.5	1.89	0.525	58
	40.1	2.29	0.681	143
	42.3	1.96	0.602	153
	15.2	5.38	1.16	121
	36.3	3.58	1.02	168
Sodium Carbonate, Mol. Wt. 106.00				
Middle soap is formed	38.2	2.60	0.457	80
	34.1	2.12	0.346	77
	43.4	1.26	0.237	135
	37.3	0.96	0.162	138
Lye is formed or soln. near phase boundary remains isotropic on cooling	7.30	10.6	1.35	...
	9.34	11.4	1.50	141
	5.66	11.7	1.48	154
	35.1	4.30	0.739	...
	4.55	11.1	1.37	133
	3.07	11.3	1.38	140
	7.92	10.9	1.40	115
	10.4	11.3	1.50	128
	15.1	11.2	1.59	105
	10.5	10.9	1.45	104
	5.64	10.4	1.29	...
	6.77	10.6	1.34	...
	3.52	10.7	1.30	112
	30.7	1.09	0.166	...
	41.5	2.92	0.549	...
	12.3	10.7	1.45	...
Neat soap is formed	22.4	11.0	1.72	156
	33.3	7.28	1.28	154
	18.5	10.8	1.60	113
	24.9	8.92	1.40	116
	15.0	11.2	1.58	70
	34.7	5.88	1.03	126
	37.0	4.43	0.788	67
	13.6	11.7	1.63	>165
	43.2	3.50	0.682	161
	32.6	5.93	1.00	80
	26.1	7.84	1.24	70
Sodium Tetraborate, Mol. Wt. 202.27				
Middle soap is formed	36.6	2.83	0.231	69
	39.4	3.01	0.258	84
	42.0	2.89	0.259	84
	40.1	0.55	0.0456	155
	40.9	3.11	0.274	71
	35.3	1.01	0.145	123
	44.6	0.97	0.0878	143
	37.5	1.07	0.0865	127
	32.7	1.19	0.0894	91
	43.2	0.91	0.0800	140
Lye is formed or soln. near phase boundary remains isotropic on cooling	39.2	4.12	0.359	...
	36.0	5.59	0.473	...
	23.9	12.4	0.976	...
	20.6	13.7	1.03	...
	18.0	15.5	1.15	...
	10.4	16.8	1.14	...
	6.97	16.9	1.10	96
	4.64	17.3	1.10	148
	2.22	17.6	1.08	152
	13.2	17.4	1.24	...
	4.06	16.8	1.05	137
	10.8	17.3	1.19	135
	14.1	17.8	1.29	138
Neat soap is formed	33.4	8.68	0.741	148
	29.2	10.8	0.893	122
	32.3	8.77	0.736	106
	24.8	14.9	1.22	163
	44.9	3.05	0.290	153
	39.0	7.02	0.643	168
	21.2	15.2	1.18	128
	16.0	17.7	1.33	138
	22.7	13.1	1.01	64
	34.2	7.35	0.622	70
	42.2	4.06	0.399	129
Trisodium Phosphate, Mol. Wt. 162.97				
Middle soap is formed	30.4	1.92	0.173	59
	42.2	0.94	0.101	150
	49.2	1.11	0.136	160
	45.1	3.23	0.381	160
	35.8	1.50	0.147	116
	43.1	2.71	0.305	142
	34.1	2.41	0.164	82
	37.1	3.63	0.373	60
	39.6	2.42	0.255	98
	44.6	2.48	0.286	151
Lye is formed or soln. near phase boundary remains isotropic on cooling	16.5	14.3	1.27	>170
	5.07	12.9	0.963	101
	13.1	13.5	1.12	101
	3.28	13.1	0.954	...
	6.17	12.2	0.909	...
	11.1	13.1	1.05	...
	16.3	13.3	1.15	...
	3.00	13.9	1.02	153
	7.48	13.5	1.04	146
	39.2	3.84	0.425	...
	33.4	5.82	0.585	...
	7.85	12.9	0.992	127
Neat soap is formed	41.2	4.20	0.470	146
	20.3	12.9	1.17	143
	27.6	10.9	1.08	162
	27.2	10.6	1.04	153
	32.6	10.1	1.07	>170
	37.0	6.16	0.661	145
	39.0	4.99	0.543	143
	23.6	11.1	1.03	81
	15.7	14.0	1.21	135
Tetrasodium Pyrophosphate, Mol. Wt. 265.95				
Middle soap is formed	31.7	2.55	0.146	71
	30.2	1.62	0.114	61
	35.1	1.58	0.0937	122
	37.4	2.98	0.188	80
	45.9	2.70	0.197	130
	42.2	1.25	0.104	149
	39.7	3.10	0.204	82
	37.5	4.83	0.315	65
Lye is formed or soln. near phase boundary remains isotropic on cooling	9.80	13.7	0.674	96
	34.4	5.81	0.366	...
	8.91	14.8	0.734	142
	3.37	15.0	0.693	151
	3.22	14.1	0.641	...
	6.57	13.1	0.612	112
	12.5	12.8	0.644	...
	17.1	12.3	0.655	...
	5.04	13.8	0.641	136
	14.9	14.0	0.743	131
Neat soap is formed	21.0	13.1	0.750	68
	22.2	13.9	0.822	148
	34.4	8.67	0.573	127
	41.0	6.99	0.505	177
	29.6	13.3	0.872	182
	40.4	5.02	0.344	115
	32.4	7.74	0.486	83
	27.0	13.0	0.775	>160
	33.1	10.5	0.703	152
Calgon, "Mol. Wt." 101.98				
Middle soap is formed	34.1	0.33	0.0326	132
	30.2	1.63	0.163	153
	32.3	0.45	0.0442	96
	43.3	0.44	0.0771	145
	39.6	0.30	0.0483	148
	41.9	1.47	0.198	160
Lye is formed or soln. near phase boundary remains isotropic on cooling	15.8	0.98	0.0972	...
	5.32	1.09	0.108	...
	28.2	0.67	0.0661	...
	5.74	1.71	0.171	>170
	3.23	1.52	0.152	167
Neat soap is formed	28.5	1.93	0.193	160
	26.4	1.41	0.140	134
	28.8	0.86	0.0855	61
	6.88	1.32	0.131	138
	23.1	1.27	0.126	122
	15.0	1.56	0.155	166
	15.7	1.22	0.121	91
	32.2	1.15	0.114	119
	25.0	1.92	0.192	162
	37.6	1.33	0.102	140
	47.6	0.85	0.029	>170
Sodium Metasilicate, Mol. Wt. 122.05				
Middle soap is formed	29.4	0.35	0.041	75
	37.6	2.75	0.278	131
	32.3	1.95	0.244	85
	37.0	1.65	0.220	140
	35.0	1.82	0.236	128
	35.4	0.52	0.067	138
	40.7	0.79	0.111	155
	33.7	1.11	0.165	100
	32.7	3.00	0.382	88
	31.5	1.45	0.192	72
	31.8	0.44	0.057	93
	46.1	2.58	0.990	139

(*Continued on page 165*)

Table V. T_i of Three-Component Systems (*Continued*)

Phase	% Soap	% NaCl	N_w of Salt	T_i*, °C.
Sodium Metasilicate, Mol. Wt. 122.05 (*Cont'd*)				
Lye is formed or soln. near phase boundary remains isotropic on cooling	10.3	14.5	1.58	88
	8.28	16.8	1.83	137
	10.1	14.2	1.54	68
	7.15	13.7	1.42	65
	3.72	14.5	1.45	61
	30.6	1.97	0.239	...
	30.6	1.26	0.151	...
	2.99	15.8	1.59	86
	1.48	15.6	1.54	87
	22.9	8.47	1.01	...
	30.3	3.71	0.461	...
	27.0	6.94	0.862	...
	16.8	16.2	1.97	>165
	11.6	17.1	1.96	>165
	4.60	17.5	1.83	>165
	6.01	14.8	1.53	89
	7.16	15.1	1.86	92
	13.5	13.1	1.46	...
Neat soap is formed	34.8	4.44	0.202	125
	14.9	12.2	1.37	71
	34.6	4.27	0.573	123
	32.5	4.83	0.632	103
	24.3	8.41	1.02	75
	26.4	8.19	1.02	93
	30.3	9.39	1.27	133
	37.8	3.83	0.537	139
	40.7	5.34	0.810	143
	31.2	10.43	1.46	140
	37.7	6.02	0.876	130
	34.7	6.88	0.965	127
	42.3	3.86	0.558	138
	44.8	3.52	0.558	142
	20.5	11.8	1.42	98
	23.0	9.45	1.15	73
	29.9	5.87	0.749	73
	28.8	7.13	0.912	84
	15.0	13.9	1.61	94
	17.0	12.0	1.38	72
	48.5	2.63	0.440	>170
	36.5	9.45	1.43	137
	38.4	9.48	1.49	157
	42.6	3.54	0.587	140
	30.2	14.2	1.98	155
Sodium Silicate (SiO_2/Na_2O Ratio, 2.46), "Mol. Wt." 210.04				
Middle soap is formed	33.3	5.73	0.419	131
	37.6	3.01	0.241	141
	34.8	1.81	0.136	127
	31.6	1.21	0.0860	90
	33.6	0.95	0.0692	121
	31.2	2.06	0.204	76
	33.7	3.50	0.265	122
	45.1	3.15	0.292	152
	41.5	3.54	0.269	156
	41.5	5.25	0.469	149
	40.5	8.25	0.767	139
	44.0	8.95	0.906	141
Lye is formed or soln. near phase boundary remains isotropic on cooling	16.8	17.9	1.30	...
	29.4	6.17	0.456	...
	25.6	10.5	0.783	...
	24.1	11.1	0.819	...
	27.6	8.49	0.633	...
	10.7	18.5	1.25	...
	4.47	24.2	1.61	>170
	10.9	22.3	1.59	>170
	5.44	20.8	1.34	76
	11.3	20.1	1.53	106
	16.3	19.6	1.45	95
	6.69	21.5	1.43	125
	8.72	20.2	1.36	122
	5.77	22.8	1.52	127
	2.77	23.5	1.52	127
	4.36	19.4	1.21	...
Neat soap is formed	31.4	5.96	0.454	89
	29.3	20.2	1.90	>170
	24.9	12.1	0.920	82
	21.3	18.7	1.48	97
	22.7	14.6	1.11	75
	27.8	9.90	0.756	106
	31.2	7.78	0.615	104
	20.3	17.9	1.38	71
	23.3	18.3	1.49	122
	25.2	17.8	1.49	128
	29.3	17.2	1.53	139
	25.4	19.4	1.67	137
	29.7	12.3	1.01	120
	38.5	12.4	1.20	145
	35.7	16.0	1.58	173
	48.6	6.50	0.689	>165
Sodium Silicate (SiO_2/Na_2O Ratio, 3.93), "Mol. Wt." 298				
Middle soap is formed	39.0	3.96	0.234	149
	30.5	4.12	0.212	90
	43.5	8.48	0.596	150
	42.5	4.84	0.308	160
	29.7	0.96	0.047	65
	32.3	5.60	0.304	115
	40.8	9.45	0.639	149
Lye is formed or soln. near phase boundary remains isotropic on cooling	7.32	22.5	1.08	120
	10.1	18.8	0.892	65
	10.3	22.1	1.10	97
	10.4	24.9	1.31	170
	27.7	5.11	0.257	...
	11.1	19.2	0.926	73
	10.5	22.9	1.16	123
	4.67	24.4	1.16	120
	4.89	20.1	0.903	...
Liquid crystal (neat soap) is formed	42.1	9.72	0.681	148
	47.3	4.45	0.311	169
	37.4	15.4	1.10	146
	27.3	19.7	1.26	150
	27.1	11.0	0.601	92
	31.6	10.0	0.581	128
	25.1	15.8	0.904	122
	27.7	6.81	0.350	70
	31.9	18.5	1.26	152
	17.2	18.6	0.980	81
	19.0	20.7	1.16	96
	25.5	13.8	0.767	82
	34.7	16.1	1.10	150
	38.5	10.9	0.721	148
	32.0	14.3	0.892	145
	29.8	21.9	1.53	142
	14.8	22.1	1.18	100
Potassium Silicate (SiO_2/K_2O Ratio, 2.04), "Mol. Wt." 200.66				
Middle soap is formed	37.2	7.23	0.648	162
	40.6	10.9	1.12	151
	33.5	1.80	0.138	114
	40.7	2.44	0.213	160
	39.7	3.76	0.331	162
	43.2	2.33	0.204	160
	43.5	2.78	0.258	161
	41.3	1.09	0.0940	160
	35.5	1.14	0.0895	118
	22.4	15.1	1.21	93
	23.0	14.5	1.16	100
	20.9	20.4	1.73	106
	19.3	18.6	1.49	69
	29.4	10.2	1.40	114
	32.1	4.42	0.643	101
	32.7	4.24	0.335	103
	17.9	22.2	1.85	75
	25.1	18.7	1.66	132
	35.1	11.4	1.06	163
	29.9	3.97	0.299	82
	31.2	7.42	0.602	114
	27.3	7.90	0.607	70
	29.5	3.62	0.270	65
	21.8	12.7	0.906	59
	38.5	6.09	0.548	159
	42.9	5.05	0.483	160
	16.8	20.3	1.61	69
	29.6	1.21	0.104	73
	31.6	1.03	0.0879	90
	34.9	5.88	0.494	145
	14.3	25.0	2.05	73
	47.6	1.81	0.178	158
	41.7	7.55	0.746	163
	36.8	8.64	0.789	162
	32.8	17.0	1.69	168
	20.6	25.0	2.29	140
	12.2	27.8	2.31	170
Lye is formed or soln. near phase boundary remains isotropic on cooling	28.9	2.31	0.167	...
	8.22	25.1	1.81	...
	3.85	25.2	1.77	...
	6.81	26.6	1.99	96
	14.6	28.6	2.50	>170
Neat soap is formed	46.8	6.53	0.698	187
	40.9	16.7	1.97	>170
	31.5	22.4	2.42	167
	35.4	18.2	1.96	158

* Temperature at which isotropic solution separates a liquid-crystalline or a second liquid phase.

various amounts of salt from 70° to 150° C. The per cent salt increased from 0.7 for Calgon, 1.0 for trisodium phosphate, 1.3 for sodium chloride, and 1.7 for the carbonate, tetraborate, and tetrasodium pyrophosphate, to 7.2 for the metasilicate, 7.3 for the 2.46-ratio silicate, 10.6 for the 3.93-ratio silicate, and 13 for the potassium silicate. The value for the metasilicate is not strictly comparable with the others, since the formation of different phases (nigre and lye) is involved at the higher temperature. The salting-out power of salts determined by the temperature coefficients given is different from that previously obtained by other methods. Temperature affects the solubility of soaps in aqueous silicate solutions far less than in solutions of the other salts.

Figure 3 shows the boundaries of the field of isotropic solution at 70° C. as a function of the weight normality of added electrolyte. For Calgon and the silicious silicates, which are colloidal electrolytes, the weight normalities were calculated using the formula weight as the molecular weight. Use of the real molecular weight (which, although unknown, is in the colloidal range) would accentuate the differences between these and the other salts. Again the solubility of electrolytes in aqueous soap systems varies widely even on a molecular basis. In general, Figure 3 shows that those salts which salt in middle soap best are also most effective in salting out an isotropic solution into neat soap, or nigre and lye. However, this is not true of Calgon or the siliceous silicates.

PHASE DATA

The data given show that the salting out of soaps by these electrolytes, some of which are alkaline as well as colloidal, is a complex process. All electrolytes do not behave in the same way, even on a molecular basis. The salting out of nonassociated electrolytes of low molecular weight involves a reduction in the amount of water which acts as a solvent, because of hydration of the added ions. The salting out of soap solutions is complicated by the existence in them of complex equilibria between free ions and various types and sizes of ion aggregates and micelles. The addition of salts is believed to increase the proportion and size of micelles until they link together and precipitate. Because of the presence of neutral molecules in the average micelle, the added salt may be incorporated in it and affect the equilibria involved. The effect of added salts on micelle formation, which can be very specific because of steric and other factors, is probably more important in determining its effect on soap solutions than is hydration of added ions.

The unusually small solubility of soap in Calgon solutions suggests some sort of complex formation. Complexes with soap could also be formed by the colloidal siliceous silicates. This may explain the decreased effect, on a molecular basis, of the silicates of higher SiO_2/Na_2O ratio in salting out soap solutions containing less than 20% soap. Another factor which may be involved is fractionation of the siliceous silicates. The salting out of soap solutions is also complicated by the multiplicity of crystalline and liquid-crystalline phases which aqueous soap systems form at various concentrations and temperatures.

In spite of the complexity of the subject, sufficient regularities exist so that the data of this paper can be used to predict phase diagrams for other soaps and concentrations. The regions of existence of isotropic solutions for other soaps in the presence of all these electrolytes should be predictable to a fairly accurate degree if this part of their diagram is known with any one salt. Phase diagrams at higher soap concentrations for this and other soaps can also be predicted from these data, although with less certainty. One of the practical industrial applications of such work is to predict the amounts of various builders which will dissolve in soaps at crutching temperatures.

LITERATURE CITED

(1) Baker, C. L., Ind. Eng. Chem., 23, 1025 (1931).
(2) Batz, dissertation, Karlsruhe, 1918.
(3) Bolton, H. L., Ind. Eng. Chem., 34, 737 (1942).
(4) Buerger, M. J., Smith, L. B., Ryer, F. V., and Spike, J. E., *Proc. Natl. Acad. Sci. U. S.*, 31, 226 (1945).
(5) Cobbs, W. W., Harris, J. C., and Eck, J. R., *Oil & Soap*, 17, 4 (1940); 19, 3 (1942).
(6) Dedrick, C. H., and Wills, J. H., Div. of Ind. Eng. Chem., A.C.S., Atlantic City, 1946.
(7) Ferguson, R. H., and Richardson, A. S., Ind. Eng. Chem., 24, 1329 (1932).
(8) Ferguson, R. H., Rosevear, F. B., and Stillman, R. C., *Ibid.*, 35, 1005 (1943).
(9) Fischer, M., "Soaps and Proteins", New York, John Wiley & Sons, Inc., 1921.
(10) Hofmeister, F., *Arch. exptl. Path. Pharmakol.*, 25, 6 (1888).
(11) Lamm, O., *Arkiv. Kemi, Mineral. Geol.*, 17A, No. 25 (1944).
(12) Leimdorfer, J., *Kolloidchem. Beihefte*, 2, 1 (1911).
(13) McBain, J. W., in Alexander's "Colloid Chemistry", Vol. I, p. 132, New York, Chemical Catalog Co., Inc., 1926.
(14) McBain, J. W., *J. Chem. Soc.*, 127, 852 (1925).
(15) McBain, J. W., Brock, G. C., Vold, R. D., and Vold, M. J., *J. Am. Chem. Soc.*, 60, 1870 (1938).
(16) McBain, J. W., Elford, W. J., and Vold, R. D., *J. Soc. Chem. Ind.*, 59, 243 (1940).
(17) McBain, J. W., and Pitter, A. V., *J. Chem. Soc.*, 1926, 893.
(18) McBain, J. W., Vold, R. D., and Gardiner, K., *Oil & Soap*, 20, 221 (1943).
(19) McBain, J. W., Vold, M. J., and Porter, J. L., Ind. Eng. Chem., 33, 1049 (1941).
(20) McBain, J. W., and Walls, E., 4th Rept. Colloid Chem., Brit. Assoc. Advancement Sci., p. 244, H.M. Stationery Office, London, 1922.
(21) Merklen, F., "Études sur la constitution des savons du commerce", Marseilles, 1906; German ed. tr. by F. Goldschmidt, 1907.
(22) Richert, T., dissertation, Karlsruhe, 1918.
(23) Shreve, R. N., "Chemical Process Industries", p. 601, New York, McGraw-Hill Book Co., Inc., 1945; U. S. Bur. of Census, private communication.
(24) Thorl, M., dissertation, Karlsruhe, 1918.
(25) Vail, J. G., Ind. Eng. Chem., 28, 294 (1936).
(26) Vaughn, T. H., and Vittone, A., *Ibid.*, 35, 1094 (1943).
(27) Vold, R. D., and Lyon, L. L., *Ibid.*, 37, 497 (1945).

Resinous Products from Petroleum Polymer Sulfurization

M. GLENN MAYBERRY, PAUL V. MCKINNEY[1], AND HARRY E. WESTLAKE, JR.[2]

Mellon Institute of Industrial Research, Pittsburgh, Pa.

A MULTITUDINOUS assortment of commercial products is produced by the general process of vulcanizing unsaturated compounds (*4*). They range from hard rubber and other resinous materials through elastometers and factices to special lubricating fluids. These products have a common feature; their manufacture involves the reaction of sulfur or sulfur-bearing compounds with unsaturates, and the ease of this reaction has led to a widespread search for useful materials. Many research projects have been reported on the sulfurization of unsaturated hydrocarbons of high molecular weight. For example, Snelling (*6*) produced rubberlike bodies from lubricating oil and sulfur chloride; Egloff (*3*) obtained a hard pitch from a cracked petroleum distillate and 5-10% sulfur at 260° C.; and Thomas (*7*) vulcanized a hydrocarbon polymer, formed by copolymerizing olefins and diolefins, in place in a mold.

REACTION OF PETROLEUM POLYMERS WITH SULFUR

Some gasolines made by the cracking of petroleum are subjected to a refining treatment in clay towers. In these towers certain gum-forming compounds, such as diolefins, are removed from cracked gasoline by polymerization. These polymers are

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[1] Present address, Sun Chemical Corporation, 100 Sixth Ave., New York N. Y.

[2] Present address, Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J.

Table I. Characteristics of Petroleum Polymers Used

Gravity, °A.P.I.	10–11
Min. flash point, ° C.	110
Fire point, ° C.	137.8
Saybolt Universal viscosity at 210° F., sec.	225–300
Max. pour point, ° C.	7
Min. iodine No.	200
Molecular weight, approx.	425

Table II. Binary Reaction of Petroleum Polymers with Sulfur

Reaction Compn., %				Properties of Product		
Petroleum polymer	Sulfur	Reaction Time, Hr.	Reaction Temp., ° C.	A.S.T.M. penetration[a], mm.	Softening point[b], ° C.	Remarks
95	5	9.2	80–108	...	...	Soft, almost liquid
90	10	10.8	80–120	...	...	Hard and brittle
85	15	9.3	80–120	35.9	51.0	Soft and plastic
85	15	9.0	105–130	2.3	72.5	Hard
70	30	4.8	90–132	15.7	60.9	Soft and plastic
70	30	5.7	70–140	5.6	64.2	Brittle
70	30	6.7	95–135	2.8	63.0	Brittle
60	40	8.2	95–130	1.2	73.2	Brittle
52	48	11.5	95–128	1.6	69.8	Contains dissolved free sulfur

[a] At 25° C., 100 grams, 5 seconds.
[b] A.S.T.M. ball and ring.

separated from the gasoline by distillation and have become available from several petroleum companies with about the same specifications; a typical range of specifications is given in Table I.

Such polymers provided a previously untried unsaturate for sulfurization. Although they dissolved little sulfur below 100° C. (*1*), above that temperature a reaction took place which resulted in the combination of sulfur, with evolution of hydrogen sulfide increasing as the temperature was raised. Above 140° C. excessive foaming occurred because of the rapid formation of hydrogen sulfide, and higher temperatures caused decomposition of the product. The details of a representative series of experiments using the same petroleum polymer are given in Table II. The properties of the products depended on time, temperature, and concentration of sulfur, and varied from viscous liquids to hard, brittle, shiny, black solids which broke with a conchoidal fracture. The most satisfactory resins were obtained by preparing a mixture of sulfur and a polymer (usually at 80° to 90° C.), which was then heated slowly to the reaction temperature during a period of about 1 hour and maintained at the higher temperature for the rest of the reaction time shown in Table II. Low concentrations of sulfur, short reaction time, and low temperature afforded soft products. Increasing any or all of these factors gave harder products. Phosphorus pentachloride and sulfur monochloride were tried unsuccessfully as catalysts for the reaction.

The properties of the products could be modified by the inclusion of unsaturates from other sources in the reaction mixture. Thus the inclusion of certain natural oils (*2*) gave tough, rubbery solids, which lost some elasticity when the reaction time was long or when the product had been allowed to age. Table III gives experimental details of such preparation. The products softened and could be molded upon heating to 160° C. but did not melt. Other natural oils were tried, but none of them gave products as tough as the ones mentioned in Table III. Dicyclopentadiene could be added to either the sulfur polymer or the sulfur polymer-natural oil mixture to cut down sulfur blooming and to give the products a more lustrous surface. Both the binary and the ternary reactions have been run on pilot plant scale with few difficulties encountered.

Although the structure of the reaction product was not investigated, certain related properties were determined (Table IV). The final product has much less unsaturation than the starting material but the molecular weight was increased by only 45 units. Since the original polymer was a mixture, it is quite probable that the sulfur added to the individual components in different proportions; and since sulfur is a good dehydrogenation element, it is also likely that some depolymerization occurred. This seems to be the best explanation of the small increase in molecular weight of the resin.

VALUE OF PRODUCTS

The sulfurized products are resistant to salts and to low concentrations of sulfuric acid. Nitric acid attacks them to form hard, brittle, easily crumbled materials. Neither sodium hydroxide nor hydrochloric acid has any apparent effect, but ammonia and calcium hydroxide have slight bleaching action.

These products are far too brittle to be of use by themselves. It was shown (*5*), however, that both the binary and ternary reaction products can be compounded to give a mastic composition which will flow to fill completely a simple mold cavity if heated under pressure. The binary product requires the addition of factice to the filler. The properties of the mastic are dependent on those of the resin and also on the type and quantity of the filler used. Fillers such as whiting, asbestos, wood flour, cottonseed hull fibers, carbon black, lignin, slag, or a combination of these materials were found to be satisfactory for the preparation of mastics suitable for floor tile, for example. Certain pigments could be used to obtain dark shades of red, brown, green, and black. The dark color of the resin prohibited lighter colors.

Table III. Reaction of Petroleum Polymers, Sulfur, and Natural Oils

Reaction Compn., %				Reaction Conditions		
Petroleum polymer	Sulfur	Natural Oil %	Natural Oil Name	Time, hr.	Temp., ° C.	Product
41	27.5	31.5	Castor	1	100–160	Stiff, rubbery
39.2	30.6	30.2	Perilla	2	115–145	Rubberlike, unmeltable
41.4	26.8	31.8	Linseed	2	141–146	Tough and elastic
51	29	20	Linseed	$2\frac{3}{4}$	140–152	Tough and elastic
50	30	20	Rapeseed	$4\frac{1}{2}$	140–162	Tough, plastic

Table IV. Chemical Properties of Sulfurized Petroleum Polymer

(70% polymer, 30% sulfur; 5.5 hours at 90–135° C.; softening point, 62.6° C.)

Mol. wt. at freezing point of benzene	470
Iodine No.	26
Sulfur content, analysis	28.8
Sulfur content used in reaction mixture	30.0

Various methods of modifying the mastic to obtain an inexpensive molding composition were inconclusive. Although the products have low tensile and impact strengths, the addition of cyclopentadiene to the original reaction mixture gave a product with both properties improved.

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LITERATURE CITED

(1) Chittick and McKinney, U. S. Patent 2,309,692 (1943).
(2) Chittick and Schlandt, *Ibid.*, 2,330,798 (1943).
(3) Egloff, *Ibid.*, 1,896,227 (1933).
(4) Ellis, "The Chemistry of Synthetic Resins", Chap. 60, New York, Reinhold Pub. Corp., 1935.
(5) McKinney and Mayberry, U. S. Patent 2,316,964 (1943).
(6) Snelling, *Ibid.*, 1,535,740 (1925).
(7) Thomas, *Ibid.*, 2,078,353 (1937).

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Cellulose Ester Melt-Coating Compositions

C. J. Malm, M. Salo, and H. F. Vivian

EASTMAN KODAK COMPANY, ROCHESTER, N. Y.

The melt-coating properties of compositions containing high-butyryl cellulose acetate butyrate have been studied. Essentially fully esterified cellulose acetate butyrates, with a butyryl content above 47% and an intrinsic viscosity of about 0.9 in acetone, have been found suitable as basic components in melt formulations. The physical properties of typical cellulose acetate butyrate melt formulations containing plasticizers, resins, and waxes are described in detail. The data include the effect of temperature and plasticizer concentration on melt viscosity, the effect of plasticizer variations on melting point, tensile strength, elongation, impact strength, blocking temperature, and plasticizer retention, and the effect of the incorporation of resins and waxes on water vapor permeability. The outstanding properties of these formulations are high gloss, high blocking temperature, good water resistance, and in some cases good water vapor resistance. Data are also presented which illustrate the properties imparted to several types of paper by melt coating with typical formulations.

THE application of coatings from molten organic thermoplastic materials appears to be a process of potential utility in various industrial coating problems. In this process, which has been referred to as dry coating or hot melt coating (*12, 18, 23*), the coating is deposited from the molten composition at a temperature sufficiently high to maintain the fluidity of the melt at the proper range for satisfactory coating at atmospheric pressure. In general, temperatures below about 180° C. are used in order to obviate the degradation of both the melt composition and the materials to be coated, such as paper and cloth, which as a rule do not possess good stability at higher temperatures. After application at elevated temperature, the molten coating converts to a desirable condition merely by cooling and does not involve the evaporation of volatile constituents, as is the case when the conventional coating material is applied either as a dispersion in volatile solvents or as an emulsion. Based upon practical melt-coating experience, the preferable viscosity for machine application of coatings on continuous webs such as paper usually lies below 250 poises. The melt-coating compositions can be applied by conventional coating methods such as dipping, knife casting, roll coating, and extrusion.

An example of practical application of this process is the melt coating of packaging paper to obtain improvement both in appearance and water resistance. One of the best known forms of melt coating is the application of molten waxes onto paper such as is used for bread wrappers.

Numerous patents have been issued covering formulations containing various heat-stable synthetic resins of low molecular weight. These formulations have followed certain patterns in regard to composition exemplified by the following classifications: (*a*) mixtures of resins and waxes of low degree of polymerization (*3, 15, 19, 20, 22, 29*); (*b*) mixtures containing as basic constituents resins and waxes with a low degree of polymerization, modified with small amounts of long-chain polymeric materials such as ethylcellulose, polyvinyl acetate, and rubber derivatives (*1, 2, 5–10, 13, 16, 17, 21, 24, 25, 26, 30, 31, 32*). Because these compositions are composed preponderantly of products with a low degree of polymerization, the coatings obtained from them exhibit one or more of the following undesirable characteristics inherent with coating materials of this type: poor flexibility or poor impact strength, low tensile strength, low melting point, and tendency of surfaces coated with these materials to adhere together or block upon storage.

The present paper deals with the development of melt formulations containing, as the basic materials, certain types of heat-stable cellulose esters having satisfactory compatibility with blending agents such as resins and plasticizers, low moisture sorption, and a sufficiently high degree of polymerization or viscosity to yield coatings of improved physical properties (*4, 27, 28*).

SELECTION OF ESTER FOR MELT COATING

The underlying factors entering into selection of proper cellulose esters for water-resistant melt-coating formulations become evident from a consideration of certain of their physical properties, such as melting point, sorption of moisture, and solubility in plasticizers.

Examination of the properties of cellulose esters of the lower aliphatic acids, as reported by Malm, Fordyce, and Tanner (*14*), shows that cellulose acetates have undesirably high melting points for melt coating (namely, about 250° C.), fairly high moisture sorption, and limited solubility in suitable high-boiling plasticizers. Cellulose esters containing increasing amounts of higher acyl groups such as propionyl or butyryl show a progressive improvement in melt-coating properties, especially in regard to lower melting point as Figure 1 shows (*14*). In the case of cellulose propionates, a satisfactory range in melt-coating properties is not quite reached, chiefly because the melting points are above 200° C. However, upon replacing the acetyl in cellulose acetate with increasing amounts of butyryl, the improvement in the desirable properties is more distinct. Mixed esters containing above about 35% butyryl have melting points below 200° C.

Preliminary experiments indicated that low-viscosity cellulose acetate butyrates having more than about 35% butyryl were usable as main components in melt formulations containing plasticizers, resins, and waxes. Further experiments showed that the optimum type of cellulose acetate butyrate for melt coating was confined to a butyryl content above about 47% and hydroxyl content below 0.1 group per anhydroglucose unit (Figure 2). The scope of the present paper is limited to a description of experiments carried out with a substantially fully esterified cellulose acetate butyrate having a butyryl content of about 50% and an intrinsic viscosity of about 0.9, determined in acetone.

TESTING PROCEDURES

COLOR STABILITY. An 18 × 150 mm. Pyrex test tube is filled with the composition and heated unstoppered in an electrically heated metal block at 180 ± 1° C. for a total of 8 hours. At the end of this period the color of the melt is compared with a set of arbitrary standards.

MELT VISCOSITY. A 38 × 150 mm. Pyrex test tube, marked with two lines 1.25 inches apart, the lower of which is about 1.5 inches above the bottom of the tube, is filled with the composition to be tested. The tube is stoppered loosely with a cork and immersed in a Pyrex constant-temperature bath containing high-boiling mineral oil or plasticizer, such as dioctyl phthalate, as the heating medium. A strong electric light is held behind the bath to facilitate observation of the viscosity. After the first portion of the composition is melted, more is added until the tube is nearly full of melt. The tube is adjusted so that its top is not more than 1 inch above the liquid level of the bath; more composition is added if necessary until the melt surface is 0.75 inch below the level of the liquid in the bath. Approximately 100 grams of composition are required. A cork carrying an accurate thermometer reading to 0.2° C. is inserted in the tube so that the bulb of the thermometer is in the portion of the melt in which the viscosity is to be measured. When the temperature desired is obtained, the time is noted, the cork and thermometer are removed, and a cork containing a glass-tube ball guide is inserted. Two or more $^1/_{16}$-inch steel balls (0.0625 ± 0.003 inch in diameter and weighing 0.163 ± 0.002 gram) are dropped through the center of the melt, and the time of fall is observed for the 1.25-inch distance between the marks on the test tube. The balls are dropped at intervals of not less than 3 minutes until values agreeing to 2 seconds are observed. The viscosity in poises is calculated as follows:

$$\text{Viscosity} = K\,(D - d)\,t$$

where K = apparatus constant
D = ball density, grams/cc. at temperature used
d = melt density, grams/cc. at temperature used
t = average time of ball drop, seconds

Apparatus constant K may be determined by standardization, using an oil of known viscosity, or it may be calculated by Faxen's correction for the Stokes law:

$$K = \frac{2 \times g \times r^2 \left[1 - 2.104\left(\frac{r}{R}\right) + 2.09\left(\frac{r}{R}\right)^3 - 0.95\left(\frac{r}{R}\right)^5\right]}{9\,L}$$

where g = acceleration of gravity, c.g.s. units
r = radius of ball, cm. at temperature used
R = radius of tube, cm. at temperature used
L = ball drop distance, cm.

Measurement of Viscosity Stability. After the viscosity has been taken as described in the preceding section, heating of the sample is continued at the prescribed temperature (170° C. in the experiments described in this paper). After a total of 6 hours from the time at which a melt is formed, the viscosity is redetermined by the same technique, and the percentage loss in viscosity calculated.

Intrinsic Viscosity of Cellulose Ester is defined by Kraemer (*11*) as:

$$[\eta] = \left(\frac{\ln \eta_r}{c}\right)_{c \to 0}$$

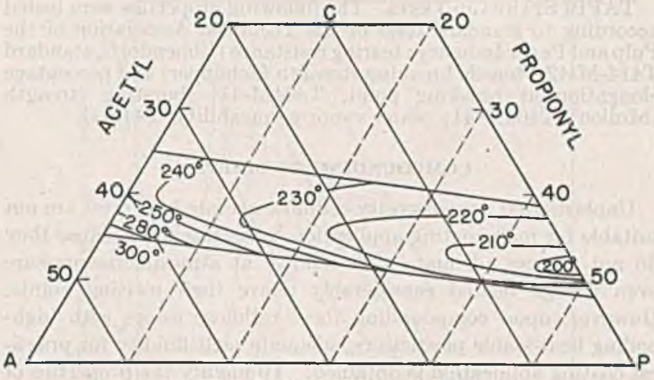
where η_r = viscosity of solution relative to that of solvent
c = concentration, grams solute/100 cc. solution

In this work the intrinsic viscosity of the cellulose ester is measured as follows: Solutions of 0.15, 0.25, and 0.35 gram of cellulose ester per 100 cc. of solution are prepared with acetone as the solvent. Viscosity of these solutions is measured at 25° C. in a capillary pipet type viscometer. The data are extrapolated to zero concentration by means of the graph of $\ln \eta_r/c$ against concentration.

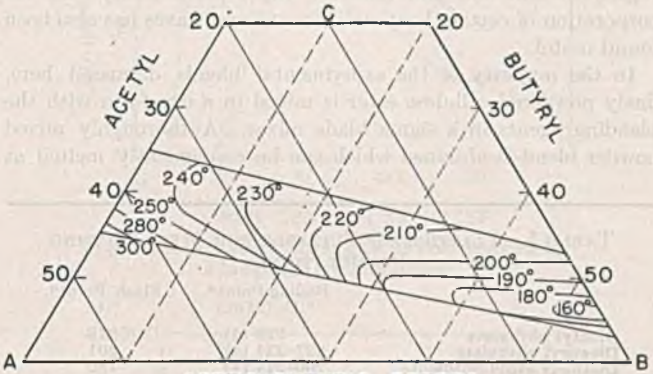
Melting Point (*14*). Pyrex test tubes of 2.5-mm. inside diameter, 4-mm. outside diameter, and 35-mm. length are filled to a height of about 1 inch (2.5 cm.) with the powdered composition to be tested and are placed in a suitable hole drilled to a depth of 2 inches (5 cm.) along the axis of a cylindrical copper block 3 inches (7.6 cm.) in diameter and 3 inches high. Other holes in the block are provided for a thermometer and for illumination of the sample. The copper block is heated at a rate of 5° C. per minute, and the point taken is the temperature at which the sample changes in physical form and becomes fused.

Izod Impact Strength. The test is made on cast-molded test pieces according to A.S.T.M. Method D256-41T. The test specimens are prepared by cast molding the composition at 170° C. in a mold giving the specified width and the notched test surface. After cooling and removal from the mold, the test pieces are accurately sawed to the specified thickness.

Tensile Strength. A uniform film (0.02–0.05 inch thick), from which the test pieces are cut, is prepared by knife coating the molten composition at 170° C. on a polished metal plate. After cooling to room temperature, the film is stripped from the plate.



ACETIC-PROPIONIC ESTERS



ACETIC-BUTYRIC ESTERS

Figure 1. Relation of Melting Point (Centigrade) to Composition of Cellulose Esters of Acetic-Propionic and of Acetic-Butyric Acids

Test pieces of the following special dimensions (in inches) are punched out from the film with a die:

Width of grip section	1.00	....
Width of center flat section	0.250	The grip section tapers to center flat section by arc of 1-inch radius
Length of center flat section	2.25	
Gage length (test marks)	2.00	Marked with grease pencil on center flat section
Distance between grips	4.00	....
Length over-all	6.00	....

Accurately measured test pieces are conditioned 96 hours and tested at $77 \pm 2°$ F. and $50 \pm 2\%$ relative humidity.

The test is made on a Scott tensile testing machine having a cross-head speed of 3 inches per minute. The tensile strength is computed from the maximum load applied during the testing. The elongation is computed from the total amount of travel between gage marks at the time of rupture:

$$\text{Tensile strength} = \frac{\text{breaking load (lb.)}}{\text{width (in.)} \times \text{thickness (in.)}}$$

$$\%\ \text{elongation over 2-in. gage marks} = \frac{\text{(inches between gage marks at point of rupture} - 2)}{2}\,100$$

Plasticizer Retention. Samples of films coated at 170° C. from the molten compositions interleaved with sheets of white writing paper are stored for 6 months or longer at normal temperature (21–35° C.). Exudation is indicated by wetting of the writing paper with the plasticizer.

Blocking Test. This property is tested at 52°, 66°, 93°, and 121° C. One-inch-square pieces of melt-coated paper are kept with coated surfaces together under a 5-pound weight for 16 hours in a constant-temperature oven. Any indication of change in surface appearance or tendency of the surfaces to adhere is considered unsatisfactory.

Wet Bursting Strength. The sample of paper is submerged for 2 hours in distilled water at 22° C. Immediately after removal from the water, the bursting strength is measured on an Ashcroft apparatus in pounds per square inch.

Wet Expansivity. A 100 × 15 mm. test strip is immersed in distilled water for 2 minutes at 22° C. and then tested on a Schopper expansion tester. The wet expansivity is the percentage gain in length of the paper.

TAPPI Standard Tests. The following properties were tested according to standard tests of the Technical Association of the Pulp and Paper Industry: tearing resistance (Elmendorf), standard T414-M-42; tensile breaking strength (Schopper) and percentage elongation at breaking point, T404M-41; bursting strength (Mullen), T403M-41; water vapor permeability, T448-41.

COMPOUNDING OF MELTS

Unplasticized, low-viscosity cellulose acetate butyrates are not suitable for melt-coating application by themselves because they do not possess adequate melt fluidity at atmospheric pressure even though heated considerably above their melting points. However, upon compounding these cellulose esters with high-boiling heat-stable plasticizers, adequate melt fluidity for practical coating application is obtained. To modify the properties of the plasticized cellulose acetate butyrate melts—for instance, in regard to adhesion and moisture vapor permeability—the incorporation of certain heat-stable resins and waxes has also been found useful.

In the majority of the experimental blends discussed here, finely powdered cellulose ester is mixed in a dry form with the blending agents in a sigma blade mixer. A thoroughly mixed powder blend is obtained which can be conveniently melted at controlled temperature for coating and testing. In a few cases, especially if resins and waxes are used as modifying agents, it is advantageous to mix the components in a fused state in a thermostatically controlled heated vessel equipped with a propeller-type mixer. For commercial uses it might be preferred to premix the components by rolling the powder blend into a sheet which is then mechanically disintegrated into granules of suitable size. The granules can be conveniently melted in a continuous manner by means of a screw or piston extruder of the type used in extrusion or injection molding of plastics.

Table I. Plasticizers Suitable for Melt-Coating Formulations

	Boiling Point[a], ° C. (Mm.)	Flash Point[a], ° C.
Dioctyl phthalate	229 (4)	218
Dicapryl phthalate	227–234 (4)	201
Diethoxy ethyl phthalate	200–214 (4)	180
Dibutyl sebacate	344–345 (760)	178
Dioctyl sebacate	248 (4)	213
Butoxy ethyl stearate	210–233 (4)	193
n-Butyl stearate	220–225 (25)	183

[a] Data obtained from Plastics Catalog Corporation's "1945 Plastics Catalog", p. 220.

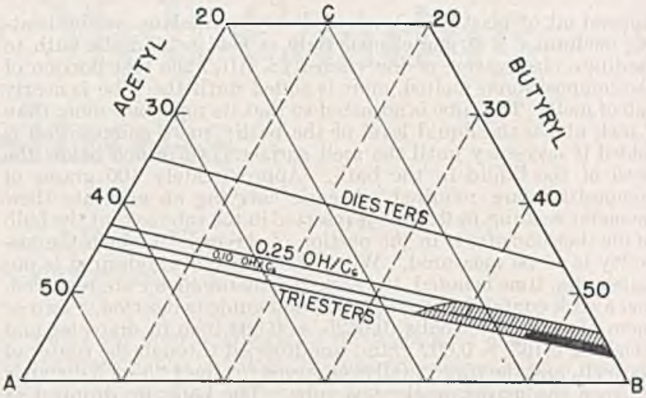


Figure 2. Composition of Cellulose Esters Suitable for Melt Coating (Black Area Shows Optimum Range)

PROPERTIES OF PLASTICIZED MELT COMPOSITIONS

The incorporation of relatively small amounts of suitable plasticizers with cellulose acetate butyrate produces a marked lowering in melt viscosity and an improvement in flexibility and

Table II. Properties of Plasticized Cellulose Acetate Butyrate Melt Compositions

Cellulose Acetate Butyrate, %	Plasticizer, %	Melt Viscosity, Poises at 170° C. 1st hr.	Melt Viscosity, Poises at 170° C. 6 hr.	M. P., ° C.	Izod (Notched) Impact Strength, Ft.-Lb./In.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %	Plasticizer Retention[a]	Blocking Test[a,b] 52° C.	Blocking Test[a,b] 66° C.	Blocking Test[a,b] 93° C.	Blocking Test[a,b] 121° C.
					Dibutyl Sebacate as Plasticizer							
86	14	Very high	...	...	0	..	..	+	..	..	..	..
83	17	458	452	146	7	1235	6	+	+	+	−	−
82	18	392	371	151	8	1190	5	+	+	+	−	−
73	27	91	93	136	5	281	31	+	−	−	−	−
64	36	26	27	130	4	92	21	+	−	−	−	−
54	46	10	10	108	3	22	21	−	−	−	−	−
					Dioctyl Sebacate as Plasticizer							
83	17	895	750	...	2	..	..	..	..	..	..	..
70	21	284	259	153	7	1185	28	+	+	+	−	−
68	32	67	66	144	6	547	66	+	+	+	−	−
58	42	20	20	132	3	366	71	−	+	+	−	−
48	52	7	7	80	2	109	47	−	+	+	−	−
					Dioctyl Phthalate as Plasticizer							
80	20	534	474	150	0.2	1660	15	+	+	+	+	−
70	30	126	119	137	8	609	50	+	+	−	−	−
60	40	35	40	135	6	312	..	+	+	−	−	−
50	50	13	13	132	3	166	74	−	+	−	−	−
					Dicapryl Phthalate as Plasticizer							
80	20	453	432	147	0.2	1550	12	+	+	+	−	−
70	30	105	103	139	6	587	44	+	+	−	−	−
60	40	32	32	135	6	355	64	+	+	−	−	−
50	50	11	11	132	4	139	50	−	−	−	−	−
					Diethoxy Ethyl Phthalate as Plasticizer							
83	17	758	741	146	0.1	1806	17	+	+	+	+	−
75	25	202	181	135	8	556	33	+	−	+	−	−
65	35	63	62	128	5	156	48	+	−	−	−	−
56	44	21	21	...	4	64	22	−	−	−	−	−
					Butoxy Ethyl Stearate as Plasticizer							
79	21	216	200	150	0.6	1021	22	+	+	+	+	−
69	31	46	44	148	6	577	46	−	+	+	−	−
59	41	15	15	146	2	358	59	−	+	+	−	−
49	51	7	7	...	1	122	26	−	+	+	−	−

[a] + = satisfactory, − = unsatisfactory.
[b] Tested under 5 lb./sq. in. pressure for 16 hours.

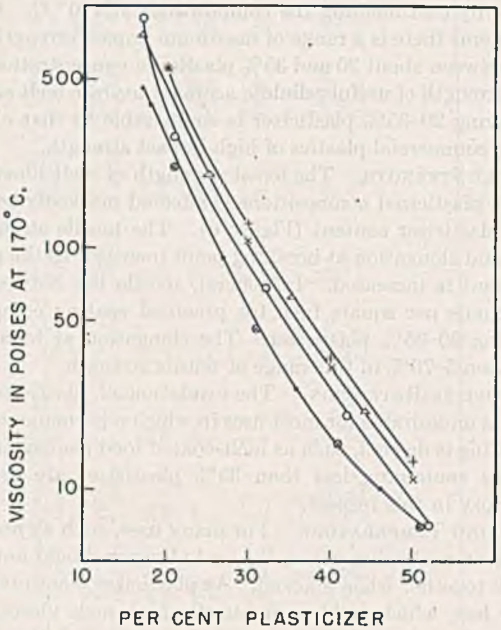


Figure 3. Melt Viscosity as Influenced by Plasticizer Variations

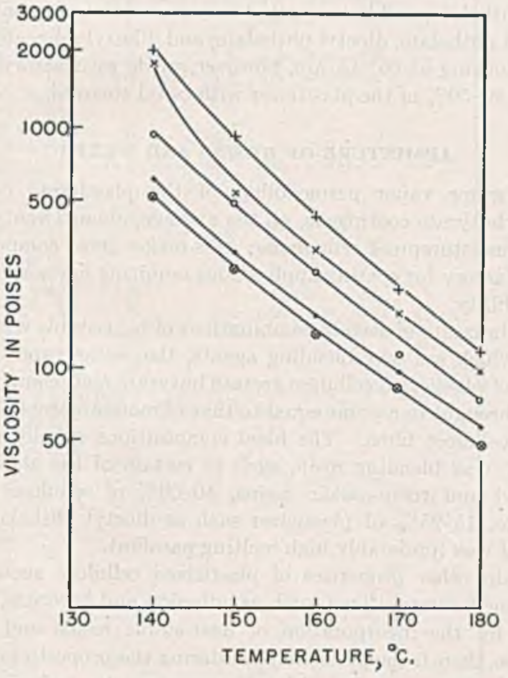


Figure 4. Melt Viscosity as Influenced by Temperature Variation (Composition Contains 25% Plasticizer)

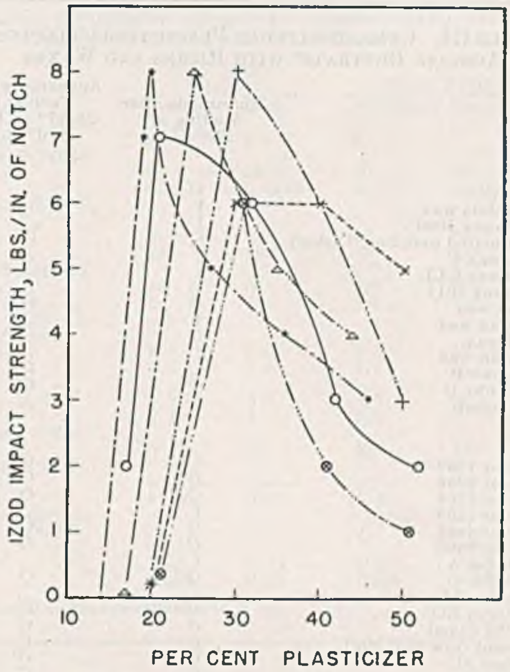


Figure 5. Impact Strength as Influenced by Plasticizer Variations

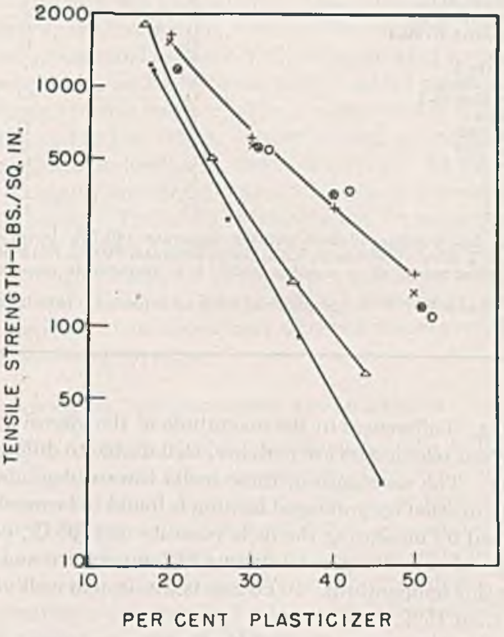


Figure 6. Tensile Strength as Influenced by Plasticizer Variations

● Dibutyl sebacate
○ Dioctyl sebacate
+ Dioctyl phthalate
× Dicapryl phthalate
⊗ Butoxy ethyl stearate
△ Diethoxy ethyl phthalate

impact strength of films coated with it. This lower melt viscosity makes it possible to apply the melt at a practical temperature range such as 150–170° C., which is considered satisfactory for high-speed machine coating of heat-susceptible materials such as paper and cloth.

The suitability of a plasticizer for these melt coating formulations is dependent on the following factors: satisfactory solvent power for the cellulose ester at high temperature, compatibility at low temperature, low toxicity, low cost, adequate heat stability at coating temperature, boiling point above about 340° C., and flash point above the coating temperature used. The commercially available ester type compounds listed in Table I are typical of melt-coating plasticizers for use with cellulose acetate butyrate. Table II shows the influence of the incorporation of plasticizer on melt-coating properties of high-butyryl cellulose acetate butyrate.

Color Stability. When incorporated with the cellulose acetate butyrate, these plasticizers give melts of excellent color stability, as shown by heating for 8 hours at 180° C.

Melt Viscosity. The incorporation of increasing amounts of plasticizer with the cellulose acetate butyrate produces a progressive decrease in melt viscosity. Figure 3 shows that melt viscosity at 170° C. plotted as a logarithmic function varies nearly linearly with change in plasticizer concentration. The rate of change in melt viscosity is approximately the same for each

Table III. Compatibility of Plasticized Cellulose Acetate Butyrate[a] with Resins and Waxes

	Appearance after Melting at 170° C.[b]	Appearance upon Cooling to 21–27° C. from 170° C.[c]
Waxes		
Beeswax	I	..
Candelilla wax	I	..
Carbowax 4000	I	..
Chlorinated paraffin (Hooker)	C	O
Flexowax C	I	..
Flexowax CLL	I	..
Halowax 1014	C	O
Japan wax	C	O
Montan wax	I	..
Opal wax	C	O
Paraffin wax	I	..
Rezowax B	C	I
Santowax O	C	O
Spermaceti	I	..
Resins		
Aroclor 1242	C	C
Aroclor 1248	C	C
Aroclor 1264	C	O
Aroclor 1269	I	..
Aroclor 4465	C	C
Aroclor 5460	C	C
Pentalyn A	I	..
Pentalyn G	O	O
Pentalyn M	I	..
Pentalyn EC	C	C
Synthe Copal	C	C
Paramit (low acid No.)	C	C
Lewisol 2L	O	O
Teglac 15	C	C
Beckacite 1111	I	..
Beckacite 1120	I	..
Paraplex G-25	C	C
Paraplex RG-9	I	..
Piccolyte S115	I	..
Piccolastic D150	I	..
Piccolastic B100-1	O	O
RH35	C	C
Nevillite 1	I	..
Cumar W$^1/_2$	I	..
Nevindine R-1	O	O
Petrex 1	I	..
Durez 550	C	C
Durez 209	C	C
Gelva V 1.5	C	C
Elemi	C	C
Rosin	C	C
Damar	C	C

[a] 37.5% by weight cellulose acetate butyrate (49.7% butyryl, 6.1% acetyl), 7.5% dibutyl sebacate, 5.0% butyl stearate, 50.0% resin or wax.

[b] C = clear melt; O = opaque melt; I = immiscible (separates into layers).

[c] C = clear solid; O = opaque solid with no separation into layers; I = immiscible.

plasticizer. Differences in the magnitude of the viscosity among the different plasticizers are perhaps attributable to differences in solvation. The resistance of these melts toward degradation or depolymerization by prolonged heating is found to be excellent, as determined by measuring the melt viscosity at 170° C., both immediately after melting and bringing to temperature and after 6 hours at this temperature. In no case is the drop in melt viscosity greater than 15%.

Figure 4 shows the effect of temperature on melt viscosity. These data were obtained with compositions containing 25% plasticizer. Melt viscosity plotted as a logarithmic function varies nearly linearly with temperature within the range of practical coating viscosity. All of the melts described here solidify as the temperature is lowered to 130–140° C. Here again it is to be noticed that differences in the magnitude of the viscosity occur among the different plasticizers.

Melting Point. Increase in plasticizer concentration reduces the melting point of plasticized compositions. Melting points varying from about 130° to 150° C. are obtained with compositions containing less than 35% plasticizer.

Impact Strength. The measurement of impact strength is an indication of the usefulness of these compositions as protective coatings on materials, such as packaging paper, which must withstand considerable rough usage. Figure 5 shows the Izod impact strength as influenced by plasticizer variation. The tests were run at 77° F. and 50% relative humidity on notched test pieces prepared by cast molding the compositions at 170° C. In most melt systems there is a range of maximum impact strength which occurs between about 20 and 35% plasticizer concentration. The impact strength of useful cellulose acetate butyrate melt compositions having 20–35% plasticizer is comparable to that obtained with the commercial plastics of high impact strength.

Tensile Strength. The tensile strength of melt films coated from the plasticized compositions is affected markedly by variation in plasticizer content (Figure 6). The tensile strength decreases and elongation at breaking point increases as the plasticizer content is increased. In general, tensile lies between 500–1000 pounds per square inch for practical coating composition containing 20–35% plasticizer. The elongation at break point varies from 5–70% in this range of tensile strength.

Plasticizer Retention. The exudation of plasticizer upon storage is undesirable for most uses in which a permanent protective coating is desired, such as melt-coated food packaging paper. Formulas containing less than 35% plasticizer are ordinarily satisfactory in this respect.

Blocking Temperature. For many uses, such as protective coatings on packaging paper, the coated paper should not adhere or block together when stacked. At plasticizer concentration of 20% or less, which yield impractically high melt viscosities for high speed coating of continuous webs, several of the cellulose acetate butyrate compositions do not block at 93° C. At plasticizer concentrations above 20%, in which range melt viscosities are low enough for high speed coating, blocking temperatures above 66° C. are obtained in the case of dioctyl sebacate, diethoxy ethyl phthalate, and butoxy ethyl stearate. Mixtures containing dicapryl phthalate, dioctyl phthalate, and dibutyl sebacate which show blocking at 66° C. are, however, made satisfactory by replacing 40–50% of the plasticizer with butyl stearate.

ADMIXTURE OF RESINS AND WAXES

The water vapor permeability of the plasticized cellulose acetate butyrate coatings is, on the average, about twenty times that of moistureproof cellophane; this makes these compositions unsatisfactory for coating applications requiring low water vapor permeability.

By admixture of certain combinations of heat-stable waxes and resins which are wax blending agents, the water vapor permeability of plasticized cellulose acetate butyrate melt compositions can be brought to a point equal to that of moistureproofed regenerated cellulose films. The ideal compositions usually contain 10–30% wax blending resin, such as certain of the chlorinated diphenyl and rosin-maleic resins, 40–60% of cellulose acetate butyrate, 15–25% of plasticizer such as dioctyl phthalate, and 1–5% of wax (preferably high melting paraffin).

Certain other properties of plasticized cellulose acetate butyrate melt compositions, such as adhesion and hardness, can be varied by the incorporation of heat-stable resins and waxes. Likewise, there is the possibility of altering the properties of melt-coatable resins and waxes by the incorporation of plasticized melt-coating-type cellulose acetate butyrate. Table III shows the compatibility of various resins and waxes.

PROPERTIES IMPARTED TO PAPER

The advantages as well as disadvantages offered by plasticized cellulose acetate butyrate melt coatings may be illustrated by the properties imparted to several types of paper by melt application. Table IV gives properties representative of those obtained with various papers melt-coated with a typical composition containing 75% melt-coating-type cellulose acetate butyrate and 25% plasticizer, composed of a 60–40 mixture of dibutyl sebacate and butyl stearate. Table V contains physical data on papers melt-coated with a typical formulation containing 65–20–15–1 parts by weight, respectively, of cellulose acetate butyrate, Aroclor 4465 (a low-

TABLE IV. PHYSICAL PROPERTIES OF PAPERS MELT-COATED WITH TYPICAL CELLULOSE ACETATE BUTYRATE COMPOSITION CONTAINING 25% PLASTICIZER

	Black Kraft Wrapper		Blue Kraft Wrapper		Hammersine		Printed Bread Wrapper							Heavy Cardboard		
Number of sides coated	Neither	Both	Neither	Both	Neither	Both	Neither	One	One	One	One	Both	Both	Neither	Both	Both
Weight of coating, lb./1000 sq. ft.	...	10 1/4	...	8	...	2 1/2	...	1 1/2	2 1/2	7 3/4	13 1/4	6 3/8	13 3/8	...	6	10
Total weight of paper, lb./1000 sq. ft.	21 1/4	31 1/2	21	29	6 1/4	8 3/4	8 3/4	10 1/4	11 1/4	16 1/2	22	15 1/8	22 1/8	66 1/2	72 1/2	76 3/4
Dry thickness, in.	0.0059	0.0061	0.0030	0.0038	0.001	0.0014	0.0019	0.0018	0.0021	0.0031	0.0048	0.0024	0.0038	0.0159	0.0167	0.0168
Tearing resistance (Elmendorf), grams																
Machine direction	80	88	44	40	12	12	12	16	20	22	36	20	22	488	352	320
Cross direction	92	108	40	40	12	12	20	16	20	24	40	16	22	624	648	600
Folding endurance (Schopper)																
Machine direction	246	85	314	206	Broke under tension on tester		30	3	10	12	6	9	13	2500+	2500+	2500+
Cross direction	98	90	473	380			5	7	11	6	5	7	6	2500+	2500+	2500+
Tensile breaking strength (Schopper), kg./15 mm.																
Machine direction	10.0	11.8	8.7	9.3	1.7	2.4	3.1	3.1	2.9	3.3	3.7	3.7	3.7	30+	30+	30+
Cross direction	5.1	5.4	5.5	5.8	1.3	2.3	1.7	1.4	2.0	2.6	3.3	2.7	2.9	10.9	10.8	10.7
Stretch, %																
Machine direction	1.5	1.5	2.0	2.0	1.0	0.5	0.50	1.0	.5	1.0	1.5	1.0	1.0	1.5	1.5	1.0
Cross direction	2.5	2.0	5.0	4.5	5.0	1.0	0.50	...	1.0	1.5	2.0	1.0	1.0	5.0	6.0	4.5
Dry bursting strength (Mullen), lb./sq. in.	42	50	45	46 1/2	11	11	10 1/2	11	13	16 1/2	22	16	16	160+	160+	160+
Wet bursting strength (Ashcroft), lb./sq. in.	5 3/4	31	5 1/2	29	1/4	7 1/2	2 3/4	6	6 1/2	8 3/4	13 1/2	13 3/4	15 1/2	47	75	140+
Wet expansivity, %	3.35	0.10	2.30	0.20	1.80	0.50	0.95	0.95	0.75	0.40	0.35	0.20	0.10	1.0	0.15	0.10
Water vapor permeability, mg./sq. cm./hr. (100° F., 95% R.H.)																
First side	18	2.5	...	...	10	4.0	...	...	...	...	...	...	...	...	...	...
Second side	21	2.7	...	...	11	4.1	...	...	...	...	...	...	...	...	...	...

TABLE V. PHYSICAL PROPERTIES OF PAPERS MELT-COATED WITH TYPICAL WATER VAPOR PROOF FORMULATION

	Blue Lucern Wrapper		Black Kraft Wrapper		
Number of sides coated	Neither	Both	Neither	One	Both
Weight of coating, lb./1000 sq. ft.	0	8	0	7	16
Total weight of paper, lb./1000 sq. ft.	4	12	20	27	36
Dry thickness, in.	0.0013	0.0023	0.0053	0.0059	0.0068
Tearing resistance (Elmendorf), grams					
Machine direction	8	12	90	94	96
Cross direction	10	16	92	108	98
Folding endurance (Schopper)					
Machine direction	12	56	456	169	30
Cross direction	1	14	163	137	163
Tensile breaking strength (Schopper), kg./15 min.					
Machine direction	1.5	3.0	9.2	10.2	11.8
Cross direction	0.8	1.8	3.8	5.1	6.0
Stretch, %					
Machine direction	1.3	2.5	2.0	2.0	2.7
Cross direction	2.5	5.7	5.5	7.3	6.0
Dry bursting strength (Mullen), lb./sq. in.	6	15	42	54	65
Wet bursting strength (Ashcroft), lb./sq. in.	0	14 1/2	5 3/4	11 1/2	65
Wet expansivity, %	3.15	0.00	4.40	1.65	0.00
Water vapor permeability, mg./sq. cm./hr. (100° F., 95% R.H.)					
First side[a]	High	0.12	High	0.36	0.038
Second side	High	0.11	High	0.16	0.051

[a] For moisture proof Du Pont cellophane, 0.10 mg.

melting chlorinated diphenyl resin), dioctyl phthalate, and paraffin. These coatings produce beneficial effects, especially on water vapor permeability, wet bursting strength, and wet expansivity. Melt-coated papers can be obtained with water vapor transmission rates in the order of those obtained with moistureproof regenerated cellulose film. Wet bursting strength is raised markedly on papers coated on both sides; papers coated on one side show a moderate improvement in this respect. The wet expansivity of papers coated on both sides is reduced to low values. Papers coated on one side, as is to be expected, show moderate reduction in wet expansivity. Tearing resistance, tensile breaking strength, and dry bursting strength are usually improved slightly by melt coating. These improvements are accompanied, however, with some decrease in folding endurance which, in most cases, is not considered to be of sufficient degree to be harmful. In addition to the changes brought about on physical properties by cellulose acetate butyrate melt coating, a marked improvement in appearance of paper occurs even with the application of low amounts of coating.

POTENTIAL COMMERCIAL APPLICATIONS

Because of their wide range of physical properties, the cellulose acetate butyrate melt compositions are being investigated for a large variety of applications. These compositions show special promise as protective coatings on paper and cloth because of their high blocking temperatures and also because of the properties they impart, such as improvements in appearance, dimensional stability, wet strength, and water vapor resistance. The resin-containing compositions show promise for the manufacture of laminates from such materials as cloth, wood, and metal webs.

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LITERATURE CITED

(1) Altman, A. M., and Shaw, E. J. (to A. B. Dick Co.), U. S. Patent 2,333,624 (Nov. 9, 1943).
(2) Asnes, Benjamin, Kallander, E. L. (to Dennison Mfg. Co.), *Ibid.*, 2,233,090 (Feb. 25, 1941).
(3) Billing, W. M. (to Hercules Powder Co.), *Ibid.*, 2,294,651 (Sept. 1, 1942).
(4) Eastman Kodak Co., Brit. Patent 540,765 (Oct. 29, 1941).
(5) Geiger, L. M. (to Neville Co.), U. S. Patent 2,247,154 (June 24, 1941).
(6) Hershberger, A. (to Du Pont Co.), *Ibid.*, 2,159,152 (May 23, 1939).
(7) Jones, W. L. (to Interchemical Corp.), *Ibid.*, 2,264,315 (Dec. 2, 1941).
(8) Kauppi, T. A. (to Dow Chemical Co.), *Ibid.*, 2,290,563 (July 21, 1942).
(9) Kauppi, T. A., and Kin, M., *Ibid.*, 2,311,609 (Feb. 16, 1943).
(10) Kauppi, T. A., and Kropcott, E. A., *Ibid.*, 2,264,316 (Dec. 2, 1941).

(11) Kraemer, E. O., Ind. Eng. Chem., 30, 1200 (1938).
(12) Long, J. H., *Tech. Assoc. Papers*, 22, 296 (1939).
(13) Lum, J. C., and Keating, T. J. (to Westinghouse Elec. & Mfg. Co.), U. S. Patent 2,367,954 (Jan. 23, 1945).
(14) Malm, C. J., Fordyce, C. R., and Tanner, H. A., Ind. Eng. Chem., 34, 430 (1942).
(15) Miller, B. C. (to Bert C. Miller, Inc.), U. S. Patent 2,117,199 (May 10, 1938).
(16) *Ibid.*, 2,117,200 (May 10, 1938).
(17) *Ibid.*, 2,190,843 (Feb. 20, 1940).
(18) Mosher, R. H., and Bracewell, R. S., *Paper Trade J.*, 122, 60 (1946).
(19) Murray, J. D. (to Murray Liquafilm Corp.), U. S. Patent 220,455 (June 18, 1940).
(20) O'Neil, J. H. (to Continental Can Co., Inc.), *Ibid.*, 2,121,404 (June 21, 1938).
(21) Ott, Emil (to Hercules Powder Co.), *Ibid.*, 2,138,192 (Nov. 29, 1938).
(22) Pullman, J. H. (to Bert C. Miller, Inc.), *Ibid.*, 2,070,553 (Feb. 9, 1937).
(23) Pullman, J. H., *Tech. Assoc. Papers*, 22, 324 (1939).
(24) Ritchie, R. S. (to Dow Chemical Co.), U. S. Patent 2,331,095 (Oct. 5, 1943).
(25) Rothrock, D. A. (to Resinous Products and Chem. Co.), *Ibid.*, 2,285,095 (June 2, 1942).
(26) Rothrock, D. A., and Cheetam, H. C., *Ibid.*, 2,294,211 (Aug. 2, 1942).
(27) Salo, M., and Vivian, H. F. (to Eastman Kodak Co.), *Ibid.*, 2,387,773 (Oct. 30, 1945).
(28) *Ibid.*, 2,387,774 (Oct. 30, 1945).
(29) Samarus, N. N. F., and Plunguian, M. (to Mead Corp.), *Ibid.*, 2,161,748 (June 6, 1939).
(30) Sermattei, J. P., U. S. Patent 2,337,939 (Dec. 28, 1943).
(31) Speicher, J. H. (to Hercules Powder Co.), *Ibid.*, 2,319,957 (May 25, 1943).
(32) Traylor, W. S., *Ibid.*, 2,271,724 (Feb. 3, 1942).

Presented before the Division of Paint, Varnish, and Plastics Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Ill.

Oxidation of GR-S and Other Elastomers

JOHN O. COLE AND JAMES E. FIELD
The Goodyear Tire & Rubber Company, Akron, Ohio

The effect of air oxidation at 100° C. on uncured natural rubber and on the following uncured emulsion polymers was studied: polyisoprene, polybutadiene, isoprene-styrene, and butadiene-styrene. The net effect of oxidation of isoprene polymers was chain scission, whereas cross linking predominated with butadiene polymers. Oxygen uptake and antioxidant consumption during aging of GR-S were measured by direct analytical methods. Aging caused a marked decrease in the antioxidant content of the acetone extract. Changes which occur in the infrared absorption spectra of unsaturated polymers during oxidation are reported. The present theories concerning the mechanism of oxidation of unsaturated polymers are reviewed, and the infrared absorption spectra data are interpreted in terms of these theories. A possible mechanism of antioxidant action is suggested.

THE effect of heat aging on the physical properties of an elastomer is generally considered the result of oxidation, which produces both chain scission and cross linking in the polymer. Early in the development of GR-S a marked difference in the aging of GR-S and natural rubber vulcanizates was observed. From the effect of aging on hardness, tensile strength, modulus, and elongation (*11, 17, 18, 21*) it appeared that cross linking occurred more rapidly than chain scission with GR-S, but the reverse was true with natural rubber.

The work reported here was undertaken to provide a better understanding of the differences in aging of GR-S and natural rubber and to introduce new experimental methods for studying the mechanism of oxidation and antioxidant action in elastomers.

EXPERIMENTAL PROCEDURE

The synthetic polymers employed were prepared by emulsion polymerization using hydroquinone as shortstop and phenyl-β-naphthylamine as antioxidant. For determination of infrared absorption spectra, with exception of the sample used in Figure 3, the polymer hydrocarbon was isolated by precipitation of the crude polymer from benzene solution. The hydrocarbon in Figure 3 was isolated by alcohol coagulation of latex containing shortstop but no antioxidant.

Samples were aged in the form of thin sheets about 2–3 mm. thick. An ordinary air oven was used for air aging. For oxygen aging, samples were placed in a vacuum oven, the oven was evacuated, and oxygen was passed in until atmospheric pressure was attained. Vacuum aging was carried out at about 20 mm. pressure in a vacuum oven which had been flushed out with commercial nitrogen. Traces of oxygen were present under these conditions.

Benzene solubility measurements were made by the static method. The oxygen uptake measurements were the difference between the oxygen content of the aged and unaged samples as determined by the method of Unterzaucher (*26*). Determination of phenyl-β-naphthylamine was made by dissolving the acetone extract from a 5-gram sample of GR-S in 60 ml. of glacial acetic acid and titrating with 0.03 *N* sodium nitrite solution. The sulfanilic acid and α-naphthylamine spot test reagents, prepared according to the directions of Feigl (*8*), were used as an external indicator. The end point was taken as the point at which a pink color was produced within a few seconds after adding a drop of the solution to a spot-plate cavity containing one drop of sulfanilic acid reagent and one drop of α-naphthylamine reagent. In some cases the antioxidant was determined by a modification of the Kjeldahl method in which the ammonia was determined colorimetrically. Since 1% antioxidant in GR-S is equal to only 0.064% nitrogen, this modification was necessary to improve the sensitivity of the method.

Infrared absorption spectra were determined with a conventional Littrow type of rock-salt prism spectrometer. Samples were prepared by evaporation of a benzene solution of the polymer on a rock salt plate or in a steel frame floating on a mercury surface. The film thickness of samples prepared on salt plates was adjusted to give approximately 10% transmission of the 1450 cm.$^{-1}$ band. For the samples suspended on a steel frame, a film thickness of approximately 0.1 mm. was maintained by controlling the concentration and volume of the solution. To prevent undue oxidation the polymer film was dried under nitrogen. Since the film thickness of the samples in each series was kept approximately constant, a fair estimate of the intensity of absorption of a particular band can be made relative to a corresponding one of another sample without transforming the absorption curves into two terms of per cent transmission. The approximate slit widths employed are given in the following table:

Spectral Region, Cm.$^{-1}$	Slit Width, Mm.
800– 900	0.25
900–1200	0.17
1200–1900	0.12
1900–3700	0.06

EFFECT OF OXIDATION ON POLYMERS

Factors involved in the aging of GR-S and natural rubber would seem to be differences in the chemical reactivity of the polyisoprene and polybutadiene systems, —$CH_2C(CH_3)$=$CHCH_2$— and —CH_2CH=$CHCH_2$—, and variations in polymer structure, such as *cis-trans* isomerism, relative amount of 1,2 and 1,4 polymerization, and degree of branching. To determine the relative importance of chemical reactivity and polymer structure, a comparison was made of the effect of oxidation on uncured natural rubber and the following uncured emulsion polymers: polyisoprene, polybutadiene, isoprene-styrene in the ratio 75 to 25 and butadiene-styrene in the ratio 75 to 25. Table I shows the effect of heating these polymers at 125° C. in an atmosphere of low oxygen content, in air, and in oxygen. Changes in benzene solubility indicate changes in the degree of cross linking. For polymers which are completely soluble in benzene or become soluble on oxidation, the decrease in intrinsic viscosity indicates approximately the degree of chain scission.

TABLE I. EFFECT OF HEATING AT 125° C. IN VACUUM, AIR, AND OXYGEN ON BENZENE SOLUBILITY AND INTRINSIC VISCOSITY OF POLYMERS DERIVED FROM ISOPRENE AND BUTADIENE

	% Benzene Solubility				Intrinsic Viscosity			
		30-hr. heating at 125° C. in:				30-hr. heating at 125° C. in:		
Polymer[a]	No heating	Vacuum	Air	Oxygen	No heating	Vacuum	Air	Oxygen
Natural crepe rubber	98	80	98	97	5.62	2.42	0.47	0.47
Polyisoprene	78	74	98	96	1.06	0.93	0.28	0.32
Isoprene-styrene, 75/25	71	69	90	95	1.33	0.83	0.47	0.33
Polybutadiene	85	39	39	53	..	..	..	..
Butadiene-styrene, 75/25	79	48	44	53	..	..	..	..

[a] Synthetic polymers contained 3% phenyl-β-naphthylamine.

On heating in a low oxygen atmosphere the butadiene polymers exhibited a somewhat greater tendency to undergo cross linking than did isoprene polymers. When heated in air or oxygen, all isoprene polymers underwent severe degradation or chain scission, as indicated by breakdown of gel and the low viscosity values. In marked contrast, however, the butadiene polymers exhibited a definite tendency to undergo further polymerization or cross linking. Synthetic emulsion polymers are known to differ from natural rubber in structural features (*9*, *14*, *25*). Since the net effect of oxidation on natural and emulsion isoprene polymers was chain scission, whereas cross linking predominated with butadiene polymers, variations in polymer structure do not seem to explain the difference observed in the aging of GR-S and natural rubber. A difference in chemical reactivity of the polyisoprene and polybutadiene systems seems to be indicated. The observation that hydrochlorination and cyclization of isoprene polymers proceed much more readily than with butadiene polymers probably indicates that the presence of a methyl group increases the reactivity of the double bond. Farmer (*4*) suggested that the presence of an alkyl group on an ethylenic carbon atom has an activating effect on α-methylenic hydrogen atoms.

TABLE II. EFFECT OF AIR OXIDATION AT 100° C. ON GR-S CONTAINING 1.5% PHENYL-β-NAPHTHYLAMINE ANTIOXIDANT

	Hr. at 100° C.	% Benzene Solubility	Intrinsic Viscosity
Sample 1	0	100	1.70
	2	100	1.58
	4	100	1.55
	6	100	1.46
	10	100	1.34
	20	100	1.17
	30	98	1.10
	60	75	1.02
	90	60	0.82
Sample 2	0	79	1.81
	4	73	1.59
	6	91	1.74
	10	100	1.50
	20	100	1.20
	30	98	1.25
	50	74	0.57
	90	52	0.44
Sample 3	0	55	1.21
	4	65	1.06
	6	72	1.07
	10	51	0.75
	20	55	0.66
	30	45	0.67
	50	41	0.68
	90	35	0.57

After the results given were obtained, a more detailed study was made of the effect of oxidation on the benzene solubility and intrinsic viscosity of uncured GR-S containing antioxidant. The results shown in Table II for the first sample were typical of many GR-S samples studied. The polymer remained completely soluble in benzene at the end of 20 hours of heating at 100° C. During this period the marked decrease observed in intrinsic viscosity indicated that chain scission was occurring more rapidly than cross linking during the early stages of oxidation. Heating for periods greater than 30 hours resulted in a gradual decrease in benzene solubility. Thus, during the later stages of oxidation cross linking occurred more rapidly than chain scission, with the formation of a gel fraction. The magnitude of the viscosity decrease and the time required for the appearance of gel varied somewhat for different GR-S samples, but no wide variations were observed.

Oxidation of GR-S samples containing gel resulted first in an increase in benzene solubility to a maximum solubility and then in a gradual decrease (Table II). Sample 2 became completely soluble after 10 hours of heating. Heating for more than 30 hours resulted in the appearance of a gel fraction. Sample 3 reached a maximum solubility of 72% after 6 hours of heating, then gradually decreased in solubility. These observations are interpreted as a further indication that, during the early stages of oxidation, chain scission occurs more rapidly than cross linking. However, during the later stages cross linking becomes the more rapid reaction. The difference observed between samples 2 and 3 was attributed to a difference in degree of cross linking of the gel fractions.

TABLE III. EFFECT OF AIR OXIDATION AT 100° C. ON GR-S HYDROCARBON

Hr. at 100° C.	% Benzene Solubility	Intrinsic Viscosity	Swelling Index[a]
0	100	1.77	...
2	99	1.69	...
3	93	1.43	120
4	81	0.91	80
6	68	0.99	54
10	62	0.94	40
30	57	0.85	33
90	54	0.86	33

[a] Grams benzene absorbed per gram insoluble polymer.

The effect of oxidation on the GR-S hydrocarbon, obtained by extraction of the nonhydrocarbon constituents, is shown in Table III. The rapid decrease in benzene solubility indicated the formation of a highly cross-linked polymer, but it was not possible to determine from the viscosity change whether a significant degree of chain scission had occurred. The sharp drop in viscosity at the gel point probably indicated that the fraction of high molecular weight had been removed from the soluble phase. Swelling index measurements, expressed as grams of benzene absorbed per gram of insoluble polymer, are a measure of the degree of cross linking in the gel fraction. The gradual decrease observed in swelling index was the result of further cross linkage in the gel fraction.

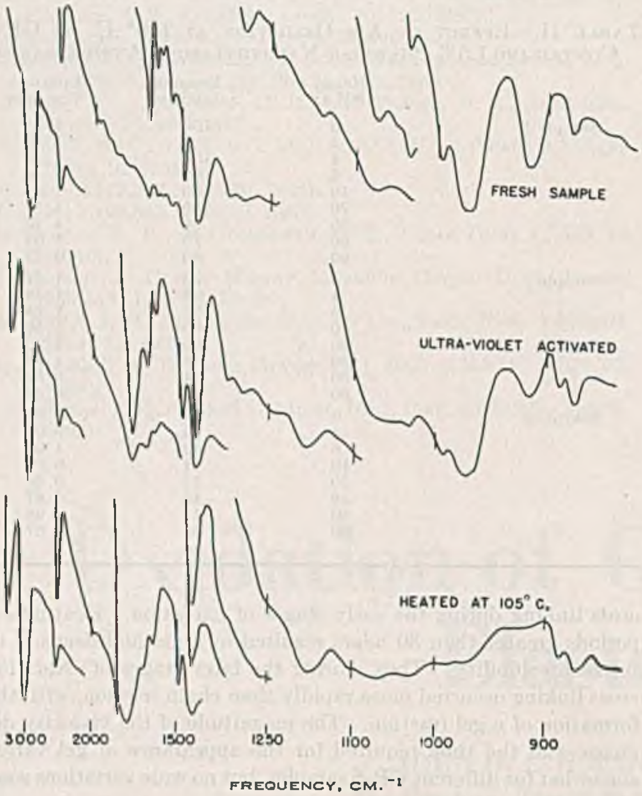


Figure 1. GR-S without Antioxidant

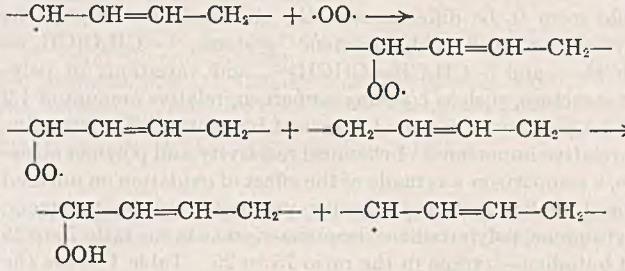
It is of interest to determine the amount of combined oxygen required to bring about changes in the solubility and viscosity of the polymer. Table IV shows the changes in oxygen content, benzene solubility, intrinsic viscosity, and antioxidant content. The values recorded for oxygen uptake are probably accurate to about ±0.1%. An oxygen uptake of less than 0.5% was sufficient to cause significant changes in the solubility and viscosity of the polymer. Oxidation caused a marked decrease in the antioxidant content. It appears that the amount of gel formed is roughly proportional to the amount of combined oxygen. This may be related to the observation of Shelton and Winn (*19*) that the increase in 200% stress of GR-S during oxidation is roughly proportional to the amount of combined oxygen. Table V gives the oxygen content for GR-S and polybutadiene samples after aging at room temperature for long periods. These were highly purified samples of the polymer hydrocarbon and contained no antioxidant. The original samples were entirely colorless; the oxidized samples were colored yellow to yellow-orange.

These observations on the effect of oxidation on uncured GR-S indicate that both chain scission and cross linking occur as the result of oxidation of the polymer. Except during the early stages of oxidation, the rate of cross linking is more rapid than chain scission. Since aging properties are fundamentally related to the chemistry of the polymer hydrocarbon, the same reactions should occur during oxidation of vulcanized polymers, though probably at a different rate. In general this prediction is confirmed by the effect of oxidation on GR-S vulcanizates (*18, 23*). Although experimental studies of the effect of aging on physical properties are useful for practical purposes, they give little information as to the mechanism oxidation.

HYDROPEROXIDE THEORY OF AUTOXIDATION

The studies of Farmer and co-workers (*4, 5, 6*) on the oxidation of simple olefins, such as cyclohexene, and more complex olefins, such as methyl oleate and natural rubber, indicated that the course of oxidation of unconjugated olefins may be represented as follows: Peroxidation takes place exclusively or almost exclusively at the methylene group adjacent to the double bond, with the formation of a hydroperoxide. Although the reaction probably has a free radical chain mechanism, the nature of the initiating step is not clear (*2, 4, 7*):

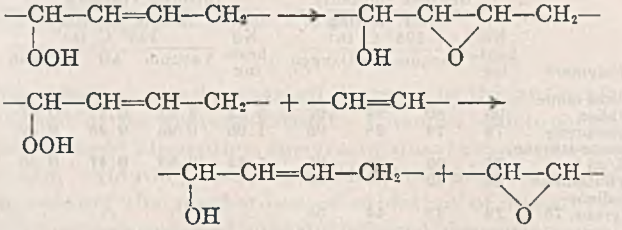
$$\mathrm{-CH_2-CH{=}CH-CH_2- + \cdot OO\cdot\ (or\ R\cdot) \longrightarrow -CH-CH{=}CH-CH_2- + \cdot OOH\ (or\ RH)} \qquad (1)$$



$$\mathrm{-\dot{C}H-CH{=}CH-CH_2- + \cdot OO\cdot \longrightarrow -\underset{OO\cdot}{CH}-CH{=}CH-CH_2-} \qquad (2)$$

$$\mathrm{-\underset{OO\cdot}{CH}-CH{=}CH-CH_2- + -CH_2-CH{=}CH-CH_2- \longrightarrow -\underset{OOH}{CH}-CH{=}CH-CH_2- + -\dot{C}H-CH{=}CH-CH_2-} \qquad (3)$$

Termination of the reaction chain occurs by combination of the radicals involved in the propagation step. Thermal decomposition of the hydroperoxide accelerates the reaction, probably by formation of a free radical capable of starting an oxidation chain. Peroxide decomposition occurs side by side with peroxide formation. This complex decomposition is not well understood, but, in general, the hydroperoxide group reverts to hydroxyl. The active oxygen reacts mainly with double bonds to form epoxides. There is some evidence that peroxide decomposition may also lead to the formation of carbonyl groups.



$$\mathrm{-\underset{OOH}{CH}-CH{=}CH-CH_2- \longrightarrow -\underset{OH}{CH}-\underset{\diagdown O \diagup}{CH-CH}-CH_2-} \qquad (4)$$

$$\mathrm{-\underset{OOH}{CH}-CH{=}CH-CH_2- + -CH{=}CH- \longrightarrow -\underset{OH}{CH}-CH{=}CH-CH_2- + -\underset{\diagdown O \diagup}{CH-CH}-} \qquad (5)$$

In view of the important effect of chain scission and cross linking on the physical properties of a polymer, the course by which these reactions occur is of particular interest. The attempts which were made by Farmer and his co-workers (*4, 7*) and also by Taylor and Tobolsky (*22*) to explain these reactions were directed along two somewhat different lines of thought. The first theory assumes that both chain scission and cross linking occur through reactions of the peroxide or its decomposition products. The second theory considers that the role of oxygen is to form free radicals, which may disproportionate to cause chain scission or attack the double bond to bring about cross linking.

Application of the hydroperoxide theory of oxidation to syn-

TABLE IV. OXYGEN UPTAKE DURING OXIDATION OF GR-S CONTAINING PHENYL-β-NAPHTHYLAMINE ANTIOXIDANT (PBNA)

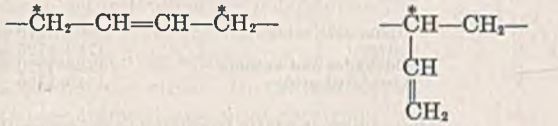
Hr. at 100° C.	Increase in % Oxygen	% Benzene Solubility	Intrinsic Viscosity	% PBNA Found
0	0	100	1.76	3.98
24	0.1	100	0.96	2.65
48	0.5	88	0.99	1.66
72	0.7	66	0.66	1.26
96	1.0	50	..	..
114	1.3	38	..	..

TABLE V. OXYGEN UPTAKE DURING AIR OXIDATION OF POLYMER HYDROCARBON AT ROOM TEMPERATURE IN ABSENCE OF ANTIOXIDANT

Sample	Aging Time, Months	% Oxygen Found	Color of Aged Sample
GR-S 1	5	9.8	Yellow
GR-S 2	5	11.7	Yellow
Polybutadiene 1	27	15.0	Yellow-orange
Polybutadiene 2	27	15.8	Yellow-orange

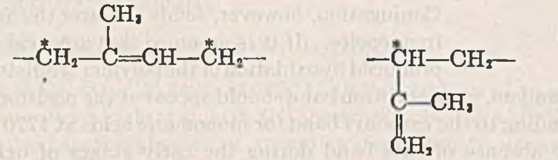
thetic elastomers is complicated by the fact that polymerization of dienes usually occurs by both 1,2 and 1,4 addition to the conjugate system. In the case of isoprene 3,4 addition also occurs (*9*). There is evidence that the C—H bond energy decreases in the order primary > secondary > tertiary. Further, the bond energy decreases when the hydrogen atom is attached to a carbon atom adjacent to the double bond (*20*). On this basis oxidation of synthetic elastomers derived from butadiene and isoprene will occur at points in the polymer chains at which secondary or tertiary hydrogen atoms are adjacent to a double bond. Such points are indicated by an asterisk:

BUTADIENE POLYMERS



$$—\overset{*}{C}H_2—CH{=}CH—\overset{*}{C}H_2— \qquad —\overset{*}{C}H—CH_2— \ (\text{with } —CH{=}CH_2 \text{ on } \overset{*}{C}H)$$

ISOPRENE POLYMERS



$$—\overset{*}{C}H_2—C(CH_3){=}CH—\overset{*}{C}H_2— \qquad —\overset{*}{C}H(C(CH_3){=}CH_2)—CH_2—$$

Accordingly, in synthetic polymers derived from butadiene and isoprene, both secondary and tertiary hydroperoxides may be formed on oxidation. Milas and Surgenor (*16*) recently presented evidence that thermal decomposition of *tert*-butyl hydroperoxide occurs in the following manner:

$$(CH_3)_3COOH \xrightarrow{95-100° \text{ C.}} (CH_3)_3COH + O \qquad (6)$$

$$(CH_3)_3COOH \xrightarrow{250° \text{ C.}} (CH_3)_3CO\cdot + \cdot OH \qquad (7)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot$$

$$CH_3\cdot + \cdot OH \longrightarrow CH_3OH$$

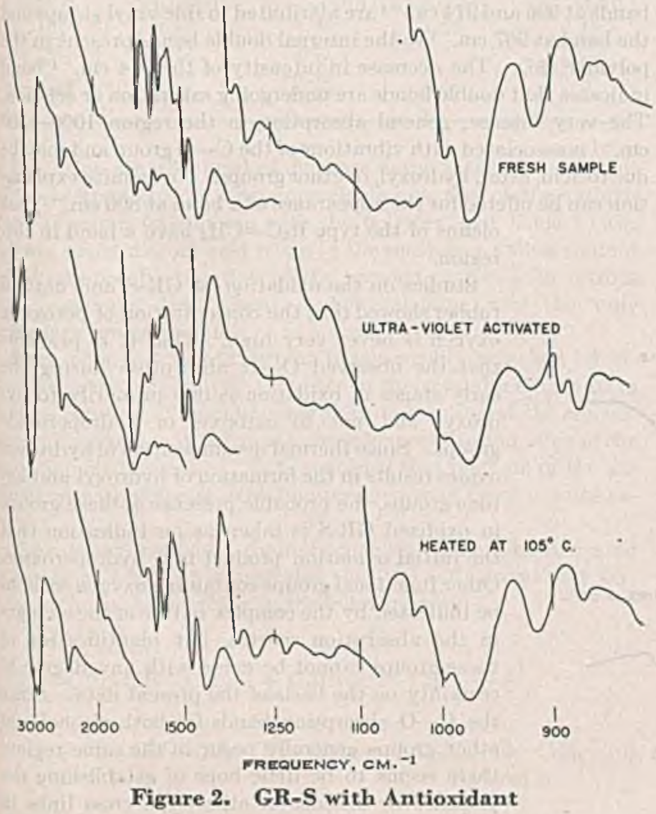


Figure 2. GR-S with Antioxidant

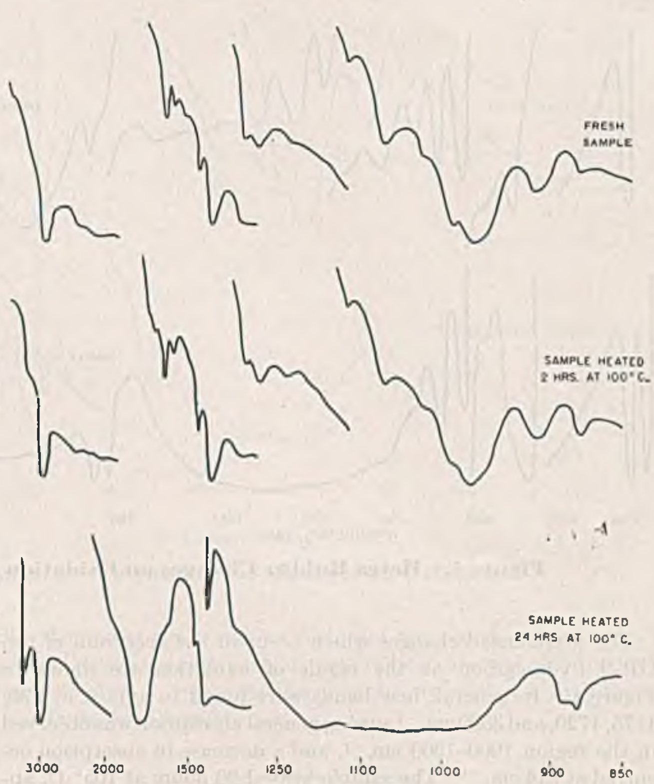
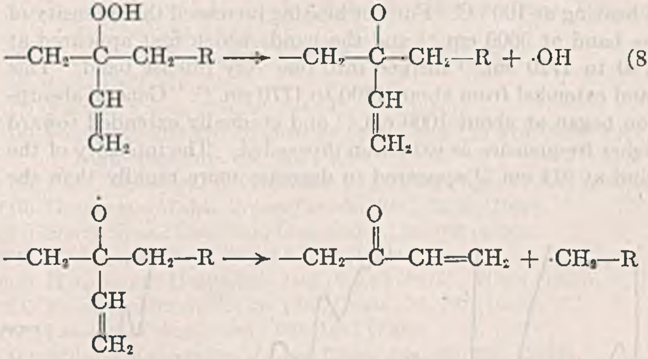


Figure 3. GR-S during Early Stages of Oxidation

The latter mode of decomposition seems to be a general reaction of tertiary hydroperoxides. George and Walsh (*10*) showed that the products obtained by oxidation of cyclopentane and cyclohexane derivatives at 80–100° C. may be readily explained on the basis of the formation and decomposition of tertiary hydroperoxides. A similar decomposition of tertiary polymer peroxides may lead to chain scission and the formation of a ketone group:



$$—CH_2—C(OOH)(CH{=}CH_2)—CH_2—R \longrightarrow —CH_2—C(\dot{O})(CH{=}CH_2)—CH_2—R + \cdot OH \qquad (8)$$

$$—CH_2—C(\dot{O})(CH{=}CH_2)—CH_2—R \longrightarrow —CH_2—C({=}O)—CH{=}CH_2 + \cdot CH_2—R$$

ABSORPTION SPECTRA OF OXIDIZED POLYMERS

Experimental study of the mechanism of oxidation of GR-S and other butadiene polymers is made difficult by the fact that these polymers become insoluble as the result of oxidation. Since infrared absorption spectra can be readily measured on a thin polymer film, this method is of particular value in such cases.

The infrared absorption spectra curves shown in Figures 1 and 2 were obtained by heating production GR-S and the GR-S hydrocarbon at 105° C. in an air oven and at 40° C. in ultraviolet light (Atlas Fadeometer). These curves are plotted as transmission, measured as a galvanometer deflection, against frequency in wave number. The present infrared data were obtained with the object of studying the oxidation of unsaturated polymers from a qualitative standpoint.

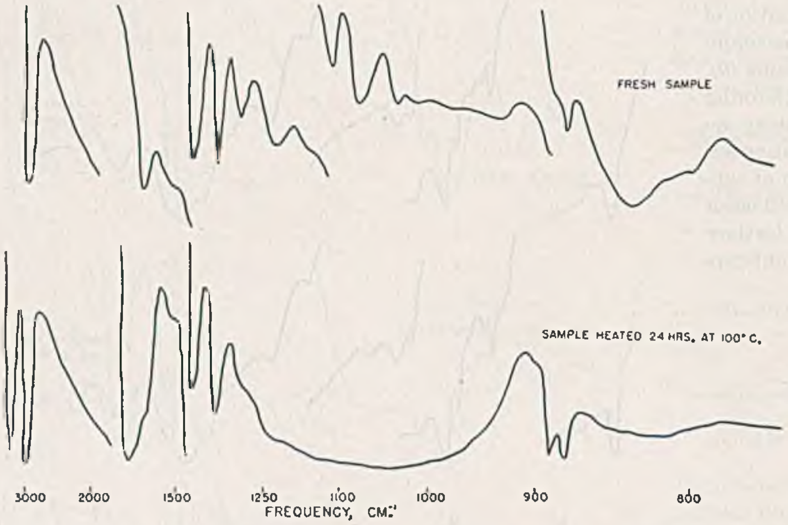


Figure 4. Hevea Rubber Changes on Oxidation

The pronounced changes which occur in the spectrum of the GR-S hydrocarbon as the result of oxidation are shown in Figure 1. In general, new bands were found to appear at 890, 1175, 1720, and 3600 cm.$^{-1}$, strong general absorption was observed in the region 1000–1300 cm.$^{-1}$, and a decrease in absorption occurred at 914 cm.$^{-1}$ The sample heated 20 hours at 105° C. appeared to have undergone a much higher degree of oxidation than the sample heated 48 hours at 40° C. in ultraviolet light.

The changes in the spectrum produced by oxidation of regular production GR-S containing phenyl-β-naphthylamine as antioxidant are shown in Figure 2. Heating for 20 hours at 105° C. caused only slight changes in the spectrum. However, heating for 24 hours at 40° C. in ultraviolet light brought about changes in the spectrum similar to those observed when oxidation was carried out in the absence of antioxidant.

Figure 3 shows the changes which occurred in the spectrum of the GR-S hydrocarbon during the early stages of oxidation. New bands appeared at 890, 1700, 1720, and 3600 cm.$^{-1}$ after 2 hours of heating at 100° C. Further heating increased the intensity of the band at 3600 cm.$^{-1}$ and the bands which first appeared at 1700 to 1720 cm.$^{-1}$ merged into one very intense band. This band extended from about 1700 to 1770 cm.$^{-1}$. General absorption began at about 1000 cm.$^{-1}$ and gradually extended toward higher frequencies as oxidation proceeded. The intensity of the band at 914 cm.$^{-1}$ appeared to decrease more rapidly than the band at 970 cm.$^{-1}$; however, the general absorption occurring in this region was a complicating factor.

DISCUSSION

The band which appears at 3600 cm.$^{-1}$ is associated with vibrations of the O—H group. The intense absorption at 1700–1720 cm.$^{-1}$ is undoubtedly due to the presence of the C=O group, but it is difficult to determine the functional groups which may be involved. The frequency usually associated with the various carbonyl groups (*1*, *3*, *12*, *13*, *15*, *24*) is given as follows:

Monomeric acids	1770 cm.$^{-1}$
Esters	1750–1725 cm.$^{-1}$
Aldehydes and ketones	1725–1690 cm.$^{-1}$
Associated acids	1740–1700 cm.$^{-1}$

These characteristic frequencies are generally valid for the higher members of a homologous series. Conjugation, however, tends to lower the assigned frequencies. If it is assumed that any acid groups produced by oxidation of the polymer are distributed at random, an absorption band should appear at the position corresponding to the carbonyl band for monomeric acids at 1770 cm.$^{-1}$. The absence of this band during the early stages of oxidation would seem to indicate that no appreciable number of carboxyl groups are present. There seems to be some evidence that this band is present in the later stages of oxidation. Although the observed bands at 1720 and 1700 cm.$^{-1}$ are probably due to ketone or ketone and aldehyde groups, it is difficult to determine the significance of this doublet. This doublet may indicate that both aldehyde and ketone groups are present, or that the frequency of part of the carbonyl groups has been shifted by conjugation. The fact that GR-S becomes yellow as the result of oxidation indicates the presence of conjugate carbonyl groups or carbonyl groups conjugated with double bonds. In either case a ketone carbonyl would be involved. Both the shape and the width of the band in the region 1770–1700 cm.$^{-1}$ suggest that several carbonyl groups are present in the later stages of oxidation. The bands at 996 and 914 cm.$^{-1}$ are attributed to side vinyl groups and the band at 967 cm.$^{-1}$ to the internal double bonds present in the polymer (*25*). The decrease in intensity of the 914 cm.$^{-1}$ band indicates that double bonds are undergoing saturation or scission. The very intense, general absorption in the region 1000–1300 cm.$^{-1}$ is associated with vibrations of the C—O group and may be due to acid, ester, hydroxyl, or ether groups. No definite explanation can be offered for the appearance of a band at 890 cm.$^{-1}$, but olefins of the type $R_2C=CH_2$ have a band in this region.

Studies on the oxidation of GR-S and natural rubber showed that the concentration of peroxidic oxygen is never very high. Thus it is probable that the observed O—H absorption during the early stages of oxidation is due primarily to hydroxyl and not to carboxyl or hydroperoxide groups. Since thermal decomposition of hydroperoxides results in the formation of hydroxyl and ketone groups, the probable presence of these groups in oxidized GR-S is taken as an indication that the initial oxidation product is a hydroperoxide. Other functional groups containing oxygen seem to be indicated by the complex nature of the changes in the absorption spectra, but identification of these groups cannot be made with any degree of certainty on the basis of the present data. Since the C—O absorption bands for both alcohol and ether groups generally occur in the same region, there seems to be little hope of establishing the presence or absence of ether-type cross links in

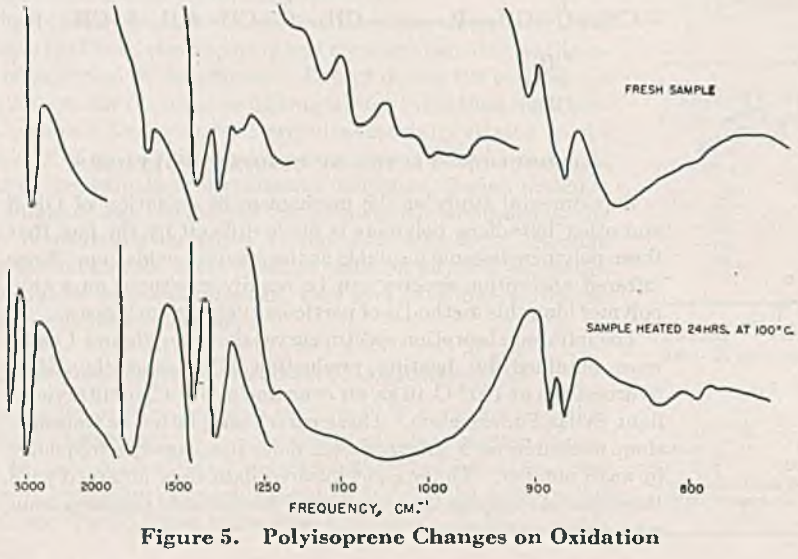


Figure 5. Polyisoprene Changes on Oxidation

oxidized GR-S. As already indicated, chain scission may result from peroxide decomposition, which leads to the formation of aldehyde and ketone groups. Although evidence for the presence of these groups has been presented, there does not appear to be much possibility of establishing the mechanism of chain scission by infrared methods alone.

Figures 4, 5, and 6 show the effect of oxidation on the spectra of the hydrocarbons derived from natural rubber, polyisoprene, and polybutadiene, respectively. The changes brought about by oxidation were similar to those observed with GR-S. In the case of natural rubber and polyisoprene the decrease in intensity of the band at 840 cm.$^{-1}$ indicates saturation or scission of the double bonds in the polymer chain. On the basis of the changes in the infrared absorption spectrum, the mechanism of oxidation of all the elastomers studied appears to be similar.

MECHANISM OF ANTIOXIDANT ACTION

Aging of GR-S for 20 hours at 105° C. in the presence of an antioxidant caused little change in the spectrum, whereas a similar aging period in the absence of an antioxidant brought about a marked change in the spectrum. In addition, the antioxidant provided much more effective protection against thermal oxidation than for oxidation catalyzed by ultraviolet light. These observations suggest that infrared methods may be of value in fundamental studies in the field of antioxidants.

There seems to be practically no data in the literature on the consumption of antioxidants during accelerated aging. Table VI shows the effect of air oven aging at 100° C. on the phenyl-β-naphthylamine content of GR-S.

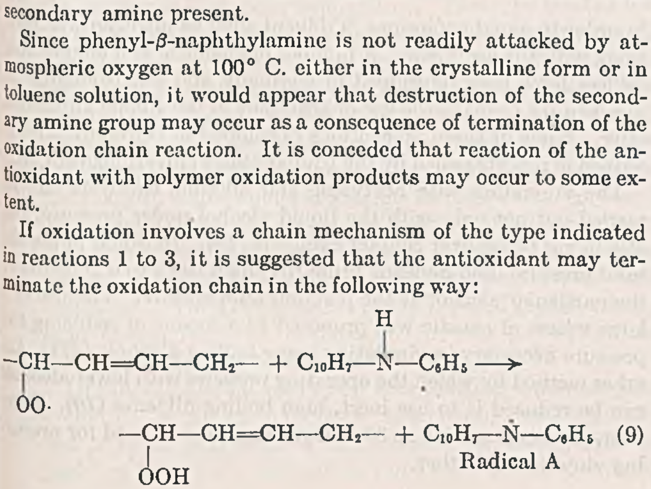
Table VI. Effect of Accelerated Aging on Phenyl-β-Naphthylamine Content of GR-S

Hr. at 100° C.	% PBNA in GR-S (Kjeldahl)	% PBNA in Acetone Extract		% PBNA in Extracted Sample (Kjeldahl)
		Nitrous acid	Kjeldahl	
0	1.43	1.36	1.35	0.15
24	1.42	0.75	..	0.37
48	1.29	0.36	..	0.61
96	1.32	0.12	..	0.88
400	1.45	0.02	0.22	1.01

Oxidation caused a marked decrease in the antioxidant content of the acetone extract. An appreciable quantity of the antioxidant appeared to combine with the polymer. In Table VI the column under nitrous acid refers to the secondary amine content as determined by titration of the acetone extract with nitrous acid, assuming that phenyl-β-naphthylamine was the only secondary amine present.

Since phenyl-β-naphthylamine is not readily attacked by atmospheric oxygen at 100° C. either in the crystalline form or in toluene solution, it would appear that destruction of the secondary amine group may occur as a consequence of termination of the oxidation chain reaction. It is conceded that reaction of the antioxidant with polymer oxidation products may occur to some extent.

If oxidation involves a chain mechanism of the type indicated in reactions 1 to 3, it is suggested that the antioxidant may terminate the oxidation chain in the following way:



$$\underset{\displaystyle OO\cdot}{-\underset{|}{CH}}-CH{=}CH-CH_2- + C_{10}H_7-\overset{\displaystyle H}{\overset{|}{N}}-C_6H_5 \longrightarrow$$

$$-\underset{\displaystyle OOH}{\underset{|}{CH}}-CH{=}CH-CH_2- + \underset{\text{Radical A}}{C_{10}H_7-\dot{N}-C_6H_5} \quad (9)$$

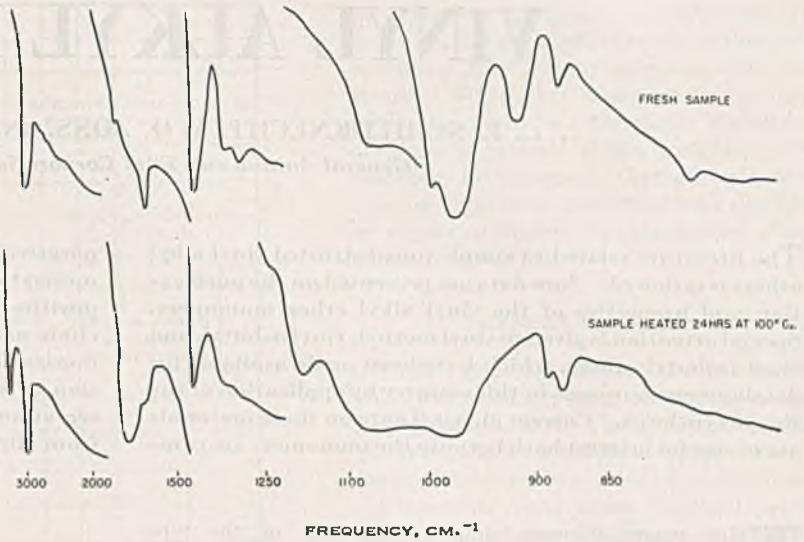


Figure 6. Polybutadiene Changes on Oxidation

Diarylamino radicals such as A do not react with oxygen. Because of resonance stabilization, such radicals are probably too inactive to start a new oxidation chain by removal of a hydrogen atom from the polymer.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Barnes, Liddel, and Williams, Ind. Eng. Chem., Anal. Ed., 15, 667 (1943).
(2) Bolland and Gee, *Trans. Faraday Soc.*, 42, 238 (1946).
(3) Davies and Sutherland, *J. Chem. Phys.*, 6, 763 (1938).
(4) Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Faraday Soc.*, 38, 350 (1942).
(5) Farmer and Sundralingam, *J. Chem. Soc.*, 1942, 121.
(6) *Ibid.*, 1943, 119, 125.
(7) Farmer, *Trans. Faraday Soc.*, 42, 228 (1946).
(8) Feigl, "Qualitative Analysis by Spot Tests", p. 215, New York, Nordeman Pub. Co., Inc., 1939.
(9) Field, Woodford, and Gehman, *J. Applied Phys.*, 17, 388 (1946).
(10) George and Walsh, *Trans. Faraday Soc.*, 42, 95 (1946).
(11) Harrison and Cole, Ind. Eng. Chem., 36, 702 (1944).
(12) Herman, *J. Chem. Phys.*, 8, 257 (1940).
(13) Herman and Hofstadter, *Ibid.*, 6, 537 (1938); 7, 461 (1939).
(14) Kemp and Straitiff, Ind. Eng. Chem., 36, 707 (1945).
(15) Lecomte, *Compd. rend.*, 180, 1481 (1925).
(16) Milas and Surgenor, *J. Am. Chem. Soc.*, 68, 205 (1946).
(17) Scott, *Trans. Inst. Rubber Ind.*, 21, 78 (1945).
(18) Shelton and Winn, Ind. Eng. Chem., 36, 728 (1944).
(19) *Ibid.*, 38, 72 (1946).
(20) Smith and Taylor, *J. Chem. Phys.*, 7, 390 (1939); 8, 543 (1940).
(21) Sturgis, Baum, and Vincent, Ind. Eng. Chem. 36, 348 (1944).
(22) Taylor and Tobolsky, *J. Am. Chem. Soc.*, 67, 2064 (1945).
(23) Tobolsky and Andrews, *J. Chem. Phys.*, 13, 19 (1945).
(24) Thompson and Tortington, *J. Chem. Soc.*, 1945, 640.
(25) Thompson and Tortington, *Trans. Faraday Soc.*, 41, 252 (1945).
(26) Unterzaucher, *Ber.*, 73B, 391 (1940).

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VINYL ALKYL ETHERS

C. E. SCHILDKNECHT, A. O. ZOSS, AND CLYDE McKINLEY

General Aniline and Film Corporation, Easton, Pa.

The literature related to simple unsubstituted vinyl alkyl ethers is reviewed. New data are presented on the purification and properties of the vinyl alkyl ether monomers. Special attention is given to vinyl methyl, vinyl *n*-butyl, and vinyl isobutyl ethers, which have been made available for development purposes in this country by application of the Reppe synthesis. Correct physical data on these materials are of special interest both because the monomers are comparatively unstable and because their behavior in polymerization is greatly influenced by certain types of impurities. Chemical reactions of the vinyl alkyl ethers include addition to the double bond, hydrolysis, and polymerization. Some preliminary work on the polymerization of vinyl alkyl ethers is described together with observations on several commercial polyvinyl alkyl ethers from abroad.

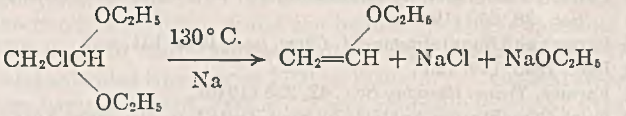
THIS paper discusses simple compounds of the type $CH_2{=}CHOR$, where R is an alkyl group free from unsaturation and both the vinyl and R groups are free from halogen or other substitution. Vinyl methyl ether, vinyl *n*-butyl ether, and vinyl isobutyl ether are the members of the series which received most attention and whose polymers are discussed.

The new data presented from this laboratory comprise the major part of the material under the headings Purification, Physical Properties, and Polymerization, as well as Properties and Stabilization of the Polymers. A large part of the information on the synthesis of vinyl alkyl ethers and their chemical reactions is taken from the literature. All data not otherwise designated are from these laboratories.

The authors examined much of the published work critically in the laboratory, including that of Reppe in Germany and Shostakovskiĭ in Russia. Some discrepancies with their work are noted.

SYNTHESIS

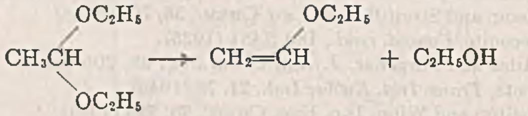
In 1878 Wislicenus (*63*) prepared vinyl ethyl ether by heating chloroacetal with sodium:



$$CH_2Cl\overset{OC_2H_5}{\underset{OC_2H_5}{CH}} \xrightarrow[Na]{130^\circ C.} CH_2{=}\overset{OC_2H_5}{CH} + NaCl + NaOC_2H_5 \quad (1)$$

It was established that the boiling point and specific gravity are higher than those of diethyl ether.

Vinyl ethyl ether was prepared by Claisen by the combined action of phosphorus pentoxide and quinoline on acetal (*7*):



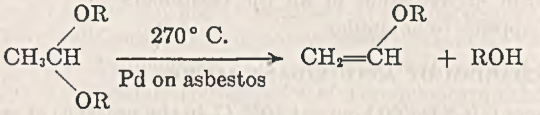
$$CH_3\overset{OC_2H_5}{\underset{OC_2H_5}{CH}} \longrightarrow CH_2{=}\overset{OC_2H_5}{CH} + C_2H_5OH \quad (2)$$

Chalmers (*5*) was unable to dehydrate ether alcohols such as 2-butoxyethanol directly but treated the bromoether with alkali to obtain vinyl *n*-butyl ether:

$$CH_2OHCH_2OC_4H_9 \xrightarrow{PBr_3} CH_2BrCH_2OC_4H_9 \quad (3)$$

$$CH_2BrCH_2OC_4H_9 + NaOH \longrightarrow CH_2{=}CHOC_4H_9 + NaBr + HOH \quad (4)$$

Vinyl alkyl ethers can be prepared by passing the vapors of acetals over hot contact catalysts such as porous clays, or silver or palladium deposited on asbestos (*2, 57*):



$$CH_3\overset{OR}{\underset{OR}{CH}} \xrightarrow[\text{Pd on asbestos}]{270^\circ C.} CH_2{=}\overset{OR}{CH} + ROH \quad (5)$$

Vinyl chloride can be used as a vinylating agent, but, under the conditions illustrated in Equation 6, the reaction is slow—about 12 hours are required for an 85% yield. An excess of the alcohol can be used as solvent for the liquid phase reaction in an autoclave (*38*):

$$CH_2{=}CHCl + NaOC_2H_5 \xrightarrow{100^\circ C.} CH_2{=}CHOC_2H_5 + NaCl \quad (6)$$

A German patent of 1918 (*37*) disclosed the reaction of acetylene with cold, concentrated sulfuric acid to obtain vinyl sulfuric acid, which gave vinyl ethyl ether on treatment with ethanol. Vinyl ethyl ether was also said to be obtained by reaction of absolute alcohol with acetylene at 80° C. using mercuric phosphate catalyst dispersed in ligroin (*8*). However, the action of acetylene upon alcohols in the presence of mercury salts or acidic catalysts gives primarily acetals, and good yields of vinyl alkyl ethers are not obtained.

In 1930 Reppe (*39*) applied for patents on the use of acetylene at relatively high pressures to prepare vinyl alkyl ethers directly from alcohols using alkaline catalysts:

$$\underset{\text{Diluted}}{CH{\equiv}CH} + ROH \xrightarrow[NaOR]{150^\circ C.} CH_2{=}CHOR \quad (7)$$

In order to avoid explosions, a diluent such as nitrogen was used along with the acetylene. A number of chemical and engineering devices have been developed in Germany and independently in this country to make the use of acetylene in the Reppe vinylation safer. Some of these precautions developed in Germany are described in reports issued by the United States Government (*3, 9*).

The vinylation with acetylene and alkaline catalysts can be carried out not only with the liquid alcohol under pressure, but also in gas phase over contact catalysts (*48*). In liquid phase the total pressure used depends primarily upon the vapor pressure of the particular alcohol at the reaction temperature. The use of a large excess of caustic was proposed as a means of reducing the pressure necessary in vinylating lower boiling alcohols (*47*). Another method by which the operating pressure with lower alcohols can be reduced is to use inert, high boiling diluents (*19*). However, pressures as high as 30 atmospheres may be used for preparing vinyl methyl ether.

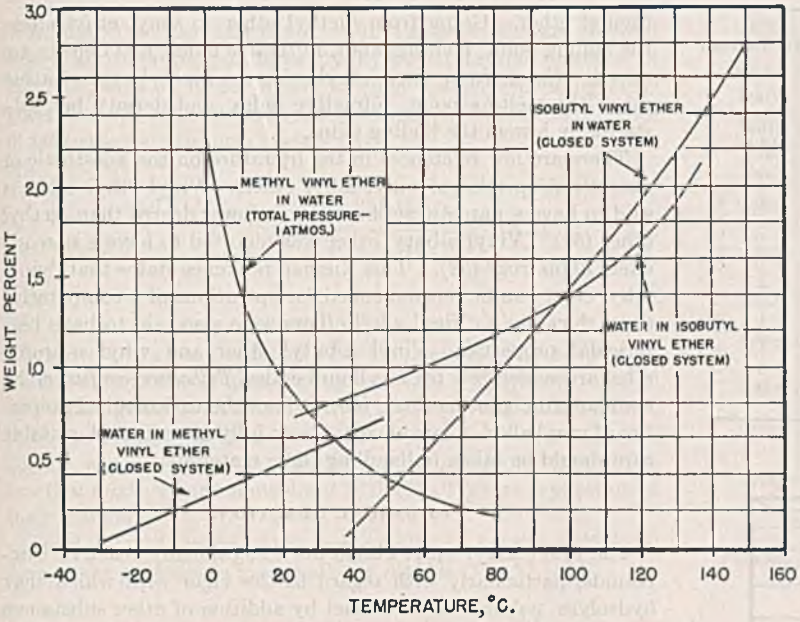


Figure 1. Mutual Solubilities of Vinyl Ethers and Water

Both primary and secondary alcohols can be vinylated readily by the Reppe process. Vinylation of tertiary alcohols usually proceeds more slowly. Varying amounts of the acetal are obtained as a side product, depending upon the conditions.

PURIFICATION

Vinyl alkyl ether monomers should normally be stored containing an alkaline stabilizing agent, such as potassium hydroxide or triethanolamine, in order to minimize or prevent such chemical changes as hydrolysis in the presence of water or polymerization from the action of acidic contaminating materials. Stabilized vinyl alkyl ethers can be stored for a year or more at room temperature. When required in a substantially pure form free of stabilizer, portions should be washed and distilled. When purified monomers are kept in refrigeration, precautions should be taken to prevent contact with water.

In order to purify vinyl n-butyl ether or vinyl isobutyl ether, which contain free alcohol and stabilizing alkali, the ether is washed several times with an equal volume of water, or until there is essentially no further change in the volume of the ether. During washing at room temperature the pH of the aqueous phase preferably should not fall below 8. The washed material is dried by a neutral or alkaline drying agent. For example, the liquid monomer may be dried by standing over solid potassium hydroxide for 24 hours at room temperature. It can be treated further for the removal of traces of alcohol and other impurities by standing over sodium wire at room temperature or by heating with metallic sodium under reflux. Finally, the vinyl alkyl ether is distilled from sodium through a glass column packed with glass helices and having an efficiency of ten to twenty plates.

Vinyl methyl ether is conveniently purified by first scrubbing the gas with water rendered alkaline to prevent hydrolysis. The gas or liquid is then thoroughly dried by a neutral or alkaline drying agent. The liquid can be treated with solid potassium hydroxide or sodium, as indicated for the vinyl butyl ethers, before it is distilled. Vinyl methyl ether can be distilled at pressures higher than atmospheric—for example, 60 pounds per square inch—without loss by polymerization.

During distillation water and acid-reacting materials must be excluded. Small amounts of calcium chloride from drying tubes and traces of acid-reacting substances from certain ceramic still packings have been sufficient in some cases to cause polymerization during distillation. Antioxidant-type stabilizers are not effective in preventing polymerization catalyzed by inorganic acidic substances. Vinyl alkyl ethers up to the vinyl butyl ethers can be satisfactorily distilled at atmospheric pressure if the precautions just described are observed. German methods of treating vinyl ether monomers were described in reports published by the United States Government (*9*, *11*).

PHYSICAL PROPERTIES

Table I gives physical properties of purified vinyl methyl ether, vinyl n-butyl ether, and vinyl isobutyl ether. Vinyl methyl ether is a gas at normal temperature and pressure but is readily condensed to a colorless mobile liquid. All the other vinyl ethers discussed in this paper are colorless liquids under ordinary conditions.

Boiling points attributed to vinyl methyl ether in the literature and in German reports (7–14° C.) are not in agreement with the value reported here. Reppe is quoted in a recent report (*60*) as giving the boiling point of vinyl methyl ether at 9° C. Russian workers reported 9° to 10° C. (*15*). The boiling range of purified vinyl methyl ether was found in this laboratory to be between 5° and 6° C. under the best conditions of distillation. The vapor pressure of vinyl methyl (Figure 2) is 760 mm. at a temperature just above 5° C.

Melting points of the three vinyl alkyl ethers have not been previously reported. Melting points were determined under dry nitrogen according to a procedure based on the work of Glasgow, Streiff, and Rossini (*17*). A copper-constantan thermocouple was used together with a Leeds & Northrup potentiometer No. 8662.

Table I. Physical Properties of Three Vinyl Alkyl Ethers of the Type $CH_2{=}CHOR$

Alkyl Group	Methy	Isobutyl	n-Butyl
Molecular weight	58.08	100.16	100.16
Boiling point, ° C.	5.0–6.0	82.9–83.2	93.3–93.8
Melting point, ° C.	−122	−112	−92
Density, d_4^{20}	0.7511	...	...
Density, d_4^{25}	...	0.7644	0.7727
Refractive index, n_D^{-25}	1.3947	...	...
Refractive index, n_D^{25}	...	1.3938	1.3997
Specific heat, cal./gram at 25° C.	...	0.555	0.553
Latent heat, cal./gram	...	74.4 (83° C.)	77.1 (93.5° C.)
Vapor pressure, mm. Hg at 25° C.	1550	77	51
Vapor pressure, lb./sq. in. abs. at 70° F.	28	1.3	0.8
Solubility in water, wt. % at 25° C.	0.82	<0.10	<0.10
Flash point (Cleveland open cup), ° F. (° C.)	−70 (−56)	20 (−7)	30 (−1)

Less than 1% by weight of vinyl methyl ether dissolves in water at 25° C. (although polyvinyl methyl ether dissolves readily in water at this temperature). Less than 0.10% of purified vinyl n-butyl ether or vinyl isobutyl ether dissolves in water at 25° C. In washing crude monomers containing considerable free alcohol, larger losses are observed because of the solubilizing effect of the alcohol on the aqueous phase. Figure 1 shows the solubility of water in vinyl methyl ether and in vinyl isobutyl ether as functions of temperature. Table II shows the miscibility of vinyl alkyl ethers with organic solvents.

Table II. Miscibility of Vinyl Alkyl Ethers with Equal Volumes of Organic Liquids

	Vinyl Methyl Ether, 0° C.	Vinyl Isobutyl Ether, 25° C.	Vinyl *n*-Butyl Ether, 25° C.
Hexane	+	+	+
Petroleum ether (b.p., 90–100° C.)	+	+	+
Mineral oil (Primol)	+	+	+
Benzene	+	+	+
Carbon tetrachloride	+	+	+
Diethyl ether	+	+	+
Ethyl acetate	+	+	+
Acetic acid	+	+	+
Dioxane	+	+	+
2-Ethoxyethanol (Cellosolve)	+	+	+
Ethanol	+	+	+
Methanol	+	+	+
Ethylene glycol	0	0	0
Glycerol	0	0	0

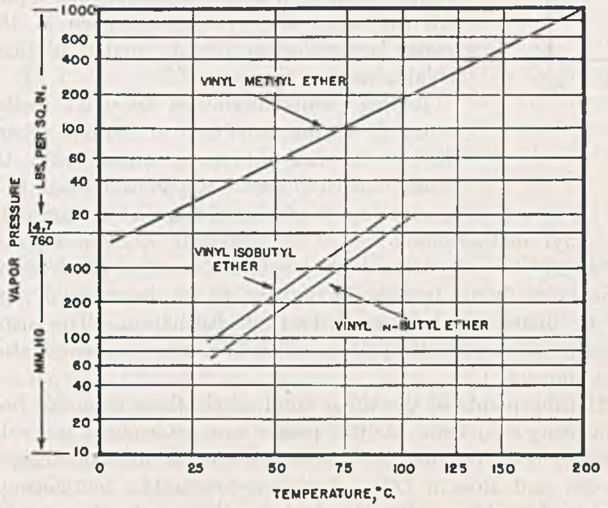


Figure 2. Vapor Pressures of Vinyl Alkyl Ethers as Functions of Temperature

Figure 2 shows the vapor pressures of the three vinyl alkyl ethers as functions of temperature. Vinyl methyl ether was transferred to an evacuated cylinder to which was attached a calibrated pressure gage. The cylinder was heated in a temperature-controlled oil bath. Vapor pressures of vinyl *n*-butyl ether and vinyl isobutyl ether were determined using an isoteniscope immersed in an oil bath (*18*). Figure 3 shows the variation of density with temperature for vinyl methyl ether, vinyl isobutyl ether, and vinyl *n*-butyl ether.

Table III shows boiling points, refractive indices, and densities of a series of vinyl alkyl ethers up to vinyl *n*-decyl ether. Some of these ethers have not yet been prepared as free from impurities as have the methyl, isobutyl, and *n*-butyl vinyl ethers. Among the isomeric vinyl propyl and vinyl butyl ethers, boiling points go down with increasing branching of the alkyl group, and the normal isomers have the highest refractive indices and densities. [Data on four of the vinyl alkyl ethers given in Table III are taken from research reports of the I. G. Farbenindustrie (*28*, *39*) and from the work of Favorskiĭ (*15*).]

It is interesting to compare the vinyl alkyl ethers with the corresponding ethyl alkyl ethers obtained by hydrogenation of the former. Incomplete published data on the ethyl alkyl ethers permit the tentative conclusion that the vinyl alkyl ethers have boiling points 1° to 3° C. higher, as well as densities higher, than the corresponding saturated ethers.

The influence of the double bond upon the physical properties of ethers is shown in Table IV, where our data for vinyl ethyl ether are compared with published values for diethyl ether and divinyl ether. Going from diethyl ether to vinyl ethyl ether, the boiling point, melting point, refractive index, and density are raised. Going from vinyl ethyl ether to divinyl ether further raises the melting point, refractive index, and density but substantially lowers the boiling point.

There are few references in the literature on the anesthetic or narcotic properties of vinyl alkyl ethers. Vinyl ethyl ether is said to have a narcotic action but to a lower degree than diethyl ether (*31*). Vinyl *n*-butyl ether was reported to have a narcotic effect upon frogs (*52*). This Russian reference states that "vinyl ethyl ether can be recommended for operations of a comparative short duration". Vinyl alkyl ethers were also said to have bactericidal properties. Vinyl *n*-butyl ether and vinyl *n*-propyl ether are moderately toxic to flour beetles, *Tribolium confusum*, by standard fumigant methods (*50*). Since the toxicological properties of vinyl alkyl ethers have not been fully investigated, suitable care should be taken in handling these materials.

CHEMICAL REACTIONS

The lower alkyl vinyl ethers are exceptionally reactive compounds, particularly with regard to the vigor with which they hydrolyze, polymerize, and react by addition of other substances to the double bond. In connection with the purification of the vinyl alkyl ethers some features of the chemical reactivity have already been pointed out. It is especially emphasized that, during syntheses with vinyl alkyl ethers, precautions must be observed to prevent polymerization and hydrolysis.

Hydrolysis. In contrast to simple dialkyl ethers, vinyl alkyl ethers hydrolyze rapidly with dilute acid at room temperature. The lower vinyl alkyl ethers are hydrolyzed on heating with distilled water, and Wislicenus observed that vinyl ethyl ether hydrolyzes very slowly even with water at room temperature (*63*):

$$CH_2{=}CHOR + HOH \xrightarrow{pH < 7} CH_3CHO + ROH \qquad (8)$$

The preparation of vinyl methyl ether from acetylene followed by hydrolysis with dilute acid was proposed as an industrial method for making acetaldehyde. The process reached a pilot plant stage of development in Germany (*41*, *46*). Reppe pointed out that vinyl alkyl ethers are similar to acetals with respect to ease of hydrolysis (*40*). A study of the comparative hydrolysis of saturated and unsaturated ethers was made by Skrabal and Skrabal (*58*). Vinyl alkyl ethers are comparatively stable to aqueous alkali.

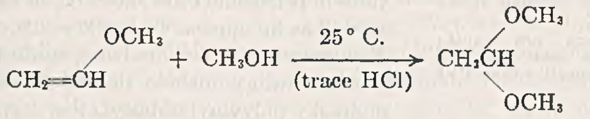
Table III. Series of Vinyl Alkyl Ethers of the Type $CH_2{=}CHOR$

Alkyl Group	B.P., ° C.	n_D^{20}	d_4^{20}
Methyl	5.5	1.3947 (−25° C.)	0.7511
Ethyl	35.5	1.3767	0.7590
n-Propyl	65.5	1.3908	0.7668
Isopropyl	55.5	1.3850	0.7534
n-Butyl	93.8	1.4022	0.7795
Isobutyl	83.2	1.3965	0.7693
sec-Butyl	81	1.3970	0.7715
tert-Butyl	75	1.3922	0.7691
n-Amyl (*39*)	111	....	....
Isoamyl (*15*)	110	1.4070	0.7833
n-Hexyl	143.5	1.4171	0.7966
2-Ethylbutyl	132.2	1.4185	0.8011
n-Octyl	58 (4 mm.)	1.4268	0.8024
2-Ethylhexyl (*28*)	61–63 (11 mm.)	....	....
Nonyl (*28*)	72–75 (12 mm.)	....	....
n-Decyl	101 (10 mm.)	1.4346	0.8123

Table IV. Effect of Unsaturation on Physical Properties of Ethers

	B.P., ° C.	M.P., ° C	n_D^{20}	d_4^{20}
Diethyl ether	34.6 (*59*)	−123β (*21*) −116α (*21*)	1.3526 (*24*)	0.7135 (*32*)
Vinyl ethyl ether	35.5	−115	1.3767	0.7590
Divinyl ether (*13*)	28.5	−101	1.3989	0.773

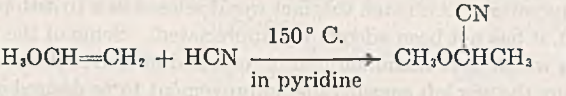
ADDITION TO DOUBLE BOND. Vinyl alkyl ethers are reduced easily at room temperatures by hydrogen in the presence of catalysts such as Raney nickel to yield the corresponding ethyl alkyl ethers. Alcohols add readily to vinyl ethers in the presence of acid catalysts to form acetals (*43*):



$$\overset{\displaystyle OCH_3}{CH_2{=}CH} + CH_3OH \xrightarrow[\text{(trace HCl)}]{25^\circ\text{ C.}} CH_3\underset{\displaystyle OCH_3}{\overset{\displaystyle OCH_3}{CH}} \qquad (9)$$

By this means unsymmetrical acetals can also be obtained. Cholesterol has been reacted with vinyl ethyl ether to give an acetal derivative soluble in ligroin (*42*). Polyvinyl alcohol suspended in chloroform reacts with the lower vinyl alkyl ethers, in the presence of hydrogen chloride as catalyst, to form partial acetals which dissolve in chlorinated hydrocarbons (*30*). The reaction mixtures are neutralized with alkali before separation of the products.

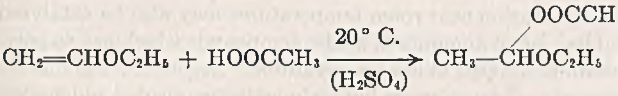
Vinyl alkyl ethers add hydrogen cyanide on heating with pyridine under pressure to give α-alkoxy nitriles (*1*):



$$CH_3OCH{=}CH_2 + HCN \xrightarrow[\text{in pyridine}]{150^\circ\text{ C.}} CH_3O\overset{\displaystyle CN}{C}HCH_3 \qquad (10)$$

The ether acids produced by hydrolysis form salts with heavy metals, some of which are soluble in organic solvents.

Acetic acid adds to the double bond of vinyl ethyl ether at 20° C. in the presence of traces of concentrated sulfuric acid to give an α-ethoxyethylidene ester boiling at 128–130° C. (*42*):



$$CH_2{=}CHOC_2H_5 + HOOCCH_3 \xrightarrow[(H_2SO_4)]{20^\circ\text{ C.}} CH_3{-}\overset{\displaystyle OOCCH_3}{C}HOC_2H_5 \qquad (11)$$

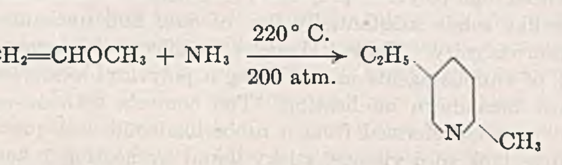
Acid catalysts used in reactions of this type must be nearly anhydrous to prevent hydrolysis of the vinyl ether. In general, simple organic acids which are free of inorganic impurities do not catalyze polymerization. Oleic acid and stearic acids are said to add to vinyl n-butyl ether by heating at 150° C. under pressure for 12 hours without catalyst (*42*).

Vinyl alkyl ethers add hydrogen chloride and hydrogen bromide but special precautions must be observed because of the tendency toward polymerization and because of the relative instability of the products. The use of inert diluents, exclusion of water, and maintenance of a uniform low temperature throughout the system are useful steps in preventing polymerization. Vinyl n-butyl ether at 0° C. can be saturated with gaseous hydrogen chloride to give n-butyl-α-chloroethyl ether distilling at 38° C. at 14 mm. (*42*):

$$CH_2{=}CHOC_4H_9 + HCl \xrightarrow{0^\circ\text{ C.}} CH_3CHClOC_4H_9 \qquad (12)$$

At atmospheric pressure the α-chloroether distills at 120° to 130° C. with decomposition.

MISCELLANEOUS REACTIONS. Krzikalla and Woldan obtained 2-methyl-5-ethyl pyridine (boiling point 62–67° C. at 14 mm.) by reaction of vinyl methyl ether with excess ammonia under pressure. Among the catalysts which they used were cuprous chloride–ammonium chloride mixtures (*29*):



$$CH_2{=}CHOCH_3 + NH_3 \xrightarrow[200\text{ atm.}]{220^\circ\text{ C.}} \qquad (13)$$

By means of nitric acid oxidation nicotinic acid was obtained from the product.

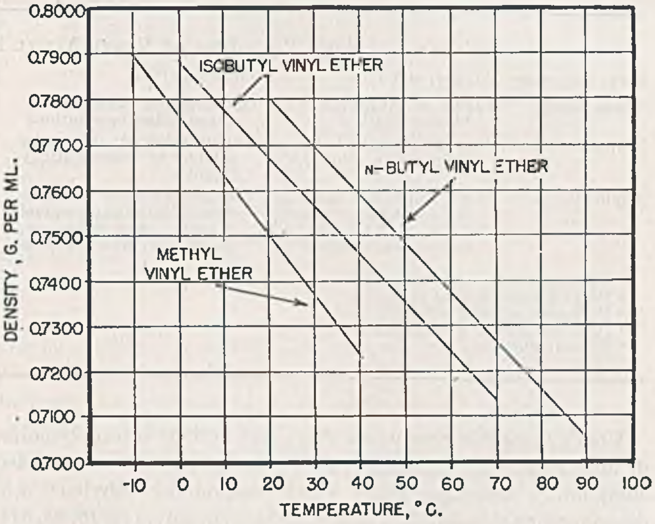


Figure 3. Densities of Vinyl Alkyl Ethers as Functions of Temperature

Pyrolysis of vinyl methyl ether can be made to yield propionaldehyde as a principal product by operating at relatively high space velocities at temperatures near 400° C. with or without a catalyst (*20*):

$$CH_2{=}CHOCH_3 \xrightarrow{400^\circ\text{ C.}} CH_3CH_2CHO \qquad (14)$$

Under different conditions the pyrolysis of vinyl ethyl ether is reported to give ethylene and acetaldehyde along with smaller amounts of other products (*62*). Butadiene was obtained as one of the products of pyrolysis of vinyl ethyl ether (*14, 35*).

ACTION OF HALOGENS. The reaction between chlorine and the lower vinyl alkyl ethers occurs with violence. Wislicenus prepared the dichloride and dibromide from vinyl ethyl ether by reaction at low temperatures with carbon disulfide or chloroform as solvents (*63*). Dibromides from a number of vinyl alkyl ethers were prepared by Shostakovskiĭ and co-workers and some of the physical properties of these compounds were determined (*15, 51, 53*). Carbon tetrachloride or chloroform was used as solvent at a temperature near 0° C. for bromination. The α,β-dibromoethyl alkyl ethers cannot be distilled at atmospheric pressure without decomposition.

Wislicenus (*63*) observed that when 1 part of iodine is added to 200 parts vinyl ethyl ether at room temperature, not only does iodine add to the double bond but polymerization to an iodine-containing nonvolatile product occurs. Chalmers (*6*) obtained a similar result on adding iodine to vinyl n-butyl ether. These results of Wislicenus and Chalmers were confirmed in this laboratory and it was found that iodine has a similar action upon purified vinyl isopropyl ether and vinyl isobutyl ether at room temperature. Purified divinyl ether does not polymerize under these conditions.

POLYMERIZATION

Purified vinyl alkyl ethers polymerize only very slowly under the influence of heat or light, even in the presence of peroxides, to give liquid low polymers. In contrast to their reluctance to polymerize with peroxides, the vinyl alkyl ethers polymerize readily or even with violence under the action of acid-type catalysts. Only at relatively low temperatures and under specially mild conditions are high polymers obtained. In some cases polymers of widely different properties may be formed depending upon the type of catalyst, temperature, diluent, and other factors (*34, 44, 45*). Active catalysts in addition to iodine include concentrated mineral acids, boron fluoride, aluminum chloride, and sulfur dioxide.

TABLE V. SOME POLYMERS OF VINYL ALKYL ETHERS

Polyvinyl ether	Methyl (PVM)	Isobutyl (PVI)	*n*-Butyl (PVN)
Trade names	Igevin M, Appretan WL, Plastomol SW[d]	Oppanol C[a], Igevin I[b, c], Cosal adhesive solutions	Not manufd. abroad
Properties	Viscous liquid or balsamlike; sol. in cold water	Tacky solid[a, b]; nontacky solid[a, b, e]: viscous sticky liquid[c]	Pressure-tacky soft rubber[a, b, e]; viscous sticky liqud[c, e]
Applications	With Buna NN latex in dip coating; plasticizer; textile size; leather treatment	Pressure-sensitive adhesives (Scotch and surgical tapes); shoe adhesives; plasticizer; wax modification	Applications are exptl.; different tack and less temp.-sensitive than PVI

[a] Polymers of highest viscosity.
[b] Polymers of medium viscosity.
[c] Polymers of lower viscosity.
[d] 70% solution in methyl acetate
[e] Experimental.

Under favorable conditions vinyl alkyl ethers interpolymerize or form mixed polymerization products with certain unsaturated compounds, including many vinyl compounds, ethylene α,β-dicarboxylic acids and their esters, and acrylic esters (*4, 16, 25, 61*). For example, by interpolymerization of vinyl chloride with minor amounts of vinyl isobutyl ether, products can be obtained of modified flexibility and solubility in organic solvents. Such an interpolymer was Vinoflex MP 400, manufactured in Germany. Interpolymers of acrylic esters with vinyl alkyl ethers were manufactured by I. G. Farbenindustrie under the name Acronals (*10, 11*). For carrying out interpolymerization, bulk, solution, or emulsion methods can be used, depending upon the particular monomers involved. If water is present in the system employed for interpolymerization, a pH of 8 or higher should be maintained throughout the process to prevent hydrolysis of the vinyl alkyl ether monomer.

Table V describes some polymers of vinyl methyl ether and vinyl isobutyl ether used abroad. These products were formerly called Lutonals, but the name was changed to Igevin followed by a letter indicating the alkyl group of the vinyl ether. Igevin I or Igevin J indicates polyvinyl isobutyl ether. Polyvinyl ethers were used abroad as adhesives and plasticizers and in compositions for impregnating and coating paper and textiles. The Igevin M or polyvinyl methyl ether products made abroad were all of relatively low solution viscosity. As prepared for textile applications, polyvinyl methyl ether was called Appretan WL (*26*).

PROPERTIES OF POLYVINYL ALKYL ETHERS. Table VI shows the solubility of polymers from vinyl methyl ether, vinyl *n*-butyl ether, and vinyl isobutyl ether in a few common solvents. It is noteworthy that polyvinyl methyl ether dissolves both in organic solvents, including benzene, and in cold water. However, the polymer precipitates from water solution on warming to near 35° C. Polyvinyl methyl ether was used abroad for heat sensitization of Buna NN and other synthetic latices in a dip coating process for fabricating gloves (*33*). This heat sensitizing process permits making relatively thick-walled articles quickly in a single step. Certain American synthetic rubber latices are sensitive to precipitation by polyvinyl methyl ether. However, the pH and other factors are critical, and temperatures higher than 35° C. must be used.

Depending upon the conditions of polymerization vinyl isobutyl ether can give (*a*) sticky balsamlike polymers, (*b*) a tacky, rubberlike solid (Oppanol C), or (*c*) a substantially nontacky, harder elastomer. Polyvinyl ether glues (Cosals) used in Europe were principally based on polyvinyl isobutyl ether. They were used as solutions in petroleum ether, acetone, or esters as well as in aqueous dispersions (*26, 27*). New polymers which are being studied by this laboratory include the substantially nontacky polyvinyl isobutyl ether (type *c*) and a rubberlike form of vinyl *n*-butyl ether. These products have not been reported from Germany. Russian workers reported viscous liquid polyvinyl alkyl ethers, but not rubberlike or solid high polymers (*54, 55, 56*). In working with the polyvinyl ethers our laboratory has found it convenient to use the abbreviations PVM, PVI, and PVN (Table V).

TABLE VI. SOLUBILITY OF POLYVINYL ETHERS AT 25° C.

(5% polymer shaken at room temperature with solvent)

	Polyvinyl Methyl Ether	Polyvinyl *n*-Butyl Ether	Polyvinyl Isobutyl Ether
Water	+	0	0
Methanol	+	0	0
Acetone	+	0	0
Methyl ethyl ketone	+	+	+
Ethyl acetate	+	+	+
Benzene	+	+	+
n-Heptane	0	+	+
Chloroform	+	+	+

STABILIZATION OF POLYVINYL ETHERS. High polymers of vinyl alkyl ether require special treatment to render them stable not only to heating and light exposure, but even to aging at room temperature. Although this fact was disclosed in a British patent (*23*), it has not been adequately appreciated. Some of the products which were manufactured abroad and offered in this country before the war left considerable improvement to be desired in this respect. The rubberlike or solid polymers without stabilizers, even after they were treated for the removal of catalyst residues or purified by reprecipitation from solvents, are transformed over a period of weeks or months at room temperature into balsamlike or liquid products. The breakdown is accelerated by heating or in light. It was observed in this laboratory that breakdown or depolymerization near room temperatures may also be catalyzed by adding small amounts of acidic compounds which act as polymerization catalysts at low temperatures. In general, degradation products are not monomers but include the free alcohol, aldehydes, and sirupy low polymers. The breakdown is retarded in atmospheres low in oxygen.

TABLE VII. STABILIZATION OF POLYVINYL *n*-BUTYL ETHER TO HEATING[a]

(Initial polymer viscosity[b] η_{sp}/C = 4.0)

Agent Added (1.0%)	η_{sp}/C after Heating 1 Hr. at 150° C.
Controls (no added agent)	0.64–0.68
Urea	0.70
Phenyl ethyl ether	0.78
Triethanolamine	1.10
Diphenylguanidine	1.14
β-Naphthylamine	3.61
Phenyl-α-naphthylamine	4.02
4,4′-Diaminodiphenylaniline	4.16
Phenyl-β-naphthylamine	4.17
1-Amino-5-naphthol	3.02
Hydroquinone	1.80
β-Naphthol	1.50
2,6-Dichloro-4-*tert*-amylphenol	1.56
4-*tert*-Butylphenol	2.60
4-*tert*-Butyl-*m*-cresol	3.46

[a] Polymers were heated in air in forced draft oven.
[b] Viscosities were determined using solutions of 1.0 gram polymer per 100 ml. benzene at 25° C. and an Ostwald-Fenske viscometer.

The incorporation of 0.5% or more of antioxidant-type stabilizers or of certain sulfur compounds is effective in preventing or retarding the breakdown and changes of properties on aging (*49*). Stabilized high polymers prepared in the summer of 1943 remain rubberlike solids substantially free of odor and unchanged in solution viscosity. Table VII shows the effects of incorporating 1.0% of various agents in stabilizing a polyvinyl *n*-butyl ether against breakdown on heating. The controls without added agent were transformed from a rubberlike solid with pressure-sensitive tack to a viscous, sticky liquid by heating 1 hour at 150° C. Stabilized polymers, which retained their chain length as measured by viscosity in benzene solution, were substantially unchanged in character. Where stabilizers were less effective, intermediate semisolid products resulted.

In addition to the results shown in Table VII, the following were found to be good or moderately effective stabilizers: diphenylamine, *N,N'*-di(β-naphthyl)-*p*-phenylenediamine, 2-naphthalenethiol, thioxane, and mercaptobenzothiazole. Among inorganic compounds which had a stabilizing effect were alkaline and alkaline earth sulfides and polysulfides (*49*). Organic compounds which had little or no effect included ammonium stearate, stearylamine, propylene diamine, cyclohexylamine, quinoline, carbazole, thioglycolic acid, diphenyl sulfone, acetic acid, and diethylene glycol. Certain oxidizing agents, such as benzoyl peroxide, catalyzed the breakdown of the polymer.

High polymers of other vinyl alkyl ethers in addition to polyvinyl *n*-butyl ether were found to require stabilization. Table VIII shows the effects of added stabilizers upon samples exposed to sunlight. The breakdown of the polymer at room temperature in brown bottles was considerable, but light had an additional action retarded by the stabilizers.

TABLE VIII. STABILIZATION OF POLYVINYL *n*-BUTYL ETHER TO SUNLIGHT[a]

Agent Added (1%)	Viscosity η_{sp}/C* Controls in brown bottle	Tests in light
None	1.37	0.41
4-*tert*-Butylmetacresol	3.50	3.00
Phenyl-α-naphthylamine	4.30	4.20

[a] Polymers exposed to diffused north light through window 12 days at room temperature.

* Viscosities were determined using solutions of 1.0 gram polymer per 100 ml. benzene at 25° C. and an Ostwald-Fenske viscometer.

Table IX shows the results of a heat stability test of 1 hour at 160° C. in a forced air draft oven on some vinyl alkyl ether polymers. A sample of Igevin J (60) procured from Sweden, but of German origin, was poorly stabilized, judging from its odor and the loss in volatiles in vacuum. Breakdown of this sirupy polymer had apparently reached equilibrium, since the viscosity was not further decreased on heating. Oppanol C (German vinyl isobutyl ether, high polymer) is not very stable to heating. An old sample of Appretan WL, polyvinyl methyl ether, became largely insoluble in benzene. A smaller amount of change was shown by three experimental polyvinyl ethers containing stabilizing agents.

TABLE IX. HEAT STABILITY TEST

	Viscosity η_{sp}/C Before heating	After heating[a]	Remarks
Igevin J (60)[b]	0.13	0.14	Odor
Oppanol C	4.3	1.7	Softer, more tacky, flowed
PVI (1527–10)	6.5	4.1	Nontacky, still granular
PVN low (G1455)[b]	0.73	0.61	Little change
PVN medium (G1259)	5.5	4.7	Pressure tack retained; still granular
Appretan WL (old sample)	Incompletely sol.		Tack retained

[a] One hour at 160° C. in air.

[b] Viscosities determined at 0.50 gram per 100 ml. benzene; others at 0.10 gram per 100 ml benzene.

In sharp contrast to the vinyl alkyl ether monomers, the polymers are resistant to hydrolysis by dilute acids. Table X summarizes an experiment in which strips of a rubberlike polyvinyl *n*-butyl ether containing an antioxidant-type stabilizer were immersed at 100° C. in water acidified with hydrochloric acid to maintain a pH of 2. That the aqueous phase penetrated into the polymer was shown by a cloudy opacity which developed during contact with the water. After the treated strips were dried, there was no evidence of change in color, tackiness, or rubberlike extensibility. Viscosities of the polymers in benzene solution using two different concentrations and two different viscometer tubes showed essentially no change. Stabilized polyvinyl alkyl ethers are also relatively stable to alkali.

TABLE X. STABILITY OF POLYVINYL *n*-BUTYL ETHER TO DILUTE AQUEOUS HYDROCHLORIC ACID AT pH 2

Time of Treatment at 100° C.	Viscosity η_{sp}/C* 0.10 g./100 ml.	0.20 g./100 ml.
Control untreated	3.8	4.1
10 minutes	3.9	4.2
1.0 hour	3.9	4.1
5.0 hours	3.9	4.1
Flow time of 10 ml. benzene, sec.	79.1 (tube II)	57.3 (tube I)

* Viscosities of benzene solutions determined at 25° C. using Ubbelohde viscometer tubes.

EFFECT OF MILLING POLYVINYL ALKYL ETHERS. The British patent mentioned (*23*) states that antioxidant-type stabilizers are effective in preventing breakdown of polyvinyl ethers by kneading and other mechanical treatment. The present authors found that this is not always true in the case of working polyvinyl alkyl ethers on the rubber mill. As in the case of many rubbers, the milling of polyvinyl ethers containing antioxidants near room temperature has more rapid degrading action than milling at moderately elevated temperatures—for example, 60° C. Whether or not profound changes occur on the rubber mill seems to depend most upon the internal structure of the polymer as related to the method of polymerization. The case of polyvinyl isobutyl ethers of higher viscosity is particularly interesting in this respect.

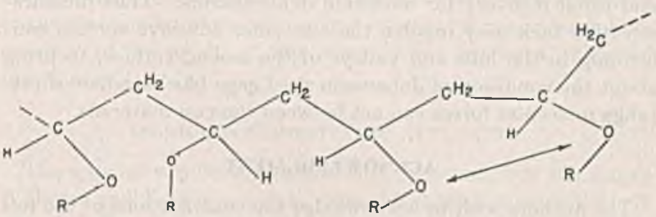


Figure 4. Representation of Polyvinyl Alkyl Ether Chain

With slow polymerization near −80° C., stabilized polyvinyl isobutyl ethers are obtained which are substantially nontacky and quite stable to milling. These polymers can be milled for half an hour at room temperature with comparatively little breakdown in viscosity or increase in tackiness. Oppanol C, vinyl isobutyl ether high polymer submitted from Germany through United States Army Intelligence, was found to behave very differently on milling under the same conditions. Oppanol C breaks down rapidly on the mill, accompanied by a loud crackling noise, to give a soft, tacky polymer of low viscosity. The experimental polyvinyl isobutyl ethers which mill quietly and with little change can have viscosities, as measured in dilute solution in benzene, which lie in the same range as the viscosity of Oppanol C. Oppanol C is reported to have been made by rapid continuous polymerization of vinyl isobutyl ether at about −40° C. using boron fluoride as catalyst (*11*). The method is similar to that described in a United States patent (*36*).

Incorporating a superior heat stabilizer into Oppanol C did not improve its stability to milling. Differences in solubility behavior of the two types of polyvinyl isobutyl ether in paraffin wax, in Nujol, and in *tert*-butanol also indicate that differences exist between the internal structures of the polymer chains in the two cases. The degree of branching or the shapes of the chains (coil or spiral), as determined by the distribution of alkoxy groups on either side of the vinyl chain, may be involved. The latter effect was suggested by Huggins (*22*) as a cause for differences between vinyl polymer chains produced by polymerization at different temperatures. For example, the repulsion or crowding of neighboring large —OR groups (Figure 4), both lying in the plane above the paper, might cause a bending of the polymer chain.

Table XI shows approximate molecular weights of some of the types of polyvinyl ethers under consideration. These data were obtained by the light scattering method by P. P. Debye. The results are tentative in that any possible dissymmetry of the angular scattering was not taken into account. All data were obtained by extrapolation to zero concentration in benzene solution. The procedure and apparatus were described recently (*12*).

TABLE XI. MOLECULAR WEIGHTS OF POLYVINYL ETHERS BY LIGHT SCATTERING

Polymer	Physical Form	η_{sp}/C	Mol. Wt.
Oppanol C	Tacky rubbery solid	4.3	600,000
PVI (302)	Nontacky solid	1.5	219,000
PVN low (G1455)	Viscous liquid	0.5	118,000
PVN medium (G1658)	Soft rubbery solid	5.0	545,000
PVN high (G1256)	Rubbery solid	7.8	810,000

The physical properties of the polyvinyl alkyl ethers are interesting in relation to the mechanism of pressure-sensitive tack and adhesion. Fractionation experiments showed that pressure-sensitive tack cannot be attributed primarily to a low viscosity sticky fraction contained in the polyvinyl ethers. Although further work is in progress, it might be said that vinyl ether polymers possessing "lively" pressure-sensitive tack are those having comparatively low yield value or modulus, together with complete and rapid recovery for moderate deformations. Thus pressure-sensitive tack may involve the elastomer adhesive surface conforming to the hills and valleys of the second surface, to bring about the condition of Johansson steel gage blocks, where short-range molecular forces can act between the two materials.

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LITERATURE CITED

(1) Baur, Karl, U. S. Dept. of Commerce, Office of Pub. Board, Rept. PB-652 (1946).
(2) Baur, Karl (to I. G. Farbenindustrie A.-G.), U. S. Patent 1,931,858 (Oct. 24, 1933).
(3) Boundy, R. H., and Hasche, R. L., U. S. Dept. of Commerce, Office of Pub. Board, Rept. PB-1069 (1946).
(4) Carothers, W. H., Collins, A. M., and Kirby, J. E. (to E. I. du Pont de Nemours & Co., Inc.), U. S. Patent 2,066,330 (Jan. 5, 1937).
(5) Chalmers, William, *Can. J. Research*, 7, 464–71 (1932).
(6) *Ibid.*, 7, 472–80 (1932).
(7) Claisen, L., *Ber.*, 31, 1021 (1898).
(8) Consortium für elektrochemische Industrie G.m.b.H., Brit. Patent 231,841 (Apr. 1, 1924).
(9) Copeland, N. A., and Youker, M. A., FIAT Final Rept. 720, U. S. Office of Military Govt. for Germany (Jan. 28, 1946).
(10) Craemer, Carl, *Kautschuk*, 15, 23–7 (1939).
(11) DeBell, J. M., Goggin, W. C., and Gloor, W. E., Q. M. C. Overseas Investigation Team Rept., Appendix 6A, 150–1, Office of Quartermaster Gen., Nov., 1945.
(12) Debye, P. P., *J. Applied Phys.*, 17, 392–8 (1946).
(13) Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., Smith, E. A., and Vaughan, W. E., *J. Am. Chem. Soc.*, 60, 441–2 (1938).
(14) Egloff, Gustav, and Hulla, George, *Chem. Revs.*, 36, 114 (1945).
(15) Favorskiĭ, A. E., and Shostakovskiĭ, M. F., *J. Gen. Chem.* (U.S.S.R.), 13, 1–20 (1943).
(16) Fikentscher, Hans (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,016,490 (Oct. 8, 1935).
(17) Glasgow, A. R., Jr., Streiff, A. J., and Rossini, F. D., *J. Research Natl. Bur. Standards*, 35, 355 (1946); Research paper RP-1676.
(18) Glasstone, S., "Textbook of Physical Chemistry", p. 439, New York, D. Van Nostrand Co., Inc., 1940.
(19) Halbig, Paul, and Rost, Theodor (to Consortium für elektrochemische Industrie G.m.b.H.), German Patent 726,547 (Sept. 3, 1942).
(20) Hasche, R. L., and Thompson, Benjamin (to Eastman Kodak Co.), U. S. Patent 2,294,402 (Sept. 1, 1942).
(21) Henning, F., *Ann. Physik.* [4], 43, 293 (1914).
(22) Huggins, M. L., *J. Am. Chem. Soc.*, 66, 1991–2 (1944).
(23) I. G. Farbenindustrie A.-G., Brit. Patent 482,512 (Mar. 28, 1938).
(24) International Critical Tables, Vol. I, p. 276 (1926).
(25) Jordan, Otto, Kollek, Leo, and Ufer, Hanns (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,054,019 (Sept. 8, 1936).
(26) Kline, G. M., U. S. Dept. of Commerce, Office of Pub. Board, OPB-8, pp. 28–32; also PB 949.
(27) Kollek, Leo, *Kunststoffe*, 30, 229–32 (1940).
(28) Krzikalla, Hans, and Flickinger, Erich, U. S. Dept. of Commerce, Office of Pub. Board, Rept. PB-601 (1946).
(29) Krzikalla, Hans, and Woldan, Ernst, *Ibid.*, Rept. PB-602 (1946).
(30) Kuehn, Erich, and Hopff, Heinrich (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,061,946 (Nov. 24, 1936).
(31) Leake, C. D., and Chen, Mei-Yu, *Anesthesia and Analgesia*, 10, 1–3 (1931).
(32) Lowry, T. M., *J. Chem. Soc.*, 105, 91 (1914).
(33) Marvel, C. S., U. S. Dept. of Commerce, Office of Pub. Board, PB-5521 and PB-11, 193 (1946).
(34) Mueller-Cunradi, Martin, and Pieroh, Kurt (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,061,934 (Nov. 24, 1936).
(35) Ostromislensky, I. I., *J. Russ. Phys. Chem. Soc.*, 47, 1487 (1915).
(36) Otto, Michael, Gueterbock, Hermann, and Hellemanns, Alfred (to Jasco, Inc.), U. S. Patent 2,311,567 (Feb. 16, 1943).
(37) Plauson's Forschungsinstitut G.m.b.H., German Patent 338,281 (May 25, 1918).
(38) Reppe, Walter (to I. G. Farbenindustrie A.-G.), U. S. Patent 1,941,108 (Dec. 26, 1933).
(39) *Ibid.*, 1,959,927 (May 22, 1934).
(40) Reppe, Walter, Office of Rubber Reserve, Tech. Rept. OPB-32 (July 25, 1945), and PB-13, 366 (1946).
(41) Reppe, Walter, U. S. Dept. of Commerce, Office of Pub. Board, Rept. PB-2437 (1946).
(42) Reppe, Walter, and Baur, Karl (to I. G. Farbenindustrie A.-G.), German Patent 566,033 (Jan. 24, 1930).
(43) Reppe, Walter, and Baur, Karl (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,000,252 (May 7, 1935).
(44) Reppe, Walter, and Kuehn, Eric, *Ibid.*, 2,098,108 (Nov. 2, 1937).
(45) Reppe, Walter, and Schlichting, Otto, *Ibid.*, 2,104,000 (Dec. 28, 1937).
(46) Reppe, Walter, and Ufer, Hanns (to I. G. Farbenindustrie A.-G.), German Patent 705,273 (Mar. 20, 1941).
(47) Reppe, Walter, and Wolff, Werner (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,021,869 (Nov. 19, 1935).
(48) *Ibid.*, 2,066,076 (Dec. 29, 1936).
(49) Schildknecht, C. E. (to General Aniline & Film Corp.), U. S. Patent 2,395,684 (Feb. 26, 1946).
(50) Seiferle, E. J., Rept. of Fellowship in School of Agr., Pa. State College, to General Aniline & Film Corp., Jan. 1, 1946.
(51) Shostakovskiĭ, M. F., *Doklady Akad. Nauk. S.S.S.R.*, 41, 124–7 (1943); *Bull. acad. sci. U.R.S.S., Classe sci. chem.*, 1943, 156–7.
(52) Shostakovskiĭ, M. F., *J. Applied Chem.* (U.S.S.R.), 16, 66–71 (1943).
(53) Shostakovskiĭ, M. F., *J. Gen. Chem.* (U.S.S.R.), 14, 102–12 (1944).
(54) *Ibid.*, 14, 889 (1944).
(55) Shostakovskiĭ, M. F., and Bogdanov, I. F., *J. Applied Chem.* (U.S.S.R.), 15, 249–59 (1942).
(56) Shostakovskiĭ, M. F., and Sidelkovskaya, *J. Gen. Chem.* (U.S.S.R.), 13, 428–35 (1943).
(57) Sigmund, Fritz, and Uchann, Reinfried, *Monatsh.*, 51, 234–52 (1929).
(58) Skrabal, Anton, and Skrabal, Roman, *Z. physik. Chem.*, A181, 449–68 (1938).
(59) Timmermans, J., *Bull. soc. belg. chim.*, 24, 244 (1910); *Chem. Zentr.*, 1910, II, 442.
(60) U. S. Dept. of Commerce, Office of Pub. Board, Rept. PB-1112, pp. 3–5 (1946).
(61) Voss, Arthur, and Dickhauser, Ewald (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,047,398 (July 14, 1936).
(62) Wang, Sheng-Nien, and Winkler, C. A., *Can. J. Research*, 21B, 97–110 (1943).
(63) Wislicenus, Johannes, *Ann.*, 92, 106 (1878).

Absorption of Oxygen by Rubbers

A. S. CARPENTER[1]

Dunlop Rubber Company, Ltd., Erdington, Birmingham, England

The rate of the rubber-oxygen reaction has been measured at constant pressure. In the absence of antioxidant the reaction is autocatalytic and in accordance with a free radical chain mechanism. In the presence of antioxidant, oxidation depends upon the formation of an equilibrium proportion of an unstable catalyst of considerable persistence, and reaches a constant dynamic equilibrium rate which is greater, the greater the oxygen pressure. Manometric methods of investigating the reaction lead to erroneous conclusions because of the autocatalytic nature of the reaction in the absence of antioxidant and because of the persistence of a high oxidation rate after a pressure reduction (due to the persistence of the unstable catalyst) in the presence of antioxidant. An approximate relation is deduced between oxidizability, specimen size, and uniformity of oxidation for rubbers containing antioxidant.

SEVERAL workers have investigated the reaction between rubber and oxygen, in the important initial stages over which the rubber retains its rubbery qualities, by following the rate of disappearance of gaseous oxygen in a closed system. Particular attention has been directed toward establishing the effect of oxygen pressure upon the rate of the reaction. This is fundamentally important. Also, in the surface of the rubber the oxygen concentration consistent with the pressure of oxygen in the gas phase is maintained by dissolution, whereas in the interior, oxygen can be supplied only by the diffusion of already-dissolved oxygen. At any point in the interior the concentration which can be built up is determined by the rate at which oxygen diffuses in from higher concentration regions and out to lower concentration regions and by the rate at which it is used up by combination. In the interior, therefore, the oxygen concentration, and hence the reaction rate, corresponds to a gas pressure different from that of the surrounding free gaseous oxygen.

One method which was used, notably by Williams and Neal (*14*) and Morgan and Naunton (*13*), for the fundamental investigation of the rubber-oxygen reaction has the advantages of simplicity and ease of operation. It consists in confining the rubber specimen in an oxygen-filled vessel connected to a vertical tube dipping into mercury. Oxygen pressure falls spontaneously as oxygen combines, and mercury ascends the vertical tube. At any particular stage in the experiment the position of the mercury meniscus in the tube gives the oxygen pressure, and its rate of movement gives the rate of combination of oxygen with the rubber. Williams and Neal, using finely subdivided acetone-extracted rubber specimens, conclude from their experiments that rate of oxygen combination is independent of oxygen pressure over most of the absorption. Morgan and Naunton, using similar specimens and continuing the work of Williams and Neal, chiefly with regard to the effect of temperature, put forward a chain reaction theory for the mechanism of the reaction, on the basis of the same conclusion.

The work of the investigators mentioned, however, is at variance with that of others using different experimental techniques (*1, 8, 11, 12*) and, furthermore, their experimental method is not free from criticism. For example, Kohman (*11*), working at constant oxygen pressure over the whole range of oxidation up to resinification, showed that the reaction is autocatalytic; consequently time effects other than those arising from the diffusion process may be operative and may vitiate the results of manometric experiments. Also, investigators in this field are generally agreed that the higher oxygen pressures favor the more rapid oxidation (usually judged by the decay of tensile properties), as shown by the common practice of assessing the oxidation resistance of technical products by accelerated aging in the Bierer-Davis pressure bomb. Furthermore, although a quantity of oxygen sufficient to cause a considerable modification of the physical properties of the rubber combines during an experiment (*10, 11*) direct comparisons are made between the initial and final stages without evidence that the changed degree of oxidation has no effect upon oxidation rate.

The investigation outlined in the present account was commenced with the following aims in view: (*a*) to try out a modified manometric apparatus which was believed would have advantages over the simple Williams and Neal type; (*b*) using this apparatus to investigate the value of the manometric method as a tool for a fundamental investigation (*1*) and as a means of determining and comparing the resistance to oxidation of specimens of technical rubbers; and (*c*) to investigate the physical chemistry of the reaction between rubber and oxygen. A preliminary note on some of the results of this investigation has been published previously (*4*).

MODIFIED MANOMETRIC APPARATUS

The apparatus differed considerably in detail from the simple Williams and Neal apparatus but was identical in principle. It was so designed that absorptions could be followed over pressure changes of about 15 cm. of mercury, starting from any desired initial pressure less than about 3 atmospheres. It was independent of the pressure of the atmosphere and its fluctuations. The apparatus was described previously (*3*) in connection with experiments to determine the solubilities and diffusion coefficients of gases in rubbers. By the use of this apparatus the rate of oxygen absorption at any pressure within the chosen range may be calculated from readily ascertainable data.

EXPERIMENTS WITH MANOMETRIC APPARATUS

The state of subdivision necessary for substantially uniform oxygen concentration and, hence, oxidation throughout a rubber specimen is dependent upon the susceptibility of the latter to oxidation, the more readily oxidizable rubber requiring the finer subdivision. It was considered possible that, with quite large specimens of more slowly oxidizing rubbers, oxidation might be substantially uniform and absorption rates little affected by diffusion. An experiment was carried out with this possibility in mind. The specimens were made from the following mixture, in parts by weight:

Rubber (smoked sheet)	100
Sulfur	3
Zinc oxide	3.5
Stearic acid	1.5
Mercaptobenzothiazole	1
Agerite white	0.25

The mixture was vulcanized by heating for 30 minutes at 148° C. in closed molds. The specimens were in the form of cylindrical rods, about 5-mm. in diameter and 15 cm. long (specimens *A* and *B*), square sectioned rods about 1 × 1 mm. in cross section and not less than 5 cm. long (specimen *C*), and cubes of about 1.5-

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[1] Present address, Courtaulds, Ltd., Foleshill Road, Coventry, England.

TABLE I. EFFECT OF OXYGEN PRESSURE ON OXYGEN ABSORPTION RATE OF CYLINDRICAL SPECIMENS OF A SLOWLY OXIDIZING RUBBER AS DETERMINED WITH MODIFIED MANOMETRIC APPARATUS

Oxygen Pressure, Cm. Hg	Absorption Rate (G. Oxygen/G. Rubber/Day) $\times 10^{-6}$				
	a	*b*	*c*	*d*	*e*
180.2	11.64	11.93	11.66	10.81	13.20
171.2	11.34	11.62	11.35	10.43	12.80
140.2	10.00	9.82	10.04	9.07	12.10
130.2	9.71	9.47	9.74	8.73	11.69
84.2	7.82	8.44	8.80	7.70	9.97
79.2	7.77	8.27	8.66	7.52	9.77
44.2	5.77	6.05	5.84	5.77	8.03
37.2	5.61	5.88	5.68	5.57	7.79
20.2	3.79	3.55	3.90	3.69	4.98
12.2	2.26	2.36	2.54	2.11	2.79

mm. side (specimen *D*). The surface areas of the specimens were, approximately, 25 cm.^{2} (*A* and *B*), 75 cm.^{2} (*C*), and 120 cm.^{2} (*D*).

The experiment was carried out in darkness at 45° C., starting at a pressure of about 80 cm. of mercury. The period allowed for solution equilibrium was 24 hours. (A calculation based on the known solubility and diffusion coefficient of oxygen in the rubber showed that, if no chemical combination had occurred between the oxygen and the rubber, the rate of solution in the cylindrical specimens, at a pressure of 1 atmosphere, would have been about 4.2×10^{-8} gram oxygen per gram rubber per day after 12 hours, and about 0.9×10^{-12} gram oxygen per gram rubber per day after 24 hours.) In each case the mercury ascended the capillary at a constant rate over the 15-cm. range. The absorption rates, calculated for the conditions when the pressure of oxygen in contact with the specimen was 1 atmosphere, were as follows:

Specimen	*A*	*B*	*C*	*D*
Absorption rate (g. O_2/g. rubber/day) $\times 10^{-6}$	4.92	5.37	5.67	4.51

The experiment was repeated using fresh specimens, one of the cylindrical specimens being given an 18-hour aging pretreatment in the Geer oven. Again in all cases the mercury ascended the capillaries at a constant rate. The absorption rates, calculated as before for an oxygen pressure of 1 atmosphere, were as follows:

Specimen	*A*	*B*	*C*	*D*
Absorption rate (g. O_2/g. rubber/day) $\times 10^{-6}$	5.40	5.27	9.54	6.06

The specimen subjected to Geer oven aging was *B*.

Although the agreement between the results of these experiments is poor, the results show that there was no consistent effect of subdivision. Thus with this slowly oxidizing rubber it appears that oxidation under these conditions is substantially uniform throughout all of the specimens. Several other investigators (*10, 11, 12*) showed that, with slowly oxidizing rubbers, it is not necessary to go to an extreme state of subdivision—for example, crumb—in order to eliminate diffusion as a rate-determining process. Calculations confirm that diffusion effects had negligible influence on the results.

In the apparatus of Williams and Neal the change in internal free volume of the specimen tube during the spontaneous pressure change was negligible. Their conclusion that the rate of oxygen combination is independent of pressure depended upon this experimental arrangement. The design of the present modified apparatus was such that the internal free volume change was an appreciable fraction of the total. In these experiments, therefore, the rate of oxygen combination was lower, the lower the oxygen pressure.

An experiment was carried out to determine the effect of oxygen pressure upon absorption rate over a wide pressure range, using five identical cylindrical specimens of 5-mm. diameter. The specimens were made from the mixture described and were kept for 3 days under vacuum in darkness before test. In this experiment the pressure of the oxygen in contact with the specimens was reduced alternately in one of two ways: (*a*) It was allowed to fall spontaneously over a small pressure range as absorption proceeded or (*b*) it was artificially reduced at intervals by withdrawing oxygen from the apparatus. In this way, starting from a pressure of about 180 cm. of mercury, absorption rates were followed over spontaneous pressure decrease steps of about 10 cm. down to about 12 cm. of mercury. When the pressure was changed by withdrawing oxygen, 24 hours were allowed for solution equilibrium. The experiment was carried out in darkness at 45° C. The results are given in Table I. The specimens were kept for 3 days under vacuum in darkness, and a repeat experiment was carried out on them. The results were in general agreement with those of the first experiment.

Starting with pressures of 180, 140, and 84 cm. of mercury, the rate of rise of mercury in the capillaries during the spontaneous pressure-fall steps was constant in any one case but was not the same for any one specimen for the three steps. With a starting pressure of 44 cm. of mercury there was a tendency in all cases for the rate to decrease with spontaneous decrease in oxygen pressure. At a starting pressure of 20 cm. of mercury the tendency was marked. In Table I absorption rates have been calculated for the oxygen pressures at the beginning and at the end of the spontaneous pressure changes.

It is seen that absorption rate is markedly dependent upon oxygen pressure. This is in agreement with the findings of Ingmanson and Kemp (*8*); by following decay of physical properties, they showed that, for oxygen pressures less than about 4 atmospheres, absorption rate increases with oxygen pressure. The results, however, are unsatisfactory, because a graph shows that, in any one case, the short curves corresponding with the spontaneous pressure decreases do not lie on one continuous curve. Very roughly, absorption rate is proportional to the square root of the oxygen pressure, a result in agreement with the findings of van Amerongen (*1*) and of Milligan and Shaw (*12*). These experiments show that results with the manometric apparatus are not independent of the arbitrary conditions of the experiment. The progressive change in the condition of the rubber at each step, due to oxidation during the preceding steps, does not affect the absorption rate at that particular step, because the repeat experiment on the same specimens gave similar results. The reproducibility of results with the same specimen, however, does not exclude the possibility that the initial stages of oxidation in a particular step might affect the later stages of that step.

In all the experiments with this modified manometric apparatus the agreement was poor among results of experiments differing only in insignificant detail. This was considered surprising in view of the known reliability of the apparatus used in a slightly different connection (*3*), and in view of the fact that the result of each individual determination could be quoted with considerable accuracy—that is, having regard only to the accuracy with which the relevant experimental data could be ascertained.

From the nature of the results of these experiments it appears that they are affected by an unappreciated factor inherent in the method. Moreover, it is fundamentally unsound to allow both of the interdependent variables, oxygen pressure and oxygen combination rate, to change without control. All further work was carried out at constant oxygen pressure.

These criticisms of the manometric method do not necessarily apply to the work of Dufraisse (*6*), who used it under carefully standardized conditions as a routine test for the estimation of the oxidizability of various rubbers.

CONSTANT PRESSURE APPARATUS

Milligan and Shaw (*12*) and van Amerongen (*1*) described apparatus for measuring the oxygen absorption of rubbers at more or less constant total gas pressure by methods involving the manual adjustment of the pressure from time to time. These methods were unsatisfactory for the present purpose. Kohman (*11*) described apparatus in which the pressure was automatically kept constant. It was, however, designed to measure the total absorption of oxygen over the complete range up to resinification, and was not considered capable of sufficient refinement to allow accurate measurement of very small oxygen absorption rates.

Figure 1 shows the apparatus designed and used for measuring oxygen absorption rates at constant pressure. It consisted of bulb *B*, of about 700-cc. capacity, with an extension, *D*, of 2-cm.

diameter and 6-cm. length connected to a horizontal capillary, *C*, 14 cm. long and uniform in bore (0.0104 cc. per cm.), marked off in centimeters by etched lines. The end of the capillary farthest from bulb extension *D* was connected directly to specimen bulb *A* (which was sealed on afresh for each new specimen) and continued through tap T_2 to the top of bulb *B*. The system contained a side tube with a tap, T_1. Bulb extension *D* served as a reservoir for a light paraffin oil freed from readily volatile constituents. The quantity of oil used was such that, when the capillary was horizontal, it rose into the capillary and the equilibrium position of its meniscus was at the end near the reservoir. Because of the great cross-sectional area of the reservoir compared with that of the capillary, movement of the oil meniscus along the capillary caused only a very small change in oil level in the reservoir. The oil meniscus in the capillary showed little tendency to move toward the reservoir when it was placed at the end of the capillary farthest from the reservoir and was free to move. Adjustment of the oil meniscus to any desired position in the capillary could be accomplished by tilting the apparatus with tap T_2 open.

For normal use the apparatus was connected by means of the side tube and tap T_1 to a mercury manometer, a vacuum pump, and an oxygen cylinder. During an experiment the whole of the apparatus shown in the diagram was contained in a thermostat of temperature constant to within 0.02° C. The oxygen absorption rate of a rubber specimen was deduced from the movement of the oil meniscus in the capillary when, with the apparatus filled with oxygen at the desired pressure, gaseous connection between the specimen bulb and the large bulb was severed by turning off tap T_2. The disappearance of oxygen from the gaseous phase in the specimen bulb caused the oxygen in the large bulb to force the oil along the capillary. The volume swept out by the oil meniscus was a measure of the volume of oxygen absorbed.

Calculation shows that using the following equation as an approximation:

$$v = bx\left[\frac{V_1 + V_2}{V_1}\right]$$

where V_1 = internal free volume on large bulb side of apparatus from oil surface in reservoir to tap T_2
V_2 = internal free volume of specimen bulb and connections from oil meniscus in capillary to tap T_2
b = cross-sectional area of capillary
v = volume of oxygen (measured at pressure of experiment) absorbed by specimen
x = movement of oil meniscus along capillary resulting from absorption

The error involved for an average actual value of V_2 = 30 cc. is about 0.7% at 1 atmosphere, 1.3% at $^2/_3$ atmosphere, and 2.5% at $^1/_3$ atmosphere. This approximation was considered to be sufficiently close; the factor $(V_1 + V_2)/V_1$ was applied in the calculation of results. The change of pressure of the oxygen surrounding the specimen, as the oil meniscus moves 10 cm. along the capillary, is about 0.02% of the original pressure. This was considered to be negligible.

The use of oil instead of mercury as the indicating liquid in the apparatus needs justification. Its main advantages and the reasons for which it was chosen are twofold: (*a*) The oil shows no tendency to stick in capillaries; (*b*) gas pressure errors arising from incorrect leveling of the capillary and from the change in liquid level in the reservoir due to movement of the meniscus in the capillary are minimized because of the low specific gravity of the oil. The disadvantages are its volatility at low pressures and its solvent power for gases. The former was overcome by never using pressures lower than 0.2 cm. of mercury. When the complete removal of oxygen from the apparatus was necessary, it was displaced by nitrogen.

The apparatus was tested in several ways to ensure that the rate of movement of the oil meniscus in the capillary was an accurate measure of the rate of disappearance of gas through the specimen tube side arm. All of the tests were satisfactory and showed that the apparatus was capable of giving trustworthy results. The only correction necessary was that arising from the dissolution of oxygen in the oil of the reservoir; the correction was necessary only in determinations with rubbers giving very slow meniscus movement rates (of the order of 10 cm. per day) during the first few hours after the pressure change. In the calculation of the results the appropriate correction, determined by experiment, was applied where necessary. The method of using the apparatus for the determination of oxygen absorption rate of rubber was as follows:

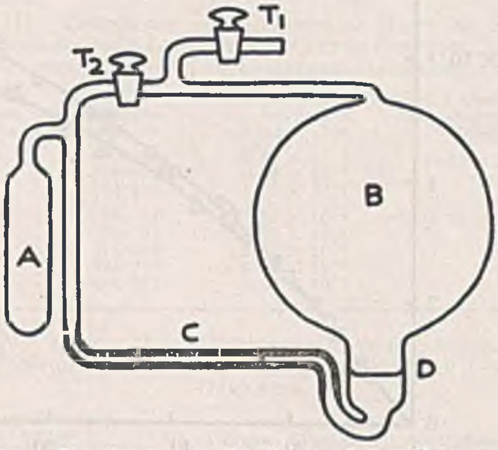

Figure 1. Apparatus for Determining Oxygen Absorption Rate of Rubbers at Constant Oxygen Pressure

The rubber specimen was sealed into a glass bulb with as little free space left as was conveniently possible. This specimen bulb was then sealed onto the apparatus, and, when required, an opaque covering was placed around it. The completed apparatus with tap T_2 open was placed in the thermostat and, together with all connecting tubes, alternately evacuated and filled with oxygen until all gases other than oxygen were removed. The apparatus was then filled with oxygen at the desired pressure. Oxygen began to dissolve in the rubber and was used up by oxidation. After a time interval determined by experiment (Table II), absorption was entirely due to chemical combination of oxygen. Tap T_2 was turned off, and the rate of disappearance of oxygen from the gas phase in the specimen bulb was measured by the rate at which the oil moved along the horizontal capillary. When the oil reached the specimen tube end of the capillary, tap T_2 was opened and the meniscus returned to the reservoir end ready for a subsequent determination. Similar determinations at other pressures could be made either by the evacuation procedure or by simply introducing or withdrawing oxygen.

The work carried out with the constant pressure apparatus and recorded here is in the nature of a preliminary investigation searching out the field for future, more rigid, treatment. Nevertheless, a broad interpretation confirms the essential invalidity of deductions based on work carried out with the manometric type of apparatus, indicates the reasons, gives the required background for a general investigation of the oxygen-rubber reaction, and gives a new basis for the theoretical treatment of the problem.

RAPIDLY OXIDIZING VULCANIZED RUBBER

In order to check the reproducibility of results on a rubber specimen, an experiment was carried out with a rapidly oxidizing rubber prepared by heating the following mixture for 40 minutes at 145° C. in a closed mold (in parts by weight):

Rubber (deproteinized by centrifugal purification of latex, and containing 0.25% added antioxidant)	100
Sulfur	3
Zinc oxide	5
Diphenylguanidine	1.5

The 8-mm.-thick slabs of the vulcanized material were kept at laboratory temperature in the dark and, when required for testing were reduced to a crumb of particle diameter about 0.3 mm. by passage through a cold friction mill at a tight nip. The temperature

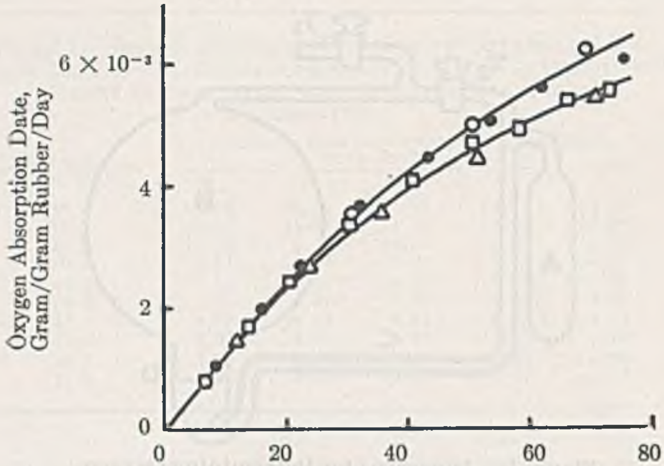

Figure 2. Effect of Oxygen Pressure on Constant-Pressure Absorption Rate of Diphenylguanidine-Vulcanized Deproteinized Rubber

	Falling Pressure	Rising Pressure
First experiment	●	○
Second experiment	□	△

of the experiment was 40° C., the oxygen pressure 75.2 cm. mercury, and the time allowed for solution equilibrium 2 hours. Five estimations were made without altering the conditions, the rates of movement of the oil meniscus being 1.80, 1.74, 1.68, 1.66, and 1.84 cm. per minute. The total consumption of oxygen during the experiment was about 0.04% by weight, 0.02% during the equilibrium period, and 0.02% during the absorption rate measurements. The results showed merely random variation; no consistent trend was apparent with increase in combined oxygen proportion.

Ingmanson and Kemp (*9*), working at more or less constant pressure and estimating combined oxygen by direct weighing and by decay of physical properties, also found that the absorption rate of antioxidanted rubbers attains a constant value. It is probable that in Kohman's work (*11*) antioxidant became oxidized away in the early stages, and the behavior noted was the autocatalytic reaction of nonantioxidized rubber. Another specimen of the same rubber mixture was used to find the effect of oxygen pressure on absorption rate. The experiment was carried out at 40° C. and the time allowed for solution equilibrium after a pressure change was 30 minutes. Two experiments were carried out on the same specimen on consecutive days, with the apparatus left evacuated overnight. Figure 2 shows the results. The total consumption of oxygen during the first experiment was about 0.13% by weight on the rubber, and during the second, about 0.16%. The good agreement between the results with increasing oxygen pressure and those with decreasing pressure shows that 30 minutes was a sufficient time for equilibrium and that an increase in combined oxygen proportion of the order of 0.15% is without considerable effect upon oxygen absorption rate. The results show that oxygen absorption rate is greater, the greater the oxygen pressure. This is contrary to the findings of Williams and Neal and Morgan and Naunton but is in agreement with the results of the experiment already described here in which the oxygen pressure was artificially reduced at intervals in the manometric type of apparatus.

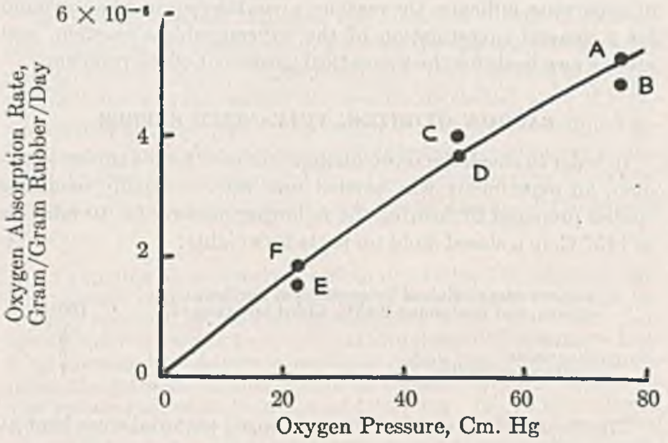

Figure 3. Effect of Oxygen Pressure on Constant-Pressure Oxygen Absorption Rate of Unvulcanized Smoked Sheet Rubber

SMOKED SHEET RUBBER

A piece of smoked sheet rubber was taken from the center of a substantial block and passed through a cold friction mill at a tight nip to reduce it to a thin, rough sheet of about 0.5-mm. average thickness. Smoked sheet rubber is known to absorb oxygen at a comparatively slow rate, and it was considered that the ratio of surface area to volume ratio of the specimen in this form was sufficiently great to ensure practically uniform oxygen concentration throughout the rubber during the oxidation. This was substantiated by calculations given later in the paper. A rectangular piece of the sheet was placed on a piece of filter paper, and filter paper and specimen were rolled together loosely on a glass rod for sealing into the specimen bulb. Absorption rate determinations were carried out on this specimen at several oxygen pressures. The equilibrium period—that is, the period during which the pressure was unaltered, immediately prior to an absorption rate determination—was in no case less than 40 hours and in most cases considerably more. The temperature of the experiment was 40° C. The results are shown in Figure 3. Determinations *A*, *D*, *E*, and *F* were, for the most part, carried out overnight—that is, in darkness—whereas *B* and *C* were carried out under conditions of feeble illumination by stray light. The total consumption of oxygen was about 0.005% by weight on the rubber. At the conclusion of the experiment the specimen was found to be unchanged, as far as could be determined from its behavior on the mill.

Table II. Rate of Dissolution in 0.2 Cm. Cubes of Gas-Free Smoked Sheet Rubber at 40° C., in Complete Darkness

Oxygen Pressure[a], Cm. Hg	Time after Start, Hr.	Rate of Movement of Oil Meniscus, Cm./Hr.
72.9	0.15	560
	0.25	220
	0.55	28
36.7	0.15	480
	0.35	105
	0.67	8
72.4	0.15	468
	0.25	242
	0.40	86
	0.50	42
	0.60	14
74.3	0.05	1590
	0.10	860
	0.15	550
	0.25	253
	0.37	105
	0.48	48
	0.80	4

[a] Rates of movement at different pressures are strictly comparable because solubility, measured as volume of gas at pressure of the experiment, is independent of gas pressure.

GR-S

Absorption rate determinations carried out on a butadiene-styrene copolymer synthetic rubber composition (GR-S) gave the results shown in Figure 4. This material is not a pure substance but contains, in addition to the polymeric material, small proportions of fatty acids, soaps, and antioxidants. It contains about 93% by weight of the copolymer. The specimen used consisted of 0.2-cm. cubes of the untreated, unvulcanized GR-S cut from a piece taken from the interior of a substantial block. It was known that GR-S absorbs oxygen at approximately the same slow rate as does smoked sheet rubber, and it was considered that this state of subdivision was sufficient to ensure substantially uniform oxygen concentration throughout the material during oxidation. Calculations show that this was justified. The temperature of the experiment was 40° C. and the equilibrium period for each determination not less than 39 hours and, in most cases, considerably more. All of the determinations were carried out for the most part in complete darkness. The total consumption of oxygen was about 0.006% by weight on the copolymer.

The specimen was examined at the end of the experiment and found to be insoluble in the usual solvents for fresh, unvulcanized GR-S. It had been in the thermostat at 40° C. for 26 days.

In these experiments with GR-S it was found that the small amount of stray, diffuse, filtered light reaching the specimen might have a measurable effect upon the absorption rate. None of the results of the experiments described, however, were considerably affected by light conditions. All of the further experiments to be described were carried out under conditions of complete darkness by enclosing the specimen tube and all adjacent glass connecting tubing in an opaque covering.

ABSORPTION RATES AFTER PRESSURE CHANGE

In the constant pressure experiments described, the oil meniscus moved along the horizontal capillary at a constant rate, and repeat determinations on the same specimen—that is, at different combined oxygen contents—gave the same results within a reasonable experimental error. There was no evidence that the absorption rate at any one pressure increased with increase in combined oxygen content. The absorption rate measurements in all cases, however, were made after an equilibrium period. This was 30 minutes in the case of the rapidly oxidizing, diphenylguanidine-vulcanized, deproteinized rubber, not less than 40 hours in the case of the smoked sheet rubber, and not less than 39 hours in the case of GR-S. These periods were allowed primarily for the attainment of solution equilibrium. An experiment was carried out, again using unvulcanized smoked sheet rubber as the specimen, first, to confirm that the dynamic equilibrium absorption rates remained constant over extended periods and, second, to investigate the absorption rate in the period immediately after the attainment of solution equilibrium in the rubber.

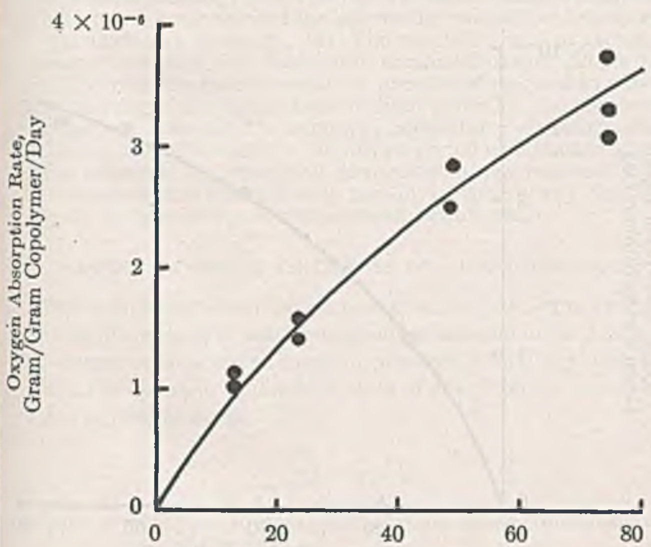

Figure 4. Effect of Oxygen Pressure on Constant-Pressure Oxygen Absorption Rate of Unvulcanized GR-S

Table III. Constancy of Absorption Rate of Smoked Sheet Rubber over Long Periods after Solution Equilibrium at 40° C. in Complete Darkness

Oxygen Pressure, Cm. Hg	Time after Start, Hr.	Absorption Rate, G. Oxygen/G. Rubber/Day	Total Absorption, G. Oxygen/G. Rubber
72.9	80–104	4.85×10^{-6}	0.36×10^{-4}
	120–132	4.83×10^{-6}	
	150–175	4.85×10^{-6}	
50.0	45– 67	3.37×10^{-6}	1.26×10^{-4}
	69– 92	3.30×10^{-6}	
	574–597	3.72×10^{-6}	
	694–723	3.57×10^{-6}	
	844–867	3.43×10^{-6}	

Table IV. Initial High Absorption Rate of Smoked Sheet Rubber after Pressure Reduction at 40° C. in Complete Darkness

Previous Exposure to Oxygen				
Pressure, Cm. Hg	Duration, Hr.	New Oxygen Pressure, Cm. Hg	Time after Pressure Change, Hr.	Absorption Rate[a], G. Oxygen/G. Rubber/Day
74.2	143	36.5	0[b]	7.0×10^{-6}
			3	6.2×10^{-6}
			6	5.3×10^{-6}
			9	4.6×10^{-6}
			12	3.9×10^{-6}
			25	3.4×10^{-6}
			30	3.0×10^{-6}
			35	2.8×10^{-6}
			40	2.8×10^{-6}
			45	2.8×10^{-6}
			65	3.1×10^{-6}
73.6	144	38.6	0[b]	7.2×10^{-6}
			3	6.6×10^{-6}
			6	6.0×10^{-6}
			9	5.1×10^{-6}
			12	4.5×10^{-6}
			30	2.7×10^{-6}
			50	2.9×10^{-6}

[a] Deduced from the slope of the tangent to the scale reading against time graph.

[b] By extrapolation to zero time of the scale reading against time graph.

The specimen consisted of rough cubes of unvulcanized smoked sheet rubber, about 0.2-cm. on each side, cut from a piece taken from the center of a substantial block. Before this experiment was begun, calculation had shown that the oxidation rate of smoked sheet was sufficiently slow to enable cubes of this size to be used with negligible error from diffusion effects.

In four experiments in which oxygen was introduced into the apparatus after a long period of evacuation (to about 0.2 cm. of mercury), the rate at which oxygen dissolved was determined from time to time soon after the start. The results (Table II) show that solution is practically complete after 0.80 hour. It was considered that gas absorbed for the attainment of solution equilibrium would be a negligibly small fraction of that absorbed for combination with the rubber after 2 hours.

Two experiments were carried out in which the oxygen pressure remained constant over a long period. Determinations carried out from time to time during that period showed that absorption rates remained constant within a reasonable experimental error (Table III).

Experiments were performed in which the specimen was exposed to oxygen at constant pressure long enough to allow attainment of the dynamic equilibrium state of absorption at a constant rate; then the pressure was quickly reduced and again kept constant. It was found that, although the absorption rate eventually became equal to the rate consistent with the new pressure, a high initial rate persisted for several hours in diminishing degree (Table IV). For a reduction of pressure from approximately 1 to approximately 0.5 atmosphere, the initial high rate was more than twice as great as that finally attained after 30- to 35-hour exposure to the lower pressure. The persistence of an effect upon absorption rate at one pressure, immediately follow-

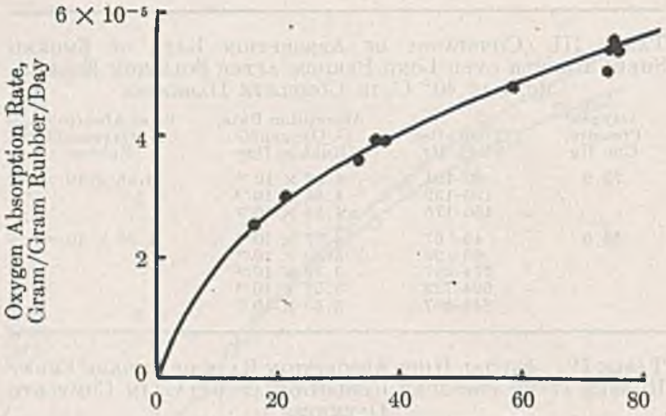

Figure 5. Effect of Oxygen Pressure on Constant-Pressure Oxygen Absorption Rate of Mercaptobenzothiazole-Vulcanized Smoked Sheet Rubber

ing previous exposure to a higher pressure, affords a possible explanation for the apparent independence of absorption rate of oxygen pressure shown in experiments carried out with the manometric type of apparatus. In this apparatus the pressure continually falls; hence the absorption rate at any stage is greater than the rate consistent with the oxygen pressure at that stage.

In the previously described experiments using unvulcanized smoked sheet rubber and GR-S, the equilibrium periods were in all cases 39 hours or more, so that the results given in Figures 3 and 4 are not vitiated by the time effects described. Although the pressure changes in the experiments using the diphenylguanidine-vulcanized, deproteinized rubber were comparatively small, the fact that equilibrium periods of 30 minutes were sufficient for the establishment of the dynamic equilibrium states suggests that the time effects already described are less marked with the more rapidly oxidizing rubber. This was confirmed in a series of experiments carried out on smoked sheet rubber vulcanized with mercaptobenzothiazole, intermediate in oxidizability between the two extremes previously investigated.

VULCANIZED SMOKED SHEET RUBBER

The unvulcanized mixture consisted of the following ingredients, in parts by weight:

Smoked sheet rubber	100
Sulfur	2.5
Zinc oxide	5
Stearic acid	1
Mercaptobenzothiazole	0.5

It was vulcanized in the form of 1-mm.-thick sheets by heating in a closed mold for 40 minutes at 138° C. These sheets were passed through a cold friction mill at a tight nip to produce an irregular sheet of 0.2-mm. average thickness, which was rolled onto a glass rod together with a sheet of filter paper for sealing into the specimen bulb. The temperature of the experiment was 40° C. Figure 5 shows the relation between the dynamic equilibrium absorption rate and oxygen pressure; Table V gives data on the time effect resulting from a pressure change.

EFFECT OF EXTRACTION WITH ACETONE

A comparison was made of the oxygen absorption behavior of a rapidly oxidizing rubber, with and without previous extraction with acetone. The mixture consisted of the following ingredients, in parts by weight:

Rubber (pale crepe)	100
Sulfur	3
Zinc oxide	5
Diphenylguanidine	1.5

It was vulcanized by heating for 90 minutes at 141° C. The vulcanizate was reduced to a finely subdivided form by passage through a friction mill at a tight nip. Part of the resulting crumb was extracted for 40 hours with acetone in a Soxhlet apparatus and, after extraction, acetone was removed by prolonged evacuation. Both the extracted and the unextracted portions were kept under vacuum at room temperature in complete darkness until required for the oxygen absorption rate determinations, which were carried out at 40° C.

Specimens taken from the portion which had not undergone extraction with acetone gave results similar to those obtained for the unextracted vulcanized and unvulcanized rubbers; that is, at constant oxygen pressure, oxygen absorption rate reached a constant value which increased with increasing oxygen pressure (Figure 6).

In an initial stage specimens taken from the acetone-extracted portion also behaved similarly. Up to a total oxygen uptake of about 1.0–1.5 × 10^{-4} grams oxygen per gram rubber, the oxidation rates reached constant values at constant pressures, the equilibrium rates being greater with the greater oxygen pressures. This stage occurred only once with each specimen.

After this proportion of oxygen had combined, however, oxidation behavior became strikingly different. At any one constant pressure the oxygen absorption rate increased as oxidation proceeded, and no dynamic equilibrium state of absorption at a constant rate was reached (Table VI). An alteration of the oxygen pressure from one constant value to a new constant value caused an approximately proportionate change in absorption

Table V. Initial High Oxygen Absorption Rate of Vulcanized Smoked Sheet Rubber after Pressure Reduction

Previous Exposure to Oxygen				
Pressure, Cm. Hg	Duration, Hr.	New Oxygen Pressure, Cm. Hg	Time after Pressure Change, Hr.[a]	Absorption Rate, G. Oxygen/G. Rubber/Day
75.4	50	33.3	1	4.4 × 10^{-5}
			24	3.6 × 10^{-5}
			72	3.7 × 10^{-5}
75.0	72	37.4	1	4.7 × 10^{-5}
			2	4.7 × 10^{-5}
			6	4.3 × 10^{-5}
			24	4.0 × 10^{-5}
			28	3.9 × 10^{-5}
			72	4.0 × 10^{-5}

[a] Time for solution equilibrium in the rubber, 30 minutes.

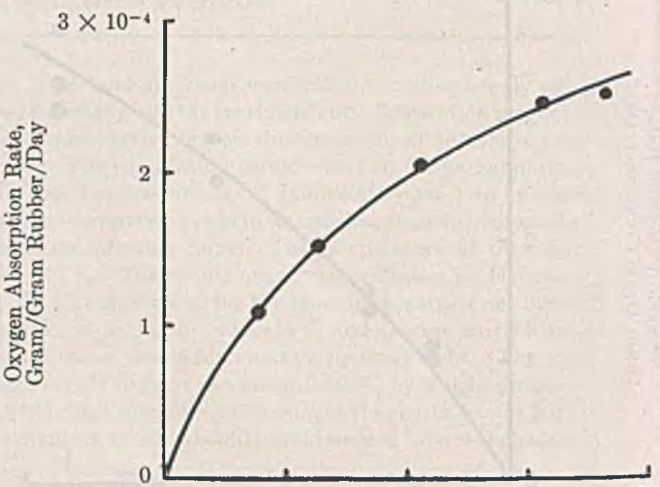

Figure 6. Effect of Oxygen Pressure on Constant-Pressure Absorption Rate of Diphenylguanidine-Vulcanized Rubber before Extraction with Acetone

Table VI. Oxygen Absorption of Acetone-Extracted Vulcanized Rubber

Time after Start, Hr.	Oxygen Pressure, Cm. Hg	Oxygen Absorption Rate, G./G. Rubber/Day	Time after Start, Hr.	Oxygen Pressure, Cm. Hg	Oxygen Absorption Rate, G/G. Rubber/Day
0	Evacuation	..	19.0	Evacuation	..
15.5	76.4	..	64.0	75.7	..
16.1	76.4	1.78×10^{-3}	64.5	75.7	2.05×10^{-3}
16.4	76.4	1.88×10^{-3}	64.9	75.7	2.22×10^{-3}
16.8	76.4	1.99×10^{-3}	65.3	75.7	2.31×10^{-3}
17.2	76.4	2.08×10^{-3}	66.3	75.7	2.62×10^{-3}
17.6	76.4	2.18×10^{-3}	67.2	75.7	2.76×10^{-3}
18.3	76.4	2.35×10^{-3}	67.5	75.7	2.92×10^{-3}
18.7	76.4	2.47×10^{-3}	68.1	75.7	3.07×10^{-3}

rate, if due account was taken of the increase which would have occurred had the pressure remained constant during the period allowed for solution equilibrium. At the new oxygen pressure the absorption rate continued to increase from the approximately proportionate value (Figure 7). When oxidation was prevented by the removal of oxygen by evacuation or by replacement with nitrogen, subsequent exposure to oxygen gave an initial absorption rate lower than that of the previous exposure (Table VI).

Extraction of natural rubber (as ordinarily produced) with acetone reduces its resistance to oxidation by removing a naturally occurring antioxidant. In the experiments recorded here, all of the rubbers examined contained either this natural antioxidant or an added antioxidant, with the single exception of the acetone-extracted specimens. It is thought that, even in the case of these specimens, a small amount of residual, natural antioxidant remained after extraction and that, during the initial oxidation stage when the behavior was similar to that of the other specimens, the residual antioxidant was being destroyed, probably by being oxidized itself. In these experiments, therefore, only the later stage of oxidation of the acetone-extracted specimens showed the oxidation behavior of a rubber in the absence of antioxidant. In all other cases either natural or added antioxidant was present.

CONCLUSIONS FROM CONSTANT PRESSURE EXPERIMENTS

Antioxidant Present. (*a*) Oxidation at constant oxygen pressure reaches a dynamic equilibrium state of reaction at a constant rate. (*b*) This rate is greater the greater the oxygen pressure but increases less rapidly than oxygen pressure. (*c*) If, after the attainment of the state of oxidation at a constant rate, the pressure is reduced to a new constant value, the reaction rate is initially greater than that consistent with the new pressure, but it falls gradually, over a period of several hours, to this value. This effect is more marked the less readily oxidizable the rubber.

Antioxidant Absent. (*d*) The reaction rate at constant pressure increases with increase in combined oxygen proportion. (*e*) The reaction rate at constant pressure is reduced to a lower new starting value by an intermediate period in the absence of oxygen. A considerable reduction necessitates an intermediate period of several hours. (*f*) If, after a period of oxidation at constant pressure, the pressure is changed to a new constant value, the reaction rate changes very rapidly in such a way that it is greater the greater the new pressure and vice versa.

EFFECT OF SHEET THICKNESS ON ABSORPTION RATE

By considering conditions in a thin lamina parallel to the faces of a uniform sheet of rubber containing antioxidant and exposed to oxygen maintained at constant pressure, it may be shown that when the dynamic equilibrium state of absorption at a constant rate has been attained,

$$\frac{d^2c}{dx^2} = \frac{\sigma}{D} F(c)$$

where c = oxygen concentration at a distance x from either face of the sheet
σ = quantity of rubber in unit volume
D = diffusion coefficient of oxygen in the rubber
$F(c)$ = quantity of oxygen which reacts with unit quantity of rubber when oxygen concentration is maintained at c

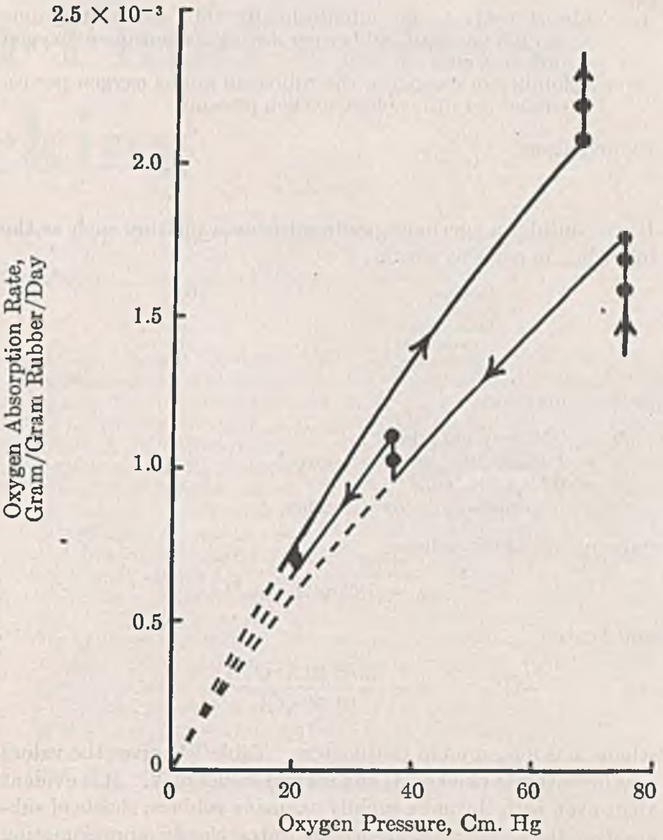

Figure 7. Constant-Pressure Oxidation Behavior of Diphenylguanidine-Vulcanized Rubber after Extraction with Acetone

By making assumptions as to the nature of the function $F(c)$, this equation may be integrated and the integration constants evaluated by using the conditions of symmetry about the center plane and of equilibrium between the oxygen in an infinitesimally thin surface film and the free gaseous oxygen (*3*, *5*). The resulting relations can be used to determine the concentration gradient at the surface and, hence, the absorption rate. Guided by the results of the experiments described, it is tentatively assumed that reaction rate is directly proportional to oxygen concentration. This assumption leads to the following relation:

$$\frac{dQ}{dt} = kc_s \frac{\tanh \frac{\lambda X}{2}}{\frac{\lambda X}{2}}$$

where $\frac{dQ}{dt}$ = oxygen absorption rate
X = thickness of sheet
c_s = solubility of oxygen in rubber at external oxygen pressure
k = proportionality constant relating $F(c)$ and c
$\lambda^2 = \frac{k\sigma}{D}$

If ψ is defined as the ratio of the absorption rate of sheets of thickness X to that of the same quantity of the rubber in the form of infinitesimally thin sheets, it may be shown that

$$\psi = \frac{\tanh \frac{\lambda X}{2}}{\frac{\lambda X}{2}}$$

This relation is applied to the particular cases of natural rubber specimens containing no fillers. Suppose that, at 40° C.,

A_0 = absorption rate for infinitesimally thin sheets in grams oxygen per gram rubber per day at 1 atmosphere oxygen pressure, and

s = solubility of oxygen in the rubber in grams oxygen per cc. rubber per atmosphere oxygen pressure

By definition,

$$k = A_0/s$$

If we consider a specimen produced from a mixture such as the following, in parts by weight,

Rubber	100
Sulfur	3
Zinc oxide	5
Stearic acid	1
Accelerator	0.5

then we may put

D = 0.231 sq. cm./day*

s = 1.16×10^{-4} gram/cc./atm.*

σ = 0.89 gram/cc.

* From unpublished work by the author.

Substituting these values,

$$\lambda = 182 \sqrt{A_0} \text{ cm.}^{-1}$$

and hence

$$\psi = \frac{\tanh 91X\sqrt{A_0}}{91\,X\sqrt{A_0}}$$

where X is measured in centimeters. Table VII gives the values of ψ for several values of A_0 and several values of X. It is evident that, even with the more rapidly oxidizing rubbers, sheets of substantial thickness give absorption rates closely approximating those for infinitesimally thin sheets. With slowly oxidizing rubbers the approximation is close for sheets of considerable thickness. Further subdivision of sheets into rods or cubes gives values for ψ still closer to unity than those shown in Table VII. The results of the experiments recorded differ negligibly from those which would have been obtained by using infinitesimally finely subdivided specimens. In other words, oxygen concentration throughout the specimens was substantially uniform, so that the graphs of absorption rate against oxygen concentration would be of the same shape as those of absorption rate against oxygen pressure.

Confirmation of these conclusions was afforded by the results of an experiment in which the absorption rate of lightly masticated pale crepe rubber was determined using specimens in the form of cubes of about 3-mm. side and a cylinder of 1.4-cm. diameter and 25-cm. length. The determinations were carried out at 40° C. with an oxygen pressure of 75.0 cm. of mercury under conditions of complete darkness. The equilibrium absorption rates were 1.32×10^{-5} and 1.39×10^{-5} gram oxygen per gram rubber per day, respectively. The good agreement shows that with both specimens oxygen concentration was substantially uniform throughout and that, at 40° C. with specimens at least as great as the cylinder, diffusion is negligible as a rate-determining factor with this particular rubber.

DISCUSSION

The oxidation behavior of natural rubber in the absence of antioxidant is in agreement with the free-radical chain reaction theory for the oxidation mechanism of simple, unconjugated olefins proposed by Bolland and Gee (*2*), which was based upon experimental work carried out chiefly on ethyl linoleate.

Sufficient data are not yet available for the extension and modification of this mechanism to include the oxidation behavior of rubbers in the presence of antioxidant. The attainment of a dynamic equilibrium oxidation state, however, suggests that an antioxidant produces its effect by controlling and maintaining at a low constant value the concentration of the first oxidation product, the hydroperoxide ROOH (7) (where RH designates the rubber molecule, H being one of its α-methylenic hydrogen atoms) or the concentration of the free radicals R— and RO_2— to which it gives rise and which are responsible for chain propagation.

Table VII. Values of ψ for Several Values of A_0[a] and X

X, Cm.	ψ $A_0 = 10^{-2}$	 $A_0 = 10^{-3}$	 $A_0 = 10^{-4}$	 $A_0 = 10^{-5}$	 $A_0 = 10^{-6}$
1.0	0.11	0.35	0.79	0.97	1.00
0.75	0.15	0.45	0.87	0.99	1.00
0.5	0.22	0.62	0.94	0.99	1.00
0.25	0.43	0.97	1.00	1.00	1.00
0.1	0.79	0.97	1.00	1.00	1.00

[a] In grams of oxygen per gram of rubber per day at 1 atmosphere oxygen pressure.

SUMMARY AND CONCLUSIONS[1]

Constant-pressure oxidation experiments on natural rubber in the absence of antioxidant confirm that the reaction is autocatalytic and essentially similar to that for the oxidation of simple, unconjugated olefins. The results are in accord with a free-radical chain reaction mechanism. In the presence of antioxidant at constant pressure, rubbers reach a dynamic equilibrium state of oxidation at a constant rate. This rate is greater, the greater the pressure, but increases less rapidly than pressure. Several graphs are given showing the relation between equilibrium oxidation rate and oxygen pressure for several rubbers. If the pressure is reduced and again maintained constant after the attainment of the equilibrium oxidation rate at one pressure, the rate at the new pressure falls slowly over several hours from an initial high value to that consistent with the new pressure. This effect is more marked the less susceptible the rubber to oxidation.

Methods of investigating the rubber-oxygen reaction in which pressure is allowed to fall spontaneously as oxidation proceeds are experimentally shown to lead to erroneous conclusions. The reasons suggested for this are the autocatalytic nature of the reaction in the absence of antioxidants and the persistence of a high oxidation rate after a pressure reduction in the presence of antioxidant. An approximate relation is deduced between uniformity of oxidation, oxidizability, and specimen dimension for rubbers containing antioxidant.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Amerongen, G. J. van, *Rev. gén. caoutchouc*, 20, 136 (1943); *Mededeel. Kunststoffeninstituut Rubber-Stichting* (Amsterdam), No. 39 (March 1944).
(2) Bolland, J. L., and Gee, G., Faraday Soc., Discussion on Oxidation, London, 1945.
(3) Carpenter, A. S., and Twiss, D. F., Ind. Eng. Chem., Anal. Ed., 12, 99 (1940).
(4) Carpenter, A. S., and Twiss, D. F., *Nature*, 154, 673 (1944).
(5) Daynes, H. A., *Proc. Roy. Soc.* (London), A97, 286 (1920).
(6) Dufraisse, C., *et al.*, *Rubber Chem. Tech.*, 11, 268 (1938).
(7) Farmer, E. H., *et al.*, *J. Chem. Soc.*, 1943, 125.
(8) Ingmanson, J. H., and Kemp, A. R., Ind. Eng. Chem., 28, 889 (1936).
(9) *Ibid.*, 30, 1168 (1938).
(10) Kemp, A. R., Ingmanson, J. H., and Mueller, G. S., *Ibid.*, 31, 1472 (1939).
(11) Kohman, G. T., *J. Phys. Chem.*, 33, 226 (1929).
(12) Milligan, A. G., and Shaw, J. E., *Proc. Rubber Tech. Conf.*, *London*, 1938, 537.
(13) Morgan, L. B., and Naunton, W. J. S., *Ibid.*, 1938, 599.
(14) Williams, I., and Neal, A. M., Ind. Eng. Chem., 22, 874 (1930).

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[1] Since the account of this investigation was written, a contribution to the literature [Shelton, J. R., and Winn, Hugh, Ind. Eng. Chem., 38, 71 (1946)] appeared which supports some of our conclusions. Working with GR-S in oxygen maintained at a more or less constant pressure of 1 atmosphere by periodic manual adjustment, they concluded: (*a*) In the presence of antioxidant, GR-S attains a constant oxidation rate; (*b*) after the elimination of antioxidant by oxidation, oxidation of the polymeric material becomes autocatalytic; and (*c*) except for high oxidation rates, diffusion of oxygen is not a rate-controlling factor with reasonably small specimens.

Naphthas from Fluid Catalyst Cracking

C. E. STARR, JR., J. A. TILTON, AND W. G. HOCKBERGER

Esso Laboratories, Standard Oil Company of New Jersey, Louisiana Division, Baton Rouge, La.

The compositions of naphthas derived from cracking with Fluid Catalyst vary within wide limits depending upon changes in operating conditions, types of catalyst employed, and feed stocks used. The compositions of nine naphthas are presented to illustrate the types of products obtained at low and high cracking temperatures with varying cracking severities, employing clay and synthetic catalysts with several paraffinic and naphthenic feed stocks. Composition data show that a number of valuable hydrocarbons, such as toluene, are present in the cracked naphthas to an extent which makes feasible their removal. The flexibility of the Fluid Catalyst cracking process permits operations for production of high quality fuels concurrent with a number of hydrocarbons that are individually valuable as raw materials for chemical manufacture.

THE versatility of the Fluid Catalyst cracking process permits wide variation of product composition. Use of cracked hydrocarbons as raw materials for chemical manufacture has necessitated detailed hydrocarbon analyses of the naphthas and light ends products. Composition studies augment the usual process and quality data and provide a basis for planning treatments to make naphtha products suitable for special uses, such as in aviation fuels. Composition studies also establish the yields and concentrations of specific hydrocarbons, such as toluene and other relatively low boiling aromatics, and certain valuable light hydrocarbons; the latter include isobutane, isobutylene, and normal butenes, which are employed in alkylation processes for the production of aviation fuels of high octane number and in chemical processes for the production of synthetic rubber.

Studies were made of the composition of more than 100 naphthas representing a wide variety of conditions encountered in the Fluid Catalyst cracking process. These conditions comprised operating temperatures of 750–1000° F., feed stock conversions of 35–90%, clay and synthetic catalysts, and low and high boiling naphthenic-type and paraffinic-type feed stocks. Process data for such operations have been described in the literature (*9*, *10*, *11*), as have data for the quality of the Fluid Catalyst–cracked products (*9*). Compositions of nine typical naphthas, selected to represent a wide variation in operating conditions, are presented in this article.

Previously published articles regarding the composition of catalytically cracked gasoline dealt with products from the Houdry fixed-bed process. One paper (*2*) concluded that the high octane number of catalytically cracked gasoline is due to the presence of a large excess of isoparaffins over normal paraffins in the lower boiling portions of the gasoline, and to a high content of aromatic hydrocarbons in the higher boiling fractions. Another paper (*1*) related the effects of feed stock boiling range and of cracking severity to the composition of the cracked gasoline.

METHODS OF ANALYSIS

Total cracked products were distilled in glass stills of approximately twenty-five theoretical plates at 10 to 1 reflux ratio. These stills had columns packed with 3/32-inch metal helices. The pots were of 12-liter capacity, and the reflux regulation was automatically timed. Ten-liter charges were segregated through this equipment into fractions of C_4 and lighter hydrocarbons, gasoline, and bottoms products boiling higher than gasoline. The fractions of C_4 and lighter hydrocarbons were then distilled through Podbielniak Hyd-Robot automatically controlled columns for the segregation of C_4 fractions, which were then analyzed by infrared absorption spectra measurements. The naphthas were distilled by precise fractionation through helix-packed columns of about 100 theoretical plates and with 20 to 1 reflux ratio. Narrow-boiling fractions (usually 2 volume % of charge) were segregated. Charges to these analytical distillation columns were 4000 ml., so that the resultant narrow fractions would amount to about 80 ml. The boiling points of these narrow fractions were obtained by Cottrell distillation. Analyses were made by refractive index measurements and gravity, boiling point, and bromine number determinations.

The olefin content was calculated as mono-olefins from a modified Francis bromine number (*5*) by the following formula:

$$\text{Wt. \% olefins} = \text{bromine number} \times \frac{\text{molecular weight}}{160}$$

The aromatic hydrocarbon content was determined by means of the specific dispersion, corrected for olefin content, according to the method of Grosse and Wackher (*7*). The specific dispersion was calculated by the following formula:

$$\frac{N_F - N_C}{d_4^{20}} \times 10^4$$

where N_F = refractive index of hydrogen F line (4861 Angström units)
N_C = refractive index of hydrogen C line (6563 Angström units)

The refractive index measurements were made with a Bausch & Lomb precision refractometer. The correlations for aromatic hydrocarbon content were checked in a number of instances by removing aromatics by extraction and adding back known amounts of aromatics to aromatic-free stocks of different compositions.

The naphthene hydrocarbon content was arbitrarily designated to include both cycloparaffins and cyclo-olefins. It was determined by means of the specific refraction according to the Lorenz-Lorentz formula:

$$\frac{N^2 - 1}{N^2 + 2} \times \frac{1}{d_4^{20}}$$

where N = refractive index of sodium D line (5893 Angström units)

The naphthene content was determined on the basis of all naphthenes having an average specific refraction value of 0.3300, whereas the average specific refraction of paraffins varies from approximately 0.3380 for a boiling point of 400° to approximately 0.3500 for a boiling point of 100° F.

Specific refractions of cracked naphtha cuts must be corrected for the effect of olefins, including cyclo-olefins and also for the effect of aromatics. After correction the specific refractions of cyclo-olefins in the 100–400° F. boiling range approximate 0.3300 fairly closely, and the specific refractions of acyclic olefins approximate the values for the corresponding paraffins. Consequently, cyclo-olefins are included once as part of the naphthenes and a second time as part of the olefins, without being determined directly as cyclo-olefins. Paraffins cannot, therefore, be determined as the difference between 100% and the sum of aromatics plus naphthenes plus olefins. In the analysis of catalytically cracked naphthas the practice was adopted of reporting one composition giving the acyclic-cyclic division and another giving the olefin-nonolefin division: (*a*) % aromatics + % naphthenes + % acyclics =

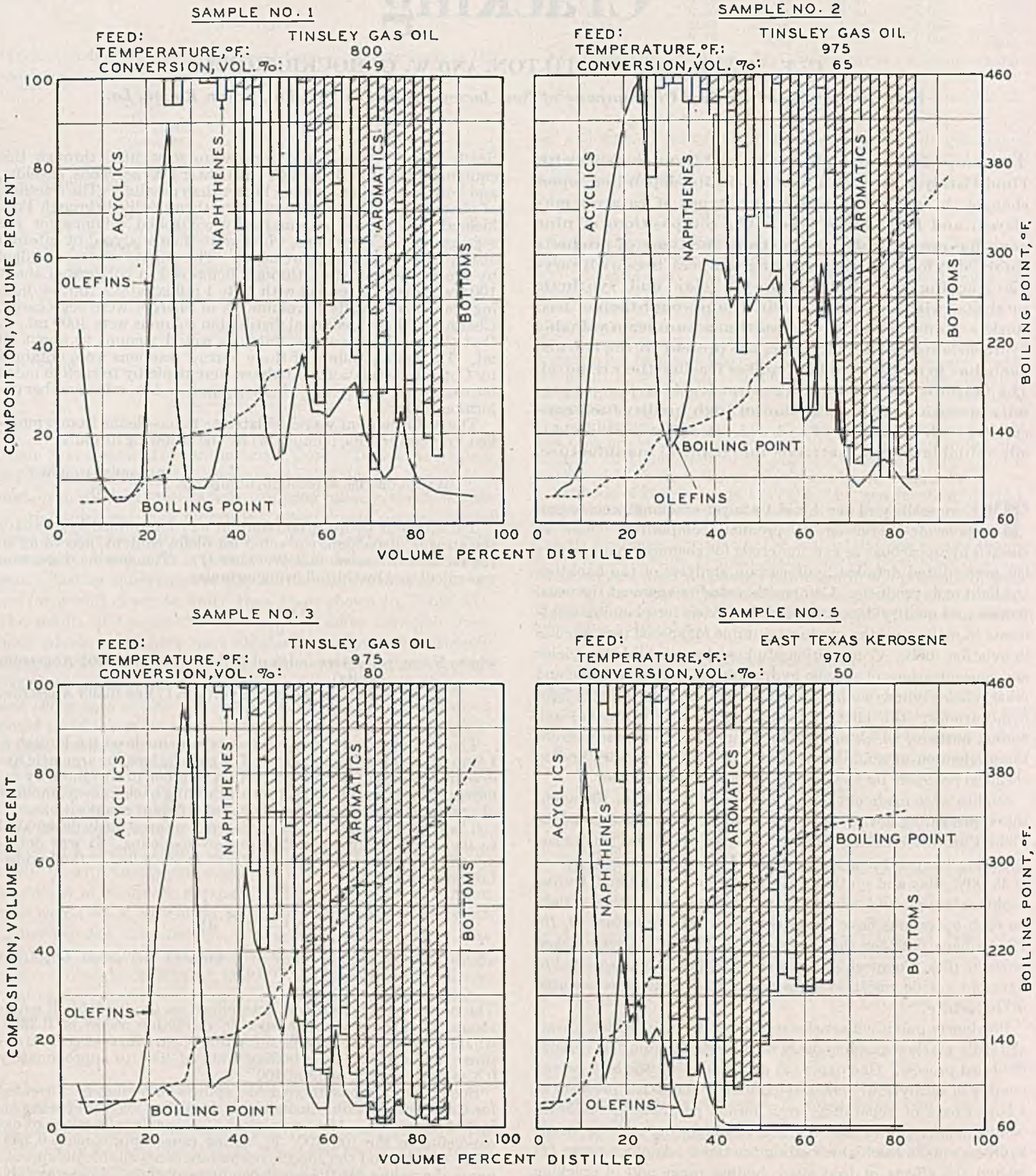

Figure 1. Compositions of Naphthas Produced from Paraffinic Feed Stocks by Cracking with Fluid Silica-Alumina Catalyst

100%; (*b*) % olefins + % nonolefins (aromatics, paraffins, cycloparaffins) = 100%.

A scheme for plotting naphtha compositions was employed (Figure 1) in which areas represent volume per cent composition and in which both acyclic-cyclic and olefin-nonolefin divisions can be shown. Acyclics are represented by the lower portion of each figure, crossed only by coordinate lines, and cyclics are shown in the upper portion of each figure in the form of an inverted block graph, the blocks representing the 2% fractions analyzed. The aromatic portions of the cyclic blocks are differentiated from the naphthene portions by cross hatching. Olefin contents of the 2% fractions are plotted as points at the middle of each fraction; the points are connected by straight lines enclosing an area at the lower portion of the plot which represents approximately the olefin content of the sample. Acyclic and olefin contents are then measured on the vertical composition scale, whereas the content of cyclic hydrocarbons is measured by inverting the composition scale. The boiling points of the 2% fractions are plotted in dashed lines with ordinates, corresponding to the temperature scales at the right-hand sides of the figures.

The feed stocks were characterized as to ring content by the method of Vlugter, Waterman, and van Westen (*13*).

The samples employed in the study of compositions were derived from Fluid Catalyst cracking pilot plants with capacities of 2 and 100 barrels per day (*3*). Operation at various levels of cracking severity and temperature, and use of both essentially naphthenic and paraffinic types of feed stock and clay and silica-alumina synthetic catalyst provided the experimental conditions. The nine samples discussed were obtained from the five feed stocks at the operating conditions given in Table I. Table I also includes the physical properties of the nine naphthas employed for composition studies.

NAPHTHAS FROM PARAFFINIC FEED STOCKS

Samples 1, 2, and 3 were produced by the cracking over silica-alumina synthetic catalyst of an essentially paraffinic-type gas oil boiling between 515° and 700° F. This gas oil (from Tinsley, Miss.) shows by analysis a content of only 11 weight % aromatic rings and 15 weight % naphthene rings. These samples represent low, moderate, and high degrees of cracking severity, respectively. Sample 4, obtained from operations on the same feed stock, represents moderately severe cracking with a clay catalyst. Sample 5 represents a moderately severe cracking operation with synthetic catalyst and a lower boiling, essentially paraffinic-type, feed stock. This feed stock is an East Texas kerosene which boils from 346° to 471° F. and shows, by analysis, 7 weight % aromatic rings and 29 weight % naphthene rings. This feed is classed as a paraffinic type since it was cut from a paraffinic crude and its acyclic carbon atom content is 65%. The aviation gasolines employed for the composition studies had octane numbers ranging from 91 to 97, according to the A.S.T.M. Aviation method, when containing 4 cc. of tetraethyllead per gallon.

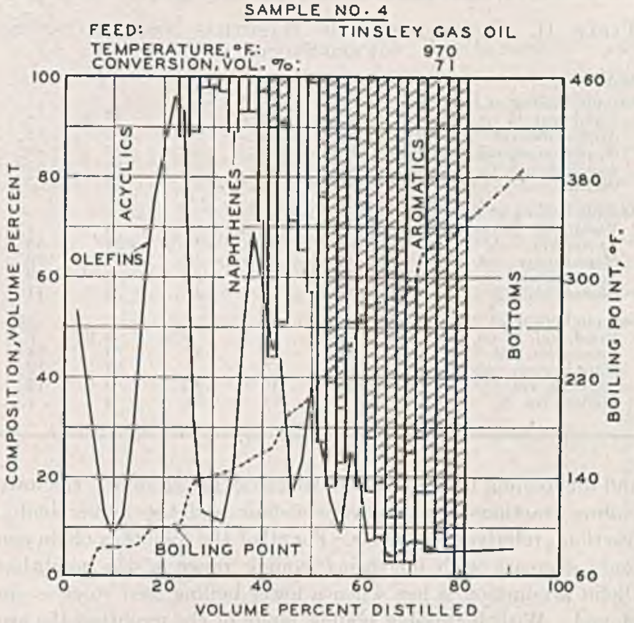

Figure 2. Composition of Naphtha Produced from a Paraffinic Feed Stock by Cracking with Fluid Clay Catalyst

FRACTIONS OF AVIATION GASOLINE BOILING RANGE. Detailed compositions of the naphthas from the paraffinic feeds are presented in Figures 1 and 2. Composition data are summarized in Table II according to the 115–200°, 200–250°, and 250–300° F. boiling range fractions, to illustrate the variant nature of the high

TABLE I. FEED STOCKS AND AVIATION GASOLINES PRODUCED FROM THEM BY FLUID CATALYST CRACKING

	Paraffinic Type					Naphthenic Type			
Feed Stock	*A*, Tinsley gas oil				*B*, E. Texas kerosene	*C*, Light Coastal gas oil		*D*, Heavy Coastal gas oil	*E*, Mirando kerosene
Gravity, ° A.P.I.	32.4				43.4	28.7		23.0	29.2
Aniline point, ° F.	177				141	141		185	112
Carbon, wt. %	86.2				86.0	87.1		86.9	87.4
Hydrogen, wt. %	13.3				14.0	12.9		12.9	12.6
Sulfur, wt. %	0.67				0.02	0.12		0.29	0.06
Composition, wt. %									
Aromatic rings	11				7	12		12	13
Naphthene rings	15				29	35		33	48
Acyclics	74				64	53		55	39
A.S.T.M. distillation, ° F.									
Initial b. p.	515				346	420		495[a]	382
10% over	577				377	515		665	424
50% over	630				404	548		791	475
90% over	695				443	591		900	518
Final	700				471	628		958	552
Cracking conditions									
Sample No.	1	2	3	4	5	6	7	8	9
Catalyst	Synthetic	Synthetic	Synthetic	Clay	Synthetic	Synthetic	Synthetic	Synthetic	Synthetic
Temperature, ° F	800	975	975	970	970	975	975	975	750
Conversion, vol. %[b]	49	65	80	71	50[c]	65	80	65	65
Aviation gasoline (7-lb. Reid vapor pressure)									
Gravity, ° A.P.I.	63.8	60.2	55.5	[d]	55.8	54.1	51.7	60.5	59.6
Aniline point, ° F.	104	66	46	..	57	40	27	71	92
Bromine No., cg./g.	41	63	36	..	29	46	21	102	11
Octane numbers									
A.S.T.M. motor	80.3	80.5	....	..	....	83.0	84.5	79.2	81.2
A.S.T.M. aviation + 4.0 cc. T.E.L./gal.	90.8	90.6	97.1	..	92.3	91.1	95.5	87.0	95.8
A.S.T.M. distillation, ° F.									
% over 158	26.5	26.0	24	..	27.0	23.0	20.5	22.5	23.5
% over 212	58.5	62.0	52.5	..	51.0	49.5	46.0	56.0	58.0
90% over	293	292	301	..	293	294	293	290	265
Final	325	338	340	..	322	326	328	322	290

[a] Distilled at 10 mm. pressure. Values shown have been converted to 760 mm.

[b] Conversion is expressed as 100% minus the per cent gas oil in the product distilling above 430° F. vapor temperature.

[c] Since a high proportion of feed *B* boils below 430° F., conversion of feed *B* is expressed as 100% minus the per cent of product above 325° F.

[d] Aviation gasoline not prepared from this product.

Table II. Compositions of Naphthas from Paraffinic Feed Stocks

Sample No.	1	2	3	4	5
Sample boiling at 115–200° F.					
Yield, vol. % on feed	10.8	10.1	8.0	12.8	6.2
Aromatics, vol. %	1	3	5	2	8
Naphthenes, vol. %	16	16	15	17	29
Acyclics, vol. %	83	81	80	81	63
Olefins, vol. %	24	44	27	33	23
Sample boiling at 200–250° F.					
Yield, vol. % on feed	4.7	4.8	4.2	4.4	4.6
Aromatics, vol. %	13	31	59	33	53
Naphthenes, vol. %	35	30	18	32	29
Acyclics, vol. %	52	39	23	35	18
Olefins, vol. %	28	40	16	23	11
Sample boiling at 250–300° F.					
Yield, vol. % on feed	4.7	5.2	5.3	4.9	7.1
Aromatics, vol. %	36	66	87	76	73
Naphthenes, vol. %	35	15	1	15	12
Acyclics, vol. %	29	19	12	9	15
Olefins, vol. %	19	21	4	8	2

and low boiling fractions of cracked aviation gasoline; the lower boiling fractions are relatively olefinic and the higher boiling fractions, relatively aromatic. For all of the naphthas olefin contents decrease with increasing boiling range of the naphthas. Olefin production is less when a lower boiling feed stock is employed. With increasing boiling range of the naphthas the aromatics content increases. The olefinic fractions can be greatly improved in leaded A.S.T.M. Aviation octane number by hydrogenation to saturate the olefins. Composition data (Figures 1 and 2) are useful for showing the optimum cut points for separation of aviation naphthas into fractions predominantly olefinic and those predominantly aromatic.

The trend of the leaded A.S.T.M. Aviation octane number with increasing boiling point is shown in Figure 3 for samples 2 and 3. (Fractions for octane ratings were distilled through the columns of twenty-five plates.) Up to about 200° F. the A.S.T.M. Aviation octane numbers of narrow fractions fall off rapidly with increasing boiling point; sample 3 shows a higher octane number level because of its lower olefin content. The octane numbers of the fractions above 200° F. show a rising trend in line with increasing aromatics content. The data in Table I show that sample 3 has the highest A.S.T.M. Aviation octane number of the naphthas from the paraffinic feeds; the composition data in Table II indicate that this is due to a low olefin content and to a high aromatics content.

Aromatics. Yields of benzene, toluene, and C_8 aromatics (xylenes and ethylbenzene) produced from paraffinic feed stocks *A* and *B* in samples 1 to 5 (Table III) reveal a tendency toward higher aromatics yield with increasing cracking severity and lower boiling feed. Benzene, a minor product, amounts to only 0.1–0.4 volume % on feed. Even with efficient fractionation the benzene distills overhead well below its boiling point (177.2° F.) and in low concentrations (Figures 1 and 2).

Table III. Yields of Benzene, Toluene, and C_8 Aromatics from Paraffinic Feed Stocks

Sample No.	1	2	3	4	5
Yield, vol. % on feed					
Benzene	0.07	0.29	0.39	0.19	0.41
Toluene	0.62	1.51	2.49	1.44	2.45
C_8 aromatics	1.71	3.39	4.72	3.75	5.21
Total	2.40	5.19	7.60	5.38	8.07

Toluene yields range from 0.6 to 2.5 volume % on feed, values roughly six times as great as the benzene yields. Toluene, like benzene, tends to distill overhead below its boiling point (231.2° F.); however, because of the higher proportions of toluene, it is relatively easier to concentrate. Figures 1 and 2 show that narrow fractions contain as high as 86 volume % toluene.

Yields of xylenes plus ethylbenzene vary from 1.7 to 5.2 volume % on feed; these yields are roughly 2 to 2.5 times as great as toluene yields. The boiling point of ethylbenzene is 277.2° F., of *p*-xylene 281.1° F., of *m*-xylene 282.6° F., and of *o*-xylene 292.1° F. Separation by straight distillation is not practicable. In this study no attempt was made to effect analyses for the individual C_8 aromatics in the naphthas from the paraffinic feeds. The concentrations of C_8 aromatics in narrow fractions from the naphthas from severe cracking of the Tinsley gas oil, or from moderately severe cracking of the lower boiling East Texas kerosene, are as high as 85 to 98 volume %. The C_8 aromatics are useful as high octane number blending constituents or as solvents. *o*-Xylene, which is estimated at about 25 volume % of the C_8 aromatics, has use as a raw material for the production of phthalic anhydride.

Naphthenes. Data given in Table II illustrate that, in general, the highest concentration of naphthenes occurs in the 200–250° F. fractions of the naphthas from the paraffinic feed stocks. Naphthene concentrations are highest when cracking severity is low; when cracking severity is high, the naphthenes in the fractions above 200° F. disappear in favor of increased aromatics content. The composition data show that the concentration of naphthenes is quite constant in the 115–200° F. fractions, regardless of the cracking severity and whether silica-alumina catalyst or clay catalyst is used. The low boiling East Texas kerosene yields a cracked naphtha having relatively higher naphthene concentrations in the 115–200° F. range.

Table IV lists the yields of C_5, C_6, and C_7 naphthenes that may be readily identified by the methods of analysis employed in this study. The cycloparaffin yields necessarily include the corresponding cyclo-olefins. Cyclopentane (boiling point, 120.6° F.) yields on feed are low, from 0.1 to 0.4 volume %. The data in Figures 1 and 2 also show that the concentrations in narrow fractions are low, the highest being 35 volume % for one fraction in sample 3.

Table IV. Yields of Naphthenes[a] from Paraffinic Feed Stocks

Sample No.	1	2	3	4	5
Yield, vol. % on feed					
Cyclopentane	0.1	0.2	0.4	0.2	0.1
Methylcyclopentane + cyclohexane	1.0	0.9	0.8	1.1	1.2
Dimethylcyclopentanes	0.8	0.7	0.4	0.9	0.7
Methylcyclohexane + ethylcyclopentane	0.9	0.6	0.4	0.8	0.7
Total	2.8	2.4	2.0	3.0	2.7

[a] Includes any cyclo-olefins present.

The yields on feed of methylcyclopentane (boiling point, 161.3° F.) and cyclohexane (boiling point, 177.4° F.) are reported together in Table IV. They vary from 0.8–1.2 volume % for the group of naphthas from paraffinic feeds. Figure 1 illustrates that, in the case of sample 5 from East Texas kerosene, the methylcyclopentane plus cyclohexane concentration is as high as 60 volume % in the narrow fractions. The boiling points of the 2% fractions indicate that methylcyclopentane predominates over cyclohexane. Calculated equilibrium compositions for a binary methylcyclopentane-cyclohexane system show 90% methylcyclopentane at 800° F. and 93% methylcyclopentane at 1000° F.

Dimethylcyclopentanes include the 1,1-isomer which boils at 189.5° F., the 1,2-isomers having *cis* and *trans* forms which boil at 211.6° and 197.4° F., respectively, and the 1,3-isomers, which include a *trans* form boiling at 195.6° and a *cis* form probably boiling at about 195° F. The yields of dimethylcyclopentanes reported in Table IV comprise the naphthenes content of the narrow fractions boiling between 180–205° F. The yields on feed of dimethylcyclopentanes amount to 0.4–0.9 volume %.

Yields of methylcyclohexane (boiling point 213.4° F.) and ethylcyclopentane (boiling point 217.6° F.) are reported together in Table IV and vary between 0.4–0.9 volume % for the paraffinic feed stocks. The detailed composition data for the naphtha from the low boiling feed stock (sample 5, Figure 1) show the presence of narrow fractions containing as much as 62 volume % of methylcyclohexane plus ethylcyclopentane.

PARAFFINS AND OLEFINS. These hydrocarbon types have not been completely differentiated by the analytical procedure employed. Unsaturated naphthenes are determined both as olefins and as naphthenes; therefore any estimation of paraffins by subtracting mono-olefins from per cent acyclics would be low by the per cent of diolefins and unsaturated naphthenes. Diolefin contents were generally found to be very low.

An indication of the branchiness of the paraffins and olefins is afforded by analyses of low boiling fractions in which naphthenes contents are negligible—for example, in the C_4, C_5, and C_6 fractions. Yields and olefin contents of C_4 and C_5 fractions are presented in Table V, and compositions of narrow-boiling C_6 fractions are illustrated in Figures 1 and 2. High olefin contents occurred in fractions from gasolines produced at high cracking temperatures with moderate conversions (samples 2 and 4). Ratios of isobutylene to normal butenes for the samples described in this article are on the order of 0.4/1 to 0.5/1, or very close to the equilibrium values calculated from thermodynamic data (*8*). A large number of light hydrocarbon analyses show values ranging from 0.4/1 to 0.7/1 for operations at the same temperature levels. Ratios of isobutane to *n*-butane are, on the other hand, very high, ranging from 4/1 to 8/1. Such ratios are far above the calculated value of 0.5/1. An explanation of the differences between the iso-to-normal ratios for the paraffins and olefins is afforded by Greensfelder and Voge (*6*). They deduce from their studies on the catalytic cracking of pure hydrocarbons that, under suitable reaction conditions, the chain-branching isomerization of normal olefins, followed by saturation by hydrogen transfer, leads to the production of isoparaffins. C_5 fractions are comparable in olefin content to the corresponding C_4 fractions, as shown in Table V.

TABLE V. COMPOSITIONS OF C_4 AND C_5 FRACTIONS FROM PARAFFINIC FEED STOCKS

Sample No.	1	2	3	4	5
C_4 fraction					
Yield on feed, vol. %	10.8	23.6	27.4	20.7	15.9
Butenes, vol. %	29	50	30	44	32
Iso-C_4H_8/n-C_4H_8					
Actual	0.35	0.41	0.46	0.39	0.43
Theoretical equil.	0.67	0.59	0.59	0.59	0.59
Iso-C_4H_{10}/n-C_4H_{10}					
Actual	. .	. .	. .	4.00	8.09
Theoretical equil.	. .	. .	. .	0.45	0.45
C_5 fraction					
Yield on feed, vol. %	9.2	12.8	13.4	14.8	5.8
Amylenes, vol. %	30	47	31	48	31

The data plotted in Figure 1 show that the olefin peaks occur regularly at certain boiling points which characterize particular olefins or groups of olefins. For example, the peak at 100–103° F. is due to trimethylethylene, at 153–158° F. to hexenes, at 203–209° F. to heptenes, at 241–251° F. to octenes, and at 297–301° F. to nonenes. Conversely, broad valleys occur in the olefin curves in the 130–150° F. boiling range; these reflect the presence of sizable proportions of 2-methylpentane and 3-methylpentane. The valleys in the 80–90° F. boiling range are due to isopentane. *n*-Hexane and the higher normal paraffins are present only in small proportions, if at all. This conclusion was confirmed by octane number determinations on narrow-boiling fractions.

NAPHTHAS FROM NAPHTHENIC FEED STOCKS

The last four of the nine samples listed in Table I were obtained by the Fluid Catalyst cracking of three essentially naphthenic-type feed stocks *C*, *D*, and *E*, representing intermediate, high, and low boiling ranges, respectively. Silica-alumina synthetic catalyst was employed in the production of all four naphtha samples. The aviation gasolines from the samples employed for these composition studies had octane numbers ranging from 87 to 96 by the A.S.T.M. Aviation method, when containing 4.0 cc. of tetraethyllead per gallon.

Samples 6 and 7 were produced at 975° F. with moderate and high cracking severities, respectively, from feed *C* (light Coastal gas oil) which distilled between 420° and 628° F.; feed *C* shows, by analysis, a content of 35 weight % naphthene rings and 12 weight % aromatic rings. Sample 8 was produced at 975° F. from feed *D* (heavy Coastal gas oil) boiling between 495° and 958° F. and containing 33 weight % naphthene rings and 12 weight % aromatic rings. High boiling feed *D* is more easily cracked than feed *C*, and, despite equal conversions of feed at the same cracking temperature, sample 8 was actually produced at less severe cracking conditions than was sample 6.

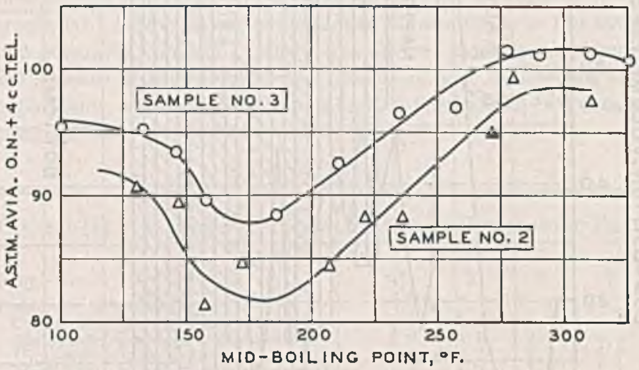

Figure 3. Octane Number Trend with Boiling Point for Cracked Naphthas from Paraffinic Feeds

(A) Sample 2: Tinsley gas oil feed, 975° F., 65% conversion
(B) Sample 3: Tinsley gas oil feed, 975° F., 80% conversion

The last fuel (sample 9) was produced at 750° F. from feed *E* (Mirando kerosene), which distills between 382° and 552° F. and contains 48 weight % naphthene rings and 13 weight % aromatic rings.

FRACTIONS OF AVIATION GASOLINE BOILING RANGE. Table VI lists yields of fractions in the aviation gasoline boiling range of the naphthas from the naphthenic feeds, along with the composition of these fractions. Composition data for these naphthas are given graphically in Figure 4.

Data are presented in Table VI and Figure 4 to show that sample 6 is moderately olefinic with the olefins concentrated in the lower boiling fractions. Relatively high naphthene and aromatic contents are also observed. Sample 7, which is comparable to sample 6 except that it was produced with greater cracking severity, has less olefins and naphthenes and considerably more aromatics. The 200–350° F. boiling range fraction of sample 7 includes many narrow cuts containing greater than 90 volume % aromatics.

In contrast to the products obtained from medium boiling range feed *C*, sample 8 derived from high boiling feed *D* shows a high olefin content. Further, the olefin content increases in the higher boiling fractions, and the olefin contents far exceed the amounts of acyclics present; this indicates that the naphthenes are mostly unsaturated. Aromatics concentrations are relatively low. Aviation gasoline from sample 8 has an A.S.T.M. Aviation octane number with 4.0 cc. of tetraethyllead of 87.0 as compared with 91.1 and 95.5 for samples 6 and 7, respectively; this illustrates the desirability of high aromatic hydrocarbon content and low olefin content in aviation fuel. Supercharged rich mixture octane numbers also are greatly influenced by aromatic hydrocarbon concentrations, the higher concentrations being the most desirable.

Sample 9 is notable for general good quality in having a low olefin content together with relatively high naphthene and aromatic hydrocarbon content; it yields an aviation gasoline having an

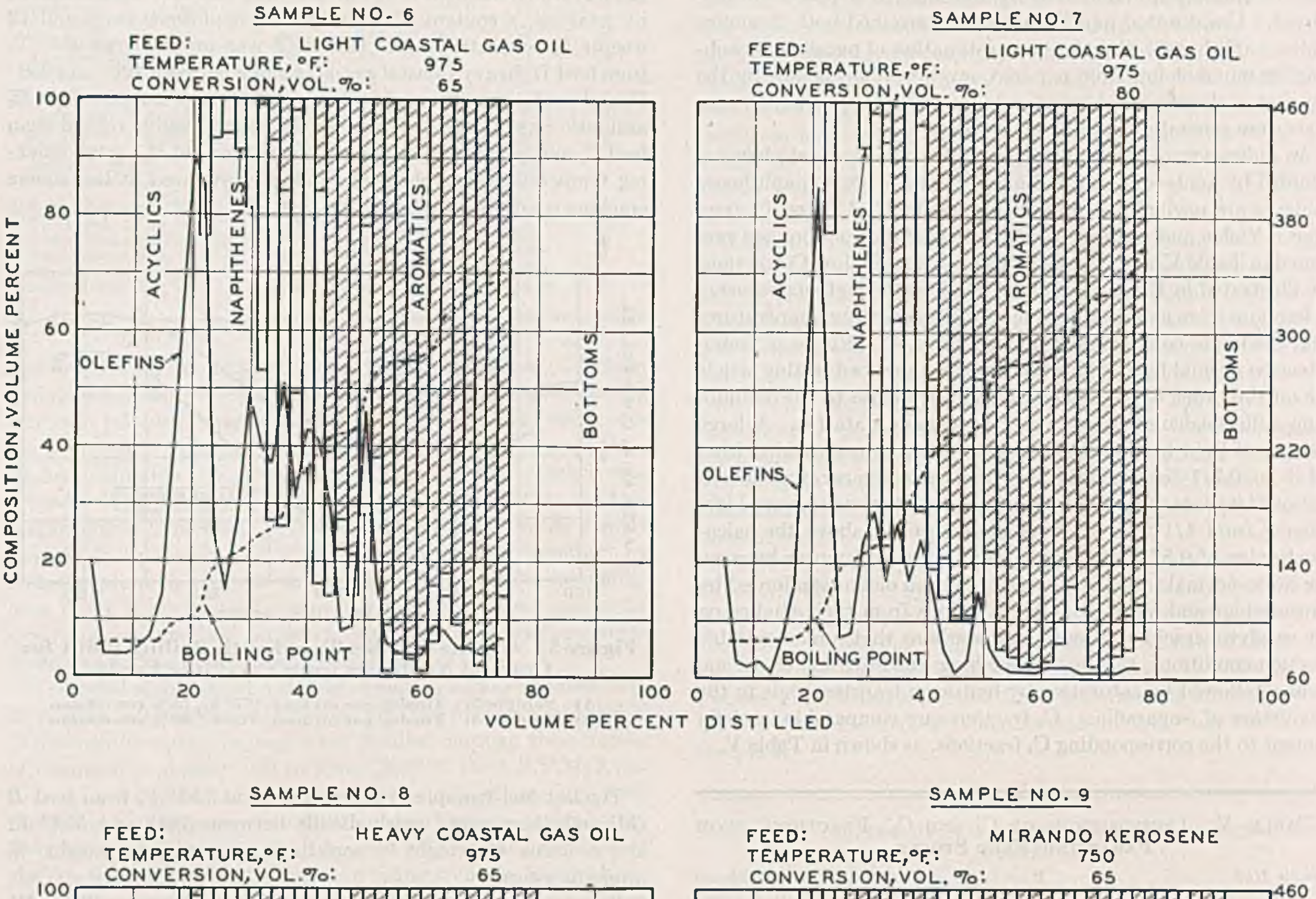

Figure 4. Compositions of Naphthas Produced from Naphthenic Feed Stocks by Cracking with Fluid Silica-Alumina Catalyst

TABLE VI. COMPOSITIONS OF NAPHTHAS FROM NAPHTHENIC FEED STOCKS

Sample No.	6	7	8	9
Sample boiling at 115–200° F.				
Yield, vol. % on feed	10.0	8.5	13.1	8.6
Aromatics, vol. %	3	6	1	4
Naphthenes, vol. %	32	29	29	40
Acyclics, vol. %	65	65	70	56
Olefins, vol. %	34	20	58	6
Sample boiling at 200–250° F.				
Yield, vol. % on feed	5.6	6.4	7.5	5.5
Aromatics, vol. %	44	60	14	30
Naphthenes, vol. %	35	25	45	52
Acyclics, vol. %	21	15	41	18
Olefins, vol. %	28	11	73	8
Sample boiling at 250–300° F.				
Yield, vol. % on feed	6.7	7.4	7.5	6.7
Aromatics, vol. %	83	93	34	55
Naphthenes, vol. %	10	1	40	38
Acyclics, vol. %	7	6	26	7
Olefins, vol. %	11	2	65	6

TABLE VII. YIELDS OF BENZENE, TOLUENE, AND C_8 AROMATICS FROM NAPHTHENIC FEED STOCKS

Sample No.	6	7	8	9
Yield, vol. % on feed				
Benzene	0.27	0.50	0.15	0.38
Toluene	2.46	3.79	1.07	1.66
C_8 aromatics	5.50	6.93	2.58	3.70
Total	8.23	11.22	3.80	5.74

A.S.T.M. Aviation octane number of 95.8 with 4.0 cc. of tetraethyllead per gallon. With few olefins to be saturated, there would be little gain in octane rating from the hydrogenation of this naphtha.

Figure 5 shows the trends of A.S.T.M. Aviation octane numbers with boiling range for samples 6 and 8. The fractions for octane number determinations were distilled through columns of twenty-five plates and show effects of only the more important composition changes. In both samples the octane number improves with increasing boiling point above 200° F.

In the higher boiling range sample 6 has fractions which reach 100 A.S.T.M. Aviation octane number plus 4 cc. of tetraethyllead per gallon. This is attributed to the high content of aromatics, 83 volume % in the 250–300° F. fraction, and to the low olefin content. In contrast, sample 8 shows but a small gain in octane number for the higher boiling fractions, with the best cuts reaching only 91 A.S.T.M. Aviation octane number plus 4 cc. of tetraethyllead per gallon. For sample 8 the aromatic hydrocarbon content is low and the degree of unsaturation is high (Table VI). The data of Table I show that sample 8 has the lowest A.S.T.M. Aviation octane number of all the samples for which data are given in this article; this is in line with the composition data.

AROMATICS. Yields of benzene, toluene, and C_8 aromatics (xylenes and ethylbenzene) produced from the naphthenic feed stocks *C* and *E* in samples 6, 7, and 9 (Table VII) are, for comparable cracking conditions with the same catalyst, higher than those obtained with the paraffinic-type feed stocks. Again a tendency is exhibited for increased aromatics yield with increasing cracking severity and lower boiling feed stocks. Even though it was cracked at the relatively low temperature of 750° F., the product from feed *E* (Mirando kerosene containing 61 weight % rings) showed a relatively high yield of aromatics.

Yields of benzene, toluene, and C_8 aromatics in the case of sample 8, which was derived from high boiling feed *D* (heavy Coastal gas oil) are definitely lower than the corresponding yields obtained from paraffinic feed *A* (Tinsley gas oil) at the same cracking temperature and conversion. These low aromatics yields are no doubt due to the relatively mild cracking conditions actually employed in cracking feed *D* to moderate conversion at 975° F. Aromatics yields and concentrations in fractions from sample 8 are notably improved above 300° F. (Figure 4).

Benzene yields from the naphthenic feed stocks are low, amounting to only 0.15 to 0.50 volume % on feed. As Figure 4 illustrates, the concentrations of benzene in the fractions analyzed are low.

With the same catalyst and under comparable cracking conditions toluene yields from the naphthenic naphthas are higher than those from the naphthas obtained by cracking the paraffinic feed stocks; these yields range from 1.1–3.8 volume % on feed and average roughly 7 times those of benzene. Narrow fractions contain as high as 88 volume % toluene (Figure 4).

Yields of xylenes plus ethylbenzene amount to 2.6–6.9 volume % on feed. These yields are roughly in a 2/1 ratio to comparable toluene yields, the same ratio as found for the paraffinic feed stocks. The yields of C_8 aromatics from the naphthenic feed stocks are, in general, considerably greater than the yields from the paraffinic feed stocks. The data plotted in Figure 4 show that narrow fractions may contain as high as 98 volume % C_8 aromatics. The high concentration of C_8 aromatics in the aviation gasolines from light Coastal gas oil feed stock, with attendant absence of the normally low octane number C_8 acyclics and naphthenes, would contribute to a high, supercharged, rich octane number.

TABLE VIII. YIELDS OF NAPHTHENES[a] FROM NAPHTHENIC FEED STOCKS

Sample No.	6	7	8	9
Yield, vol. % on feed				
Cyclopentane	0.3	0.2	0.5	0.1
Methylcyclopentane + cyclohexane	1.9	1.6	2.5	2.1
Dimethylcyclopentanes	1.1	0.7	1.7	1.7
Methylcyclohexane + ethylcyclopentane	1.3	1.1	1.7	1.7
Total	4.6	3.6	6.4	5.6

[a] Includes any cyclo-olefins present.

Analysis of the C_8 aromatics contained in samples 6, 7, and 8 was made by the Petroleum Refining Laboratory of the Pennsylvania State College with Raman spectra measurements (*4*). The analyses showed that, within the limit of error of the determination, the proportion of ethylbenzene in the C_8 aromatics was the same for each of the three samples (9 to 13 volume % on the total C_8 aromatics). Also the proportions of *p*-xylene (15 to 22%), *m*-xylene (43–48%), and *o*-xylene (20–32%) were not appreciably different in the three samples. The C_8 aromatics from a naphtha comparable to sample 3 have approximately the same distribution of the four C_8 aromatics. Equilibrium data obtained at the National Bureau of Standards (*12*) show that at 975° F. the ethylbenzene concentration in C_8 aromatics is 14 volume %, the *p*-xylene concentration is 20 volume %, the *m*-xylene 42 volume %, and the *o*-xylene 24 volume %. These values agree reasonably well with the analyses obtained on the Fluid Catalyst–cracked C_8 aromatics.

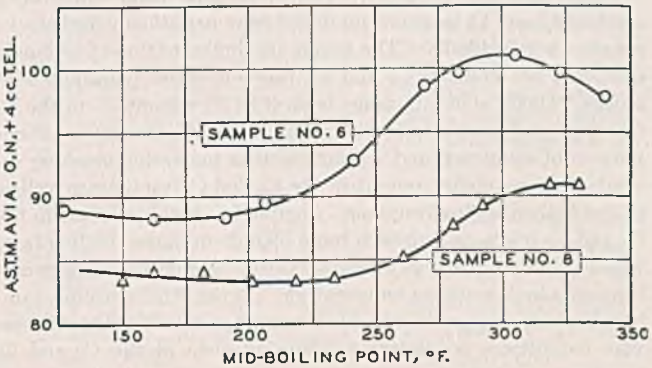

Figure 5. Octane Number Trend with Boiling Point for Cracked Naphthas from Naphthenic Feeds

(A) Sample 6: light Coastal gas oil feed, 975° F., 65% conversion
(B) Sample 8: heavy Coastal gas oil feed, 975° F., 65% conversion

NAPHTHENES. As in the case of the products from paraffinic feed stocks, the naphthene contents of the naphthas from naphthenic-type feed stocks are higher at conditions of low cracking severity and higher boiling feed stocks from a given type of feed. Very high concentrations of naphthenes in the fractions of aviation gasoline boiling range are obtained by low temperature cracking of Mirando kerosene, a feed that has 61 weight % rings. The olefin contents of the fractions boiling higher than 200° F. in the naphtha from heavy Coastal gas oil feed stock are greater than the content of acyclics; this indicates the presence of unsaturated naphthenes (cyclo-olefins).

Table VIII furnishes yield data for the main naphthene hydrocarbons identified in the cracked samples obtained from naphthenic feed stocks. Cycloparaffin yields necessarily include the corresponding cyclo-olefins. Cyclopentane yields are low, as was the case with the paraffinic feed stocks; they range from 0.1–0.5 volume % on feed. The data of Figure 4 show that the highest concentration of cyclopentane measured in a narrow fraction is 28 volume % (sample 8).

Yields of methylcyclopentane plus cyclohexane are about twice as great as those obtained from the paraffinic feed stocks; they range from 1.6–2.5 volume % on feed. Narrow fractions from all of the naphthas studied have relatively high concentrations of naphthenes, on the order of 70 volume %, in the 150° to 180° F. boiling range (Figure 4).

TABLE IX. COMPOSITIONS OF C_4 AND C_5 FRACTIONS FROM NAPHTHENIC FEED STOCKS

Sample No.	6	7	8	9
C_4 fraction				
Yield on feed, vol. %	17.7	23.6	14.6	10.8
Butenes, vol. %	31	23	56	9
Iso-C_4H_8/n-C_4H_8				
Actual	0.48	0.46	0.55	..
Theoretical equil.	0.59	0.59	0.59	..
Iso-C_4H_{10}/n-C_4H_{10}				
Actual	5.25	5.06	4.27	..
Theoretical equil.	0.45	0.45	0.45	..
C_5 fraction				
Yield on feed, vol. %	12.5	12.7	11.3	6.5
Amylenes, vol. %	31	20	58	8

Dimethylcyclopentenes are present to the extent of 0.7–1.7 volume % on feed, or in amounts approximately twice as great as were found to occur with paraffinic feed stocks. Concentration of the dimethylcyclopentanes in narrow fractions is, however, not exceptionally high; it is only about 50 volume % in the most concentrated fractions.

The yields of methylcyclohexane plus ethylcyclopentane range from 1.1 to 1.7 volume % on feed. Again, these yields are about twice as great as the yields of methylcyclohexane plus ethylcyclopentane from the paraffinic feed stocks. The concentration of these naphthenes in narrow fractions is generally high, and, in the case of sample 9, shows as much as 80 volume %.

PARAFFINS AND OLEFINS. The yields and olefin contents of cracked C_4 and C_5 fractions produced from naphthenic feed stocks are shown in Table IX. The trends are similar to those previously discussed for cracked C_4 and C_5 fractions from paraffinic feed stocks. Olefin contents range from 9 to 56 volume % in the C_4 fractions and from 8 to 58 volume % in the C_5 fractions. Comparison of samples 6 and 7 indicates that increasing cracking severity reduces olefin content in the C_4 and C_5 fractions as well as in the higher boiling fractions. Sample 8 is highly olefinic in the C_4 and C_5 fractions but even more olefinic in higher boiling fractions. Sample 8 is really representative of mild cracking conditions at a high cracking temperature. At the other extreme, sample 9, which was produced at low temperature with otherwise severe conditions, is relatively saturated even in the C_4 and C_5 fractions.

Cyclo-olefins (unsaturated naphthenes) are believed to be present in all of the cracked naphthas here considered. Particularly with the samples from naphthenic feed stocks the evidence points to large concentrations of unsaturated naphthenes. It has already been noted that sample 8 has amounts of olefins far in excess of the acyclics. One narrow fraction from sample 8 boiling at 258° F. is indicated to contain 72 volume % naphthenes and 95 volume % olefins (Figure 4). The olefin peaks previously described for samples from paraffinic feeds are supplemented by a well defined peak at 165–172° F. denoting methylcyclopentenes (Figure 4).

To demonstrate that the analytical procedure employed in these studies is capable of consistent evaluation of naphthene contents regardless of the presence of cyclo-olefins, a cracked 205–225° F. fraction having an olefin content in excess of acyclics content was analyzed for methylcyclohexane-methylcyclohexene in three ways: (*a*) untreated, (*b*) mildly hydrogenated to saturate only the olefins, and (*c*) extracted to remove all olefins and aromatics. Based on the original fraction the methylcyclohexane yields for (*a*) and (*b*) were approximately the same, but a marked reduction occurred in (*c*) due to removal of cyclo-olefins.

CONCLUSIONS

The salient compositional features of Fluid Catalyst–cracked light naphthas comprise the olefin content and the concentrations of toluene and C_8 aromatics. High octane numbers are favored by a composition such that the fractions of 200–300° F. boiling range contain toluene plus C_8 aromatics in a concentration on the order of 50 to 80 volume %. Olefin contents of the fractions below 200° F. boiling point may vary over the range of 10 to 60 volume % and require selections in regard to finishing treatment and use, since olefins are desirable in motor fuels but are objectionable in aviation fuels.

Naphthas from naphthenic-type feed stocks are characterized by high yields on feed together with high aromatics concentrations; this reflects higher yields of toluene and C_8 aromatics than are obtained by cracking paraffinic-type feed stocks under comparable conditions. Yields of naphthenes and cyclo-olefins tend to be higher in naphthas from naphthenic feed stocks, but yields of the C_4-C_7 paraffins and olefins are reduced.

The Fluid Catalyst cracking process is highly flexible, and the cracked naphthas obtained are sources for a number of valuable hydrocarbons or groups of hydrocarbons that are useful as raw materials for chemical manufacture or for production of high quality polymers, alkylates, and solvents. Such hydrocarbons are toluene, C_8 aromatics, moderately branched C_4-C_8 paraffins and olefins, straight-chain C_4-C_5 olefins, and C_6-C_7 alkylnaphthenes and cyclo-olefins. Fluid Catalyst–cracked naphthas are less promising as direct sources of benzene, cyclopentane, cyclohexane, normal paraffins, and diolefins.

LITERATURE CITED

(1) Ardern, D. B., Newton, R. H., and Barcus, G. L., IND. ENG. CHEM., 37, 546 (1945).
(2) Bates, J. R., Rose, F. W., Jr., Kurtz, S. S., Jr., and Mills, I. W., *Ibid.*, 34, 147 (1942).
(3) Carlsmith, L. E., and Johnson, F. B., *Ibid.*, 37, 451 (1945).
(4) Fenske, M. R., private communication, Mar. 19, 1945.
(5) Francis, A. W., IND. ENG. CHEM., 18, 821 (1926).
(6) Greensfelder, B. S., and Voge, H. H., *Ibid.*, 37, 983 (1945).
(7) Grosse, A. V., and Wackher, R. C., IND. ENG. CHEM., ANAL. ED., 11, 614 (1939).
(8) Kilpatrick, J. E., Prosen, E. J., Pitzer, K. S., and Rossini, F. D., *J. Research Natl. Bur. Standards*, 36, 559 (1946).
(9) Mateer, G. L., and Haney, J. D., *Oil Gas J.*, 43, No. 9, 87 (1944).
(10) Murphree, E. V., Brown, C. L., Gohr, E. J., Jahnig, C. E., Martin, H. Z., and Tyson, C. W., *Trans. Am. Inst. Chem. Engrs.*, 41, 19 (1945).
(11) Murphree, E. V., Fischer, H. G. M., Gohr, E. J., Sweeney, W. J., and Brown, C. L., *Petroleum Refiner*, 22, 371–6 (1943); *Natl. Petroleum News*, 35, R577–8 (1943).
(12) Taylor, W. J., Wagman, D. D., Williams, M. G., Pitzer, K. S., and Rossini, F. D., *J. Research Natl. Bur. Standards*, 37 95 (1946).
(13) Vlugter, J. C., Waterman, H. I., and Westen, H. A. van, *J. Ins Petroleum Tech.*, 21, 661 (1935).

Optimum Dilution in Viscous Liquid Filtration

E. J. REEVES

Magnolia Petroleum Company, Beaumont, Texas

A useful relation is derived for calculating optimum dilution in viscous liquid filtration. This relation is based on an empirical equation which was developed for expressing viscosity of filtrate as a function of solvent dilution. By using pertinent mathematical equations, the method can be adapted to dilution filtration of any viscous liquid. Observed and calculated data are shown to be in good agreement.

VISCOSITY of the liquid subjected to filtering operation is one of the major factors governing filtering rates. Assuming all other variables constant, the rate of filtration is inversely proportional to the absolute viscosity of the filtrate; this suggests dilution of viscous liquids with nonviscous solvents in order to increase the filter output.

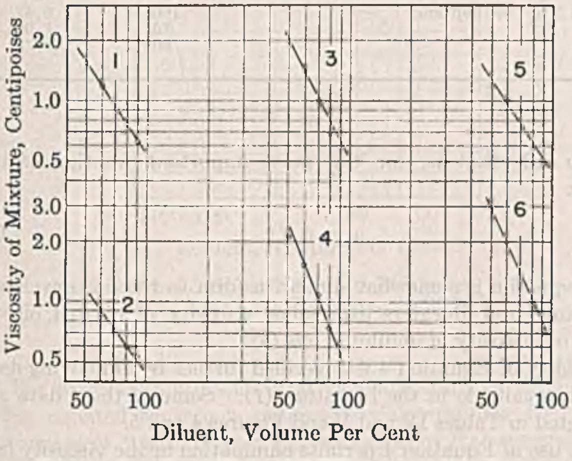

Figure 1. Paraffinic Oil Mixtures with Low Viscosity Diluents at 54.4° C.

Curve numbers on all figures refer to system numbers in corresponding tables.

In applying this procedure to practical problems, the major consideration is not an increase in the total quantity of filtrate, but an increase in the amount of the solvent-free material in the filtrate. This shows that for raising the efficiency of filtering operations dilutions should not exceed a certain optimum, which varies with the nature of the material to be filtered. The optimum dilution is determined normally on the basis of plant experience; however, it can be calculated mathematically from the known properties of the involved materials. The method described in this paper applies to filtration of petroleum oils in dewaxing operations but may be easily adapted to other engineering problems of a similar nature by employing pertinent mathematical relations.

The general Poiseuille equation (*2*) for homogeneous sludges may be presented in the following form:

$$\frac{dV}{Ad\theta} = \frac{P}{\mu[\alpha(W/A) + r]} \qquad (1)$$

Integration of Equation 1 for constant pressure filtration gives the relation between time and filtrate.

$$\frac{\theta}{V/A} = \frac{\mu\alpha}{2P}\left(\frac{W}{A}\right) + \frac{\mu r}{P} \qquad (2)$$

Assuming that F represents the fraction of solvent in the total filtrate, the rate of oil flow through the filter may be obtained by dividing Equation 2 by $(1-F)$; this leads to the expression

$$\frac{\theta}{V/A(1-F)} = \frac{1}{R} = \frac{\mu\alpha}{2P(1-F)}\left(\frac{W}{A}\right) + \frac{\mu r}{P(1-F)} \qquad (3)$$

The solvent fraction and viscosity of the total filtrate in Equation 3 are interdependent variables and should be expressed in the same terms in order to permit further analysis of the problem. This requires determination of the function connecting the two variables.

Up to the present time no satisfactory relation has been found which could be employed for this purpose. This work was undertaken, therefore, to derive a relation which would hold over a reasonable dilution range commonly encountered in commercial practice. A large number of blends involving various types of commercial products and solvents was prepared and tested:

Oil A = dewaxed mid-continent distillate of 160-second S.U.V. at 100° F.
Oil B = solvent-treated and dewaxed mid-continent neutral of 105-second S.U.V. at 100° F.
Oil C = solvent-treated and dewaxed mid-continent residual oil of 103-second S.U.V. at 210° F.
Oil D = solvent-treated and dewaxed mid-continent residual oil of 98-second S.U.V. at 210° F.
Oil E = solvent-treated and dewaxed mid-continent neutral of 150-second S.U.V. at 100° F.
Oil F = solvent-treated and dewaxed mid-continent neutral of 150-second S.U.V. at 100° F.
Oil G = solvent-treated and dewaxed mid-continent residual oil of 98-second S.U.V. at 210° F.
Oil H = solvent-treated and dewaxed mid-continent residual oil of 125-second S.U.V. at 210° F.

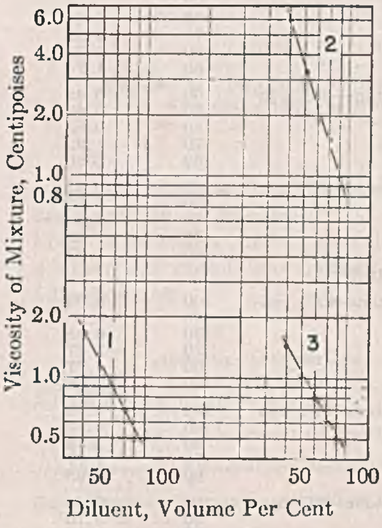

Figure 2. Paraffinic Oil Mixtures with Low Viscosity Diluents at 37.8° C.

On the basis of this information, the most pertinent portions of which are presented in Tables I, II, and III, and Figures 1, 2, and 3, the following relation was found to hold for the values of F ranging from

Table I. Paraffinic Oil Mixtures with Low Viscosity Diluents at 54.4° C.

	Diluents, Vol. %	Viscosity, Centipoises
1. Oil A + methyl ethyl ketone	90	0.63
	80	0.77
	70	0.92
	60	1.20
	50	1.54
2. Oil B + toluene	90	0.54
	80	0.60
	70	0.73
	60	0.92
3. Oil C + 50% methyl ethyl ketone–50% toluene	90	0.62
	80	0.69
	70	1.04
	60	1.41
	50	1.97
4. Oil D + toluene	90	0.56
	80	0.75
	70	1.10
	60	1.55
	50	2.16
5. Oil A + toluene	90	0.52
	80	0.61
	70	0.75
	60	0.99
	50	1.27
6. Oil C + 50% toluene–50% isopropyl alcohol	90	0.72
	80	1.03
	70	1.40
	60	1.99
	50	2.88

Table II. Paraffinic Oil Mixtures with Low Viscosity Diluents at 37.8° C.

	Diluents, Vol. %	Viscosity, Centipoises
1. Oil D + methyl ethyl ketone	90	0.50
	80	0.69
	70	..
	60	1.19
	50	1.68
2. Oil D + naphtha	90	0.98
	80	1.51
	70	2.21
	60	3.31
	50	5.84
3 Oil E + 50% methyl ethyl ketone–50% toluene	90	0.52
	80	0.63
	70	0.81
	60	1.04
	50	1.43

Table III. Paraffinic Oil Mixtures with Low Viscosity Diluents at 37.8° C. and 15.5° C.

	Diluents, Vol. %	Viscosity, Centipoises
At 37.8° C.		
1. Oil F + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.42
	90	..
	80	0.66
	70	0.85
	60	1.21
	50	1.74
3. Oil H + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.42
	90	0.59
	80	0.83
	70	1.22
	60	1.90
5. Oil G + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.42
	90	0.58
	80	0.82
	70	1.20
	60	1.81
At 15.5° C.		
2. Oil F + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.54
	90	..
	80	0.88
	70	1.17
	60	1.77
	50	2.68
4. Oil H + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.54
	90	0.78
	80	1.14
	70	1.77
	60	2.98
6. Oil G + 40% methyl ethyl ketone–40% benzene–20% toluene	100	0.54
	90	0.76
	80	1.12
	70	1.73
	60	2.80

Table IV. Paraffinic Oil Mixtures with Low Viscosity Diluents at 20° C. (*1*)

	Diluents, Vol. %	Viscosity, Centipoises
1. Oil No. 1 + heptane	100	0.47
	74.7	1.15
	54.2	3.41
2. Oil No. 1 + benzene	100	0.65
	74.8	1.26
	49.6	3.26
3. Oil No. 2 + kerosene	100	1.92
	74.4	6.15
	61.3	12.47
	59.8	14.01
4. Oil No. 3 + ligroin	100	0.66
	69.3	2.69
	50.4	8.35

Table V. Naphthenic Oil Mixtures with Low Viscosity Diluents at 0° and 20° C. (*1*)

	Diluents, Vol. %	Viscosity, Centipoises
At 0° C.		
1. Oil No. 5 + heptane	100	0.57
	75.0	1.39
	50.0	4.96
3. Oil No. 6 + heptane	100	0.57
	74.9	1.54
	49.9	6.35
At 20° C.		
2. Oil No. 5 + heptane	100	0.47
	75.2	1.01
	50.2	2.98
4. Oil No. 6 + heptane	100	0.47
	75.1	1.09
	50.2	3.66
5. Oil No. 7 + heptane	100	0.47
	75.1	1.00
	50.1	2.72

0.5 to 1.0—that is, for the most important fraction of the curve:

$$\mu = \beta F^{\gamma} \tag{4}$$

This equation is somewhat similar in form to the one developed by Tausz and Roegiers expressing viscosity of diluted oils in terms of viscosity of undiluted oils (*3*).

Validity of Equation 4 was verified further by employing data already available in the literature (*1*). Some of these data are presented in Tables IV and V and Figures 4 and 5.

The use of Equation 4 permits elimination of the viscosity factor from Equation 3, which is reduced to the following form:

$$\frac{1}{R} = \frac{F^{\gamma}}{1 - F}\left[\frac{\beta\alpha}{2P}\left(\frac{W}{A}\right) + \frac{\beta r}{P}\right] \tag{5}$$

Equation 5 can be used for determining the optimum dilution by differentiating R with respect to F and equating the resulting derivative to zero to find the maxima of the function. The first derivative is equal to

$$\frac{\delta R}{\delta F} = \frac{2P}{\beta\alpha\left(\frac{W}{A}\right) + 2\beta r}\left[\frac{(\gamma - 1) - \gamma F^{-1}}{F^{\gamma}}\right] \tag{6}$$

When equating Equation 6 to zero the only equation of interest is

$$(\gamma - 1) - \gamma F^{-1} = 0 \tag{7}$$

From this equation it follows that the optimum dilution is equal to

$$F = \frac{\gamma}{\gamma - 1} \tag{8}$$

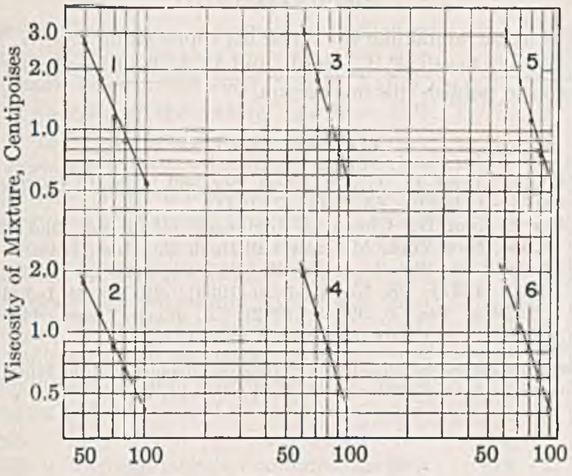

Figure 3. Paraffinic Oil Mixtures with Low Viscosity Diluents at 37.8° and 15.5° C.

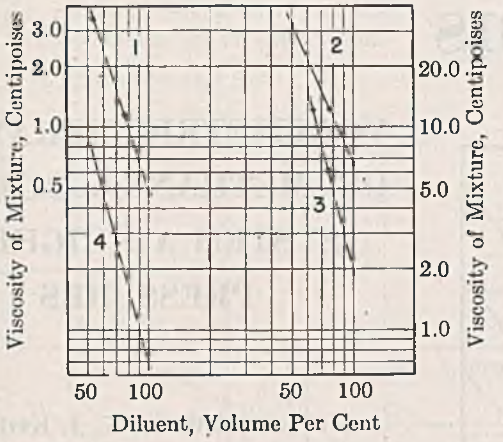

Figure 4. Paraffinic Oil Mixtures with Low Viscosity Diluents at 20° C.

The proof that Equation 6 gives a maximum of the function when equated to zero is obtained by determining the partial derivative of R with respect to F at values of F above and below the maximum point. These points are

$$F = \frac{\gamma}{\gamma - 1} + x \qquad (9)$$

$$F = \frac{\gamma}{\gamma - 1} - x \qquad (10)$$

The first partial derivative at the point determined by Equation 9 is negative, and that determined by Equation 10 is positive. This change in the slope of the curve defined by Equation 5 definitely proves the existence of a maximum.

The use of Equation 8 for solution of practical problems is demonstrated by the following example; the laboratory data were secured on diluting a wax-free oil with solvent. The table presents the properties of a dewaxed lubricating oil of 126-second Saybolt Universal Viscosity (S.U.V.) at 210° F. diluted with methyl ethyl ketone–benzene–toluene mixture:

Solvent fraction, vol. %	0.60	0.90
Viscosity at filtering temp., centipoises	6.26	1.02

Substituting these data in Equation 4 the value of the constant γ is

$$\gamma = -4.48 \qquad (11)$$

The optimum quantity of solvent is determined by substituting this value of γ in Equation 8:

$$F = \frac{\gamma}{\gamma - 1} = \frac{-4.48}{-4.48-1} = 0.818 \qquad (12)$$

Optimum composition of the filtrate is, therefore,

Solvent, vol. %	81.8
Oil, vol. %	18.2

In actual plant operations, dilutions are not based on wax-free filtrate, but on oil charge. Correction for the wax fraction is therefore important and can be made by using the relation

$$S = \frac{F}{F + \dfrac{1 - F}{1 - v}} \qquad (13)$$

Assuming 14 volume % wax in the oil charge, the optimum dilution of the oil charge is

$$S = \frac{0.818}{0.818 + \dfrac{1 - 0.818}{1 - 0.14}} = 0.794 \qquad (14)$$

Thus, optimum filter charge composition is

Solvent, vol. %	79.4
Waxy oil, vol. %	20.6

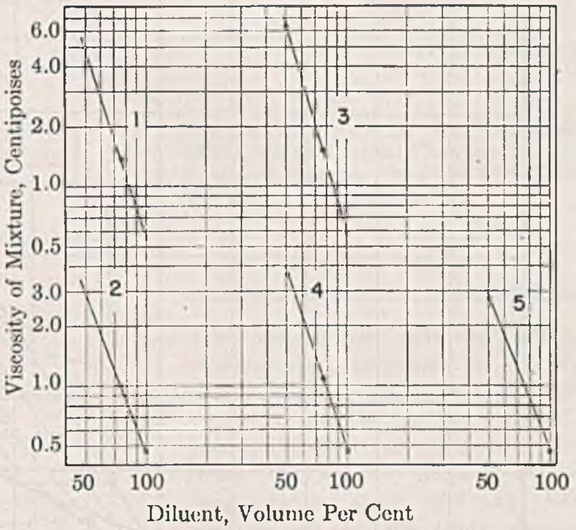

Figure 5. Naphthenic Oil Mixtures with Low Viscosity Diluents at 0° and 20° C.

The recommended method was tested in commercial practice and found to be satisfactory for establishing operating conditions at dewaxing units. Calculated and observed optimum dilutions for various lubricating oil fractions are shown in the following table:

Lubricating Oil Fraction	Optimum Dilution Calcd.	Optimum Dilution Obsvd.[a]
Mid-continent distillate 145-sec. S.U.V. at 100° F.	67	67
Solvent-treated, mid-continent neutral 105-sec. S.U.V. at 100° F.	66	67
Solvent-treated, mid-continent neutral 185-sec. S.U.V. at 100° F.	68	68
Solvent-treated, mid-continent residual 96-sec. S.U.V. at 210° F.	76	76
Solvent-treated, mid-continent residual 120-sec S.U.V. at 210° F.	78	79
Acid-treated, mid-continent residual 190-sec. S.U.V. at 210° F.	82	82

[a] Observed dilutions were determined in commercial operation of a methyl-ethyl-ketone dewaxing unit.

NOMENCLATURE

A = area of filtering surface
F = fraction of solvent in total filtrate
P = pressure drop through filter medium and cake
r = filter medium resistance
R = solvent-free liquors rate per unit area
S = fraction of solvent in waxy oil charge
v = volume per cent wax in oil charge
V = volume of filtrate
W = weight of dry cake solids
α = average specific cake resistance
β = viscosity of diluent
γ = slope of viscosity–solvent fraction curve
θ = time
μ = viscosity of filtrate
χ = incremental value of F

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LITERATURE CITED

(1) Irany, Ernest P., *J. Am. Chem. Soc.*, 60, 2106–15 (1938); 61, 1734–9 (1939); 63, 2611–17 (1941).
(2) Perry, John H., Chemical Engineers' Handbook, 2nd ed., p. 1654, New York, McGraw-Hill Book Co., Inc., 1941.
(3) Tausz *et al.*, *Petroleum Z.*, 26, 1117–24, 1129–40 (1930); 26, 41–3 (1931); 28, No. 45, 1–10 (1933); 29, No. 24, 1–3 (1933); *Erdöl u. Teer*, 8, 396–8 (1932); *Z. angew. Chem.*, 44, 884–6 (1931); Roegiers, *Ibid.*, 45, 320–3 (1932).

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Phase Equilibria in Hydrocarbon Systems

VOLUMETRIC BEHAVIOR OF METHANE–*n*-BUTANE SYSTEM AT HIGHER PRESSURES

H. H. REAMER, K. J. KORPI,
B. H. SAGE, AND W. N. LACEY
California Institute of Technology,
Pasadena, Calif.

THE volumetric behavior of the methane–*n*-butane system was studied earlier in this laboratory at temperatures between 70° and 250° F. and at pressures up to 3000 pounds per square inch for a number of experimental compositions in the one- and two-phase regions (*9*, *10*). Beattie *et al.* (*2*) investigated three mixtures approximating 0.25, 0.50, and 0.75 mole fraction methane in the single-phase area from 167° to 572° F. and up to 5300 pounds per square inch. The pressure-volume-temperature properties of the separate components, methane (*4–7*) and *n*-butane (*1*, *3*, *8*), were determined by several investigators. Since this binary system is of importance industrially and constitutes a part of the ternary methane–*n*-butane–decane system which is under investigation, the experimental data on four mixtures were extended to include temperatures from 100° to 460° F. at pressures up to 10,000 pounds per square inch, the measurements being confined to the single-phase region.

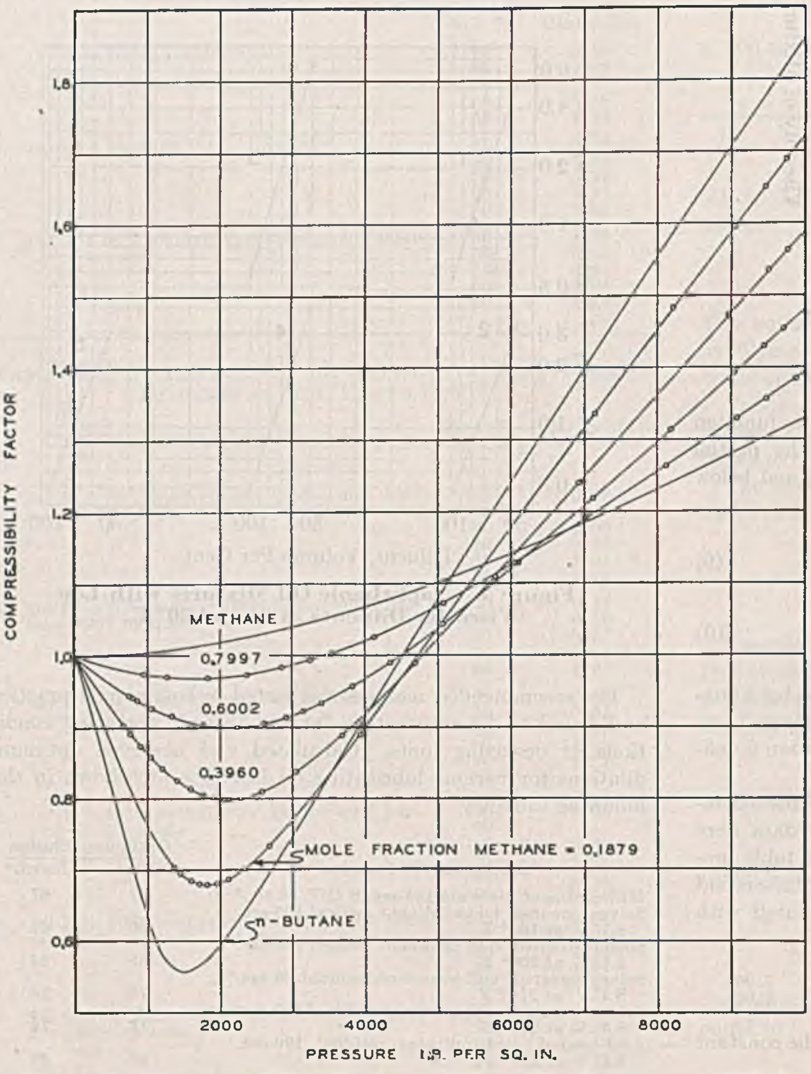

Figure 1. Compressibility Factor as Affected by Pressure at 460° F. for Four Mixtures of Methane and *n*-Butane

MATERIALS AND METHOD

The methane was obtained through the courtesy of The Texas Company from the Bowerbank field in the San Joaquin Valley, Calif. Analysis of the natural gas from this field revealed the presence of less than 0.1% of materials other than methane, mainly carbon dioxide. The purification (7) was effected by passing the gas through a drying and absorption tube at pressures in excess of 500 pounds per square inch over calcium chloride, activated charcoal, potassium hydroxide, and Drierite (a specially prepared anhydrous calcium sulfate). The *n*-butane, obtained from the Phillips Petroleum Company, was stated to contain not less than 0.99 mole fraction *n*-butane. This material was fractionated twice in a 4-foot, vacuum-jacketed column; the first and last tenths were discarded each time, and the middle fraction was collected at liquid-air temperature in a continuously evacuated ampoule in order to remove traces of noncondensable gases. Checks made on the vapor pressure of the resulting sample over a wide range of total volumes in the pressure-volume-

(*Continued on page 208*)

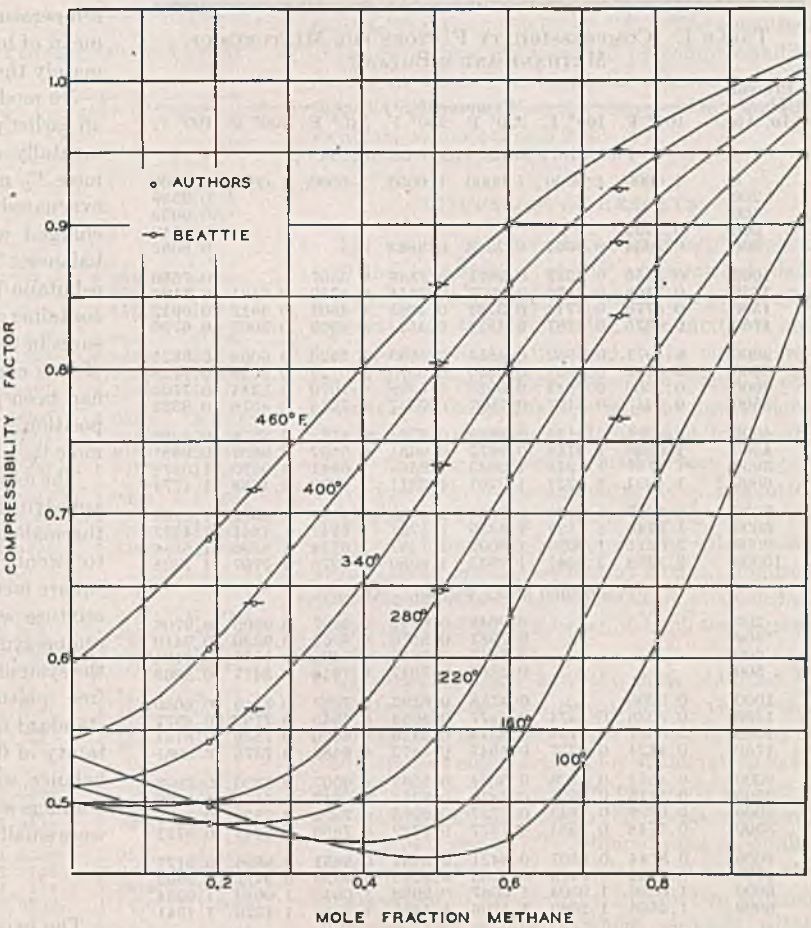

Figure 2. Variation of Compressibility Factor with Change in Composition at 2000 Pounds Per Square Inch

The volumetric behavior of four experimental mixtures of methane and *n*-butane, approximately evenly spaced as to mole fraction, was explored at seven temperatures from 100° to 460° F. and at pressures from near 400 to 10,000 pounds per square inch absolute, to supplement previous measurements for this system. The experimental data, interpolated to even values of pressure, are presented in tabular form as molal volumes and compressibility factors. Diagrams illustrating the behavior in some regions are included, and the new data are compared with those of another group of experimenters.

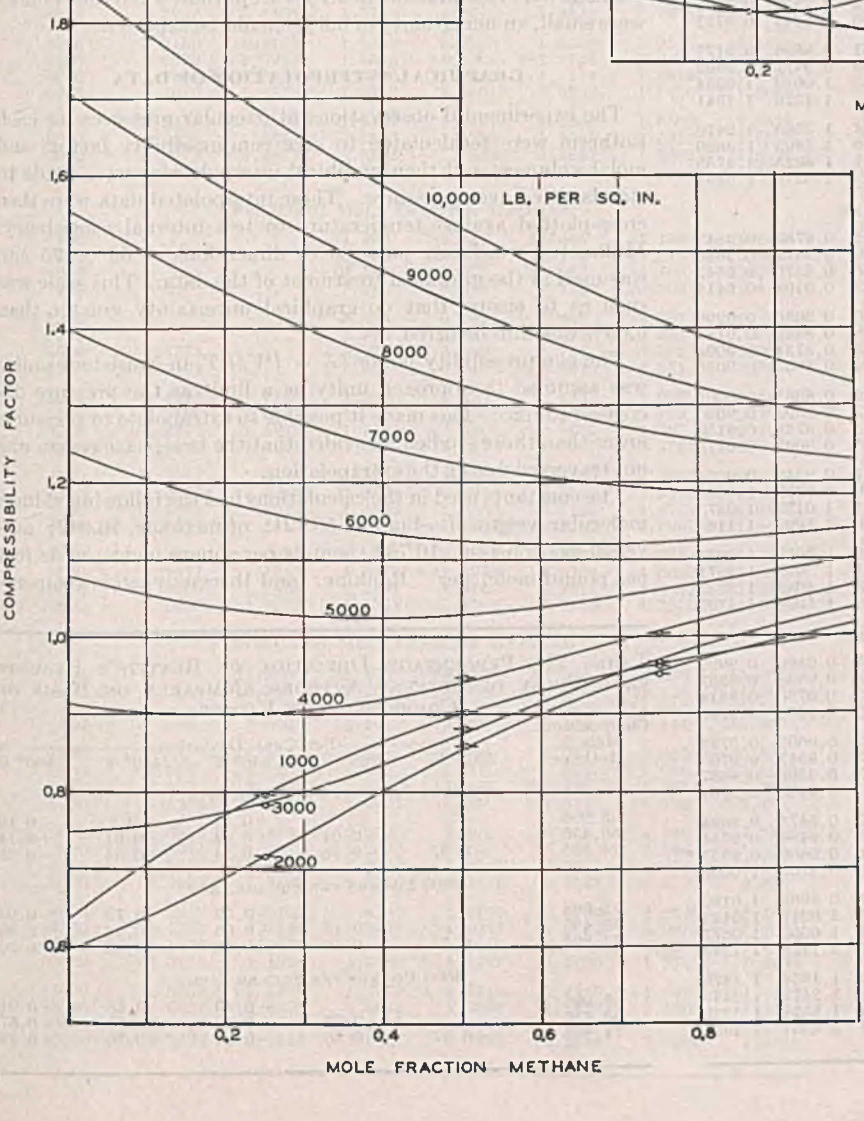

Figure 3. Isobaric Effect of Composition on Compressibility Factor at 460° F.

-○- Data of Beattie

TABLE I. COMPRESSIBILITY FACTORS FOR MIXTURES OF METHANE AND n-BUTANE

Pressure, Lb./Sq. In. Abs.	Compressibility Factor 100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
			FOR 0.1879 MOLE FRACTION METHANE				
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
200	...	...	...	...	...	...	0.9539
400	...	...	...	...	...	...	0.9052
600	0.1552	...	...	...	...	...	0.8549
800	0.2054	0.2057	0.2383	0.3863	...	...	0.8062
1000	0.2555	0.2537	0.2671	0.3366	0.5337	...	0.7630
1250	0.3166	0.3126	0.3233	0.3641	0.4783	0.6184	0.7197
1500	0.3776	0.3714	0.3781	0.4065	0.4801	0.5912	0.6912
1750	0.4375	0.4287	0.4322	0.4521	0.5069	0.5903	0.6796
2000	0.4971	0.4852	0.4854	0.5005	0.5420	0.6064	0.6825
2500	0.6146	0.5957	0.5895	0.5976	0.6229	0.6636	0.7158
3000	0.7300	0.7041	0.6913	0.6928	0.7070	0.7334	0.7702
3500	0.8447	0.8107	0.7907	0.7857	0.7915	0.8078	0.8323
4000	0.9564	0.9155	0.8889	0.8764	0.8763	0.8838	0.8989
4500	1.0666	1.0184	0.9877	0.9681	0.9597	0.9602	0.9681
5000	1.1767	1.1215	1.0833	1.0504	1.0441	1.0370	1.0378
6000	1.3931	1.3221	1.2701	1.2311	1.2072	1.1885	1.1771
7000	1.6057	1.5194	1.4536	1.4038	1.3663	1.3372	1.3165
8000	1.8140	1.7129	1.6338	1.5727	1.5242	1.4841	1.4532
9000	2.0211	1.9039	1.8092	1.7381	1.6774	1.6295	1.5884
10000	2.2238	2.0941	1.9845	1.8980	1.8279	1.7707	1.7221
			FOR 0.3960 MOLE FRACTION METHANE				
200	...	...	0.9048	0.9297	0.9497	0.9609	0.9706
400	...	...	0.7081	0.8576	0.8966	0.9220	0.9410
600	...	...	0.6247	0.7818	0.8435	0.8839	0.9134
800	...	...	0.5267	0.7017	0.7916	0.8477	0.8868
1000	0.3206	...	0.4738	0.6295	0.7427	0.8146	0.8630
1250	0.3038	0.3574	0.4277	0.5664	0.6945	0.7792	0.8377
1500	0.3581	0.3739	0.4314	0.5436	0.6620	0.7539	0.8191
1750	0.4124	0.4237	0.4647	0.5472	0.6482	0.7375	0.8061
2000	0.4663	0.4726	0.5034	0.5662	0.6507	0.7320	0.7993
2500	0.5715	0.5696	0.5876	0.6258	0.6847	0.7475	0.8062
3000	0.6739	0.6643	0.6727	0.6975	0.7374	0.7851	0.8332
3500	0.7748	0.7581	0.7577	0.7722	0.7986	0.8341	0.8721
4000	0.8744	0.8507	0.8421	0.8482	0.8651	0.8896	0.9177
4500	0.9722	0.9413	0.9263	0.9245	0.9326	0.9477	0.9692
5000	1.0696	1.0304	1.0087	0.9988	1.0012	1.0089	1.0234
6000	1.2596	1.2069	1.1706	1.1486	1.1380	1.1329	1.1341
7000	1.4464	1.3791	1.3298	1.2955	1.2734	1.2565	1.2470
8000	1.6283	1.5483	1.4865	1.4410	1.4070	1.3805	1.3620
9000	1.8088	1.7141	1.6401	1.5824	1.5411	1.5025	1.4759
10000	1.9878	1.8760	1.7893	1.7230	1.6723	1.6215	1.5891
			FOR 0.6002 MOLE FRACTION METHANE				
200	...	...	0.9448	0.9606	0.9715	0.9783	0.9843
400	...	...	0.8888	0.9207	0.9429	0.9571	0.9686
600	...	...	0.8324	0.8825	0.9155	0.9370	0.9542
800	...	...	0.7770	0.8453	0.8893	0.9194	0.9414
1000	...	...	0.7256	0.8114	0.8660	0.9036	0.9296
1250	...	...	0.6743	0.7758	0.8418	0.8862	0.9181
1500	0.4688	...	0.6419	0.7483	0.8228	0.8734	0.9094
1750	0.4402	...	0.6265	0.7314	0.8094	0.8633	0.9035
2000	0.4753	0.5347	0.6286	0.7237	0.8012	0.8581	0.9005
2500	0.5610	0.5987	0.6602	0.7340	0.8042	0.8591	0.9030
3000	0.6481	0.6693	0.7118	0.7674	0.8243	0.8738	0.9159
3500	0.7347	0.7437	0.7715	0.8131	0.8585	0.9003	0.9375
4000	0.8199	0.8109	0.8362	0.8659	0.9001	0.9348	0.9664
4500	0.9045	0.8961	0.9022	0.9218	0.9469	0.9737	1.0005
5000	0.9884	0.9713	0.9696	0.9798	0.9971	1.0173	1.0373
6000	1.1509	1.1199	1.1033	1.0993	1.1026	1.1099	1.1193
7000	1.3100	1.2659	1.2374	1.2196	1.2109	1.2059	1.2071
8000	1.4665	1.4096	1.3679	1.3388	1.3201	1.3050	1.2971
9000	1.6194	1.5516	1.4980	1.4579	1.4282	1.4048	1.3885
10000	1.7712	1.6919	1.6242	1.5754	1.5350	1.5034	1.4797
			FOR 0.7997 MOLE FRACTION METHANE				
200	...	0.9614	0.9728	0.9807	0.9865	0.9899	0.9929
400	...	0.9229	0.9466	0.9619	0.9733	0.9808	0.9867
600	...	0.8853	0.9210	0.9448	0.9613	0.9730	0.9814
800	...	0.8491	0.8984	0.9280	0.9509	0.9661	0.9769
1000	...	0.8163	0.8771	0.9138	0.9422	0.9602	0.9734
1250	0.6937	0.7810	0.8537	0.8989	0.9325	0.9547	0.9703
1500	0.6564	0.7536	0.8352	0.8872	0.9257	0.9506	0.9687
1750	0.6223	0.7341	0.8210	0.8783	0.9205	0.9483	0.9684
2000	0.6121	0.7244	0.8120	0.8726	0.9177	0.9471	0.9694
2500	0.6428	0.7311	0.8095	0.8706	0.9185	0.9496	0.9754
3000	0.6924	0.7589	0.8250	0.8823	0.9271	0.9600	0.9857
3500	0.7518	0.7998	0.8531	0.9026	0.9439	0.9757	1.0008
4000	0.8153	0.8485	0.8905	0.9321	0.9677	0.9968	1.0199
4500	0.8807	0.9032	0.9333	0.9669	0.9960	1.0219	1.0423
5000	0.9466	0.9573	0.9792	1.0045	1.0283	1.0500	1.0677
6000	1.0766	1.0707	1.0759	1.0881	1.1007	1.1128	1.1243
7000	1.2063	1.1857	1.1777	1.1768	1.1792	1.1834	1.1876
8000	1.3347	1.3000	1.2801	1.2681	1.2613	1.2575	1.2543
9000	1.4597	1.4132	1.3819	1.3606	1.3439	1.3324	1.3228
10000	1.5862	1.5256	1.4829	1.4521	1.4262	1.4051	1.3921

temperature apparatus at 100° F. showed a deviation from the mean of less than 0.1 pound per square inch, this being approximately the limit of precision in the pressure measurements.

No modifications were necessary in the equipment described in an earlier paper (*11*). The four compositions investigated experimentally were prepared so as to approximate 20, 40, 60, and 80 mole % methane. The n-butane was first introduced into the evacuated cell from a small steel weighing bomb. The amount charged was determined by direct weighings in an analytical balance. The required amount of methane was then added to the n-butane in the cell by transfer from a high pressure isochoric container; the quantity added was determined from the pressures in the container before and after the addition. Calibration of this container for methane content as a function of pressure had been previously made by gravimetric technique. The composition of the mixtures is estimated to be known within 0.05 mole %.

The experimental mixtures were then subjected to a pressure of approximately 10,000 pounds per square inch, and, under isothermal conditions, equilibrium volumes were observed at fifteen to twenty randomly spaced pressures down to 400 pounds per square inch, or until the two-phase region was reached (*9*). Each mixture was studied in this manner at seven uniformly spaced temperatures; this made a total of twenty-eight isotherms for the system. The temperature measurements, made with a strain-free platinum resistance thermometer calibrated against a standard instrument of the same type, have an estimated uncertainty of 0.02° F. The pressure readings, made with a pressure balance, were accurate to 0.2 pound per square inch. The volume readings were reproducible to 0.1% except that, when the volumes were small, an uncertainty of 0.3% should be expected.

GRAPHICAL INTERPOLATION OF DATA

The experimental observations at irregular pressures for each isotherm were recalculated to give compressibility factors and molal volumes, and then graphical interpolations were made to standardized even pressures. These interpolated data were then cross-plotted against temperature to test internal consistency. Millimeter coordinate paper with dimensions of 50 × 75 cm. was used in the graphical treatment of the data. This scale was such as to ensure that no graphical uncertainty greater than 0.05% was thus incurred.

The compressibility factor ($Z = PV/RT$, in consistent units) was assumed to approach unity as a limit as the pressure decreased to zero. This made it possible to extrapolate to pressures lower than those studied, provided that the two-phase region was not traversed during the extrapolation.

The constants used in the calculations had the following values: molecular weight of n-butane, 58.121; of methane, 16.042; universal gas constant, 10.732 (pounds per square inch) (cubic feet per pound-mole) per ° Rankine; and thermodynamic tempera-

TABLE II. PERCENTAGE DEVIATION OF BEATTIE'S RESULTS FROM THOSE OF PRESENT AUTHORS, COMPARED ON BASIS OF COMPRESSIBILITY FACTORS

Composition, Mole % Methane	Per Cent Deviation 220° F.	280° F.	340° F.	400° F.	460° F
		1000 POUNDS PER SQUARE INCH			
25.066	...	...	+0.51	0	−0.10
50.436	...	+0.04	+0.04	+0.01	+0.14
74.895	−0.57	−0.20	−0.24	−0.34	−0.26
		2000 POUNDS PER SQUARE INCH			
25.066	...	...	−0.59	−0.72	−0.03
50.436	...	+0.15	+0.66	+0.44	+0.30
74.895	−0.55	−0.19	−0.60	−0.46	−0.26
		4000 POUNDS PER SQUARE INCH			
25.066	...	...	−0.40	−0.28	+0.01
50.436	...	+0.39	+0.48	+0.56	+0.57
74.895	−0.37	−0.26	−0.31	−0.30	−0.28

Table III. Molal Volumes for Mixtures of Methane and n-Butane

Pressure, Lb./Sq. In. Abs.	Molal Volume						
	100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
	For 0.1879 Mole Fraction Methane						
200	...	...	...	...	...	...	47.075
400	...	...	...	...	...	...	22.335
600	1.5533	...	...	...	...	...	14.063
800	1.5425	1.7100	2.1725	3.834	...	...	9.946
1000	1.5350	1.6870	1.9480	2.672	4.578	...	7.531
1250	1.5216	1.6632	1.8864	2.3120	3.282	4.564	5.682
1500	1.5120	1.6467	1.8387	2.1513	2.745	3.636	4.548
1750	1.5017	1.6291	1.8017	2.0509	2.4846	3.112	3.833
2000	1.4930	1.6135	1.7705	1.9865	2.3260	2.798	3.368
2500	1.4768	1.5848	1.7200	1.8976	2.1372	2.4488	2.826
3000	1.4617	1.5610	1.6810	1.8333	2.0213	2.2553	2.5340
3500	1.4497	1.5406	1.6480	1.7820	1.9397	2.1294	2.3471
4000	1.4363	1.5223	1.6210	1.7393	1.8790	2.0385	2.2180
4500	1.4238	1.5051	1.6011	1.7078	1.8291	1.9687	2.1233
5000	1.4136	1.4918	1.5804	1.6772	1.7910	1.9134	2.0486
6000	1.3947	1.4655	1.5442	1.6288	1.7257	1.8275	1.9363
7000	1.3779	1.4436	1.5147	1.5920	1.6741	1.7624	1.8561
8000	1.3620	1.4240	1.4898	1.5606	1.6341	1.7115	1.7929
9000	1.3489	1.4069	1.4663	1.5331	1.5986	1.6704	1.7419
10000	1.3358	1.3927	1.4476	1.5067	1.5678	1.6336	1.6997
	For 0.3960 Mole Fraction Methane						
200	...	...	33.000	36.900	40.730	44.325	47.900
400	...	...	14.555	17.020	19.225	21.265	23.218
600	...	...	7.595	10.343	12.058	13.592	15.025
800	...	...	4.803	6.963	8.488	9.776	10.940
1000	1.9260	...	3.456	4.997	6.370	7.515	8.518
1250	1.4600	1.9016	2.4960	3.597	4.766	5.751	6.614
1500	1.4340	1.6580	2.0980	2.877	3.785	4.637	5.389
1750	1.4154	1.6103	1.9371	2.4823	3.177	3.888	4.546
2000	1.4005	1.5715	1.8360	2.2475	2.791	3.377	3.945
2500	1.3732	1.5152	1.7144	1.9872	2.3504	2.758	3.183
3000	1.3493	1.4727	1.6357	1.8457	2.1083	2.4143	2.741
3500	1.3297	1.4406	1.5791	1.7514	1.9571	2.1986	2.4591
4000	1.3130	1.4145	1.5358	1.6833	1.8550	2.0518	2.2643
4500	1.2978	1.3911	1.5016	1.6309	1.7776	1.9429	2.1258
5000	1.2850	1.3706	1.4716	1.5858	1.7174	1.8616	2.0202
6000	1.2610	1.3378	1.4232	1.5197	1.6268	1.7420	1.8655
7000	1.2411	1.3103	1.3857	1.4691	1.5603	1.6560	1.7583
8000	1.2226	1.2871	1.3554	1.4299	1.5085	1.5920	1.6804
9000	1.2072	1.2667	1.3293	1.3958	1.4687	1.5402	1.6186
10000	1.1940	1.2477	1.3052	1.3678	1.4343	1.4960	1.5684
	For 0.6002 Mole Fraction Methane						
200	...	...	34.460	38.130	41.665	45.130	48.575
400	...	...	16.208	18.273	20.218	22.075	23.900
600	...	...	10.120	11.677	13.087	14.408	15.697
800	...	...	7.085	8.388	9.535	10.603	11.614
1000	...	...	5.293	6.441	7.428	8.337	9.175
1250	...	...	3.935	4.927	5.776	6.541	7.249
1500	1.8773	...	3.121	3.960	4.705	5.372	5.984
1750	1.5109	...	2.611	3.318	3.967	4.551	5.095
2000	1.4275	1.7780	2.2925	2.873	3.436	3.959	4.444
2500	1.3480	1.5928	1.9264	2.3308	2.756	3.170	3.565
3000	1.2977	1.4837	1.7307	2.0307	2.3567	2.687	3.013
3500	1.2609	1.4131	1.6080	1.8443	2.1037	2.3731	2.644
4000	1.2313	1.3633	1.5250	1.7185	1.9300	2.1560	2.3845
4500	1.2073	1.3244	1.4624	1.6262	1.8049	1.9962	2.1944
5000	1.1874	1.2920	1.4146	1.5556	1.7104	1.8772	2.0476
6000	1.1522	1.2413	1.3413	1.4545	1.5762	1.7067	1.8412
7000	1.1241	1.2027	1.2894	1.3831	1.4837	1.5894	1.7020
8000	1.1011	1.1719	1.2473	1.3285	1.4154	1.5050	1.6003
9000	1.0808	1.1466	1.2141	1.2859	1.3611	1.4401	1.5227
10000	1.0639	1.1252	1.1848	1.2506	1.3166	1.3870	1.4604
	For 0.7997 Mole Fraction Methane						
200	...	31.970	35.480	38.925	42.305	45.665	49.000
400	...	15.345	17.263	19.090	20.870	22.623	24.345
600	...	9.813	11.197	12.500	13.742	14.962	16.143
800	...	7.059	8.191	9.209	10.195	11.141	12.053
1000	...	5.429	6.398	7.254	8.081	8.859	9.607
1250	3.334	4.155	4.982	5.709	6.398	7.046	7.662
1500	2.629	3.341	4.061	4.605	5.293	5.847	6.374
1750	2.1360	2.790	3.422	3.984	4.511	4.999	5.462
2000	1.8385	2.4090	2.962	3.464	3.936	4.369	4.784
2500	1.5444	1.9448	2.3620	2.764	3.151	3.504	3.851
3000	1.3863	1.6823	2.0060	2.3347	2.651	2.952	3.243
3500	1.2903	1.5197	1.7780	2.0471	2.3131	2.5720	2.822
4000	1.2243	1.4108	1.6240	1.8498	2.0750	2.2990	2.5165
4500	1.1756	1.3349	1.5129	1.7058	1.8984	2.0951	2.2860
5000	1.1372	1.2734	1.4286	1.5948	1.7640	1.9374	2.1076
6000	1.0778	1.1868	1.3080	1.4397	1.5735	1.7112	1.8495
7000	1.0351	1.1266	1.2273	1.3346	1.4449	1.5597	1.6744
8000	1.0021	1.0808	1.1673	1.2584	1.3523	1.4503	1.5475
9000	0.9742	1.0443	1.1200	1.2001	1.2808	1.3659	1.4507
10000	0.9528	1.0146	1.0817	1.1527	1.2233	1.2963	1.3740

ture in ° Rankine, 459.69 + ° F. The smoothed volumetric data are recorded as compressibility factors in Table I and as molal volumes in Table III. It is believed that the values do not deviate from fact by more than 0.2%.

DISCUSSION OF RESULTS

The extent of interpolation and extrapolation and the consistency of the experimental data are illustrated in Figure 1, which is a graph of Z against P at 460° F. for the four mixtures and the two components involved. The curves represent the data as they appear in Table I, and the circles represent the experimental observations. The internal consistency of the tabulated results with respect to composition may be seen in Figure 2, in which the compressibility factor is plotted against mole fraction methane at 2000 pounds per square inch for seven isotherms; the values taken from Table I are represented by circles. Figure 3 presents the isobaric curves resulting at a constant temperature of 460° F. when Z is plotted against composition.

In order to learn how the data obtained by Beattie and co-workers compared with the present results, their isochoric values were converted to the system of units here employed and interpolated graphically in terms of compressibility factors to comparable physical states. The results are shown in Figures 2 and 3. To eliminate the possibility of errors in interpolation, both sets of results were interpolated to the chosen states by two different methods, the results of which checked within 0.05%. In spite of the fact that each set of data is internally consistent, rather large discrepancies between them are apparent. The deviations found in this comparison are recorded in Table II. It may be seen from the tabulation and from Figures 2 and 3 that the deviations are all positive for the mixture near 50 mole %, and predominantly negative at the other two compositions studied by Beattie.

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LITERATURE CITED

(1) Beattie, Simard, and Su, *J. Am. Chem. Soc.*, 61, 24 and 26 (1939).
(2) Beattie, Stockmayer, and Ingersoll, *J. Chem. Phys.*, 9, 871 (1941).
(3) Kay, Ind. Eng. Chem., 32, 358 (1940).
(4) Keyes and Burks, *J. Am. Chem. Soc.*, 49, 1403 (1927).
(5) Kvalnes and Gaddy, *Ibid.*, 53, 394 (1931).
(6) Michels and Nederbragt, *Physica*, 3, 569 (1936).
(7) Olds, Reamer, Sage, and Lacey, Ind. Eng. Chem., 35, 922 (1943).
(8) *Ibid.*, 36, 282 (1944).
(9) Sage, Budenholzer, and Lacey, *Ibid.*, 32, 1262 (1940).
(10) Sage, Hicks, and Lacey, *Ibid.*, 32, 1085 (1940).
(11) Sage and Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, 136, 136 (1940).

Paper 48 in the series "Phase Equilibria in Hydrocarbon Systems". Previous articles have appeared during 1934–40, 1942–46, and in January 1947.

Emulsion Polymerization of Diene Hydrocarbons

H. W. Starkweather[1], *P. O. Bare, A. S. Carter, F. B. Hill, Jr., V. R. Hurka,*
C. J. Mighton, P. A. Sanders, H. W. Walker, and M. A. Youker

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

The results of an exploratory study of the emulsion polymerization of conjugated diene hydrocarbons to yield rubberlike polymers are summarized. Such polymerization variables are discussed as purity of reagents, nature and amount of a second monomer, emulsifying agents, alkali concentration, catalysts, catalyst activators, modifying agents, temperature, and yield. An investigation of the influence of some 214 different compounds copolymerized with butadiene reveals wide differences in the polymerization rate and properties of the copolymers, depending upon the structure of the second monomer. Such vinyl compounds as methacrylic acid esters, methyl vinyl ketone, dimethyl vinyl ethynyl carbinol give with butadiene potentially useful copolymers. Convenient forms of equipment for the small scale preparation, compounding, and testing of new types of elastomers are described.

LESS than a century ago Williams obtained isoprene by the thermal decomposition of natural rubber. This discovery was an essential step in a series of researches in several different countries which has culminated in the production of over a million tons of synthetic rubberlike products in a single year. The chemist, like the rubber tree, is able to produce various types of rubber as aqueous emulsions, although the actual processes of manufacture are undoubtedly far different. Liquid butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and chloroprene have been polymerized to rubberlike materials without the addition of other chemicals, but the chemist and chemical engineer have been more successful in producing uniform products by commercially practical methods since the emulsion processes for polymerization were developed.

This paper is an attempt to summarize the results obtained in investigating the emulsion polymerization of conjugated diene hydrocarbons in these laboratories from 1935–42. During the past four years other commercial and academic laboratories have investigated certain phases of this problem in more detail than is presented in this paper.

Before discussing the properties of the products obtained from specific polymerizable compounds, it seems advisable to consider certain factors, such as purity of reagents, monomer-water ratio, etc., which may have a marked effect on the rate of polymerization or properties of the products.

PURITY OF REAGENTS

The purity of all materials used to prepare the emulsions must be carefully controlled since the addition of almost any compound is likely to accelerate or to retard polymerization or to affect the quality of the product. In preliminary work at least, all monomers should be freshly distilled, preferably at reduced pressure, in order to minimize polymerization during distillation. The effect of exposure to air and possible formation of peroxides must be considered. Many of these peroxides are not only hazardous, but may have either a favorable or an unfavorable influence on polymerization. It is also advisable to use distilled water in preliminary experiments since the presence of even minute traces of impurities, such as copper or iron, may alter the polymerization. In one series of experiments the shift from distilled water to the tap water available reduced the product yield from 90 to 40%.

While oxygen is generally considered to be a catalyst for polymerization, the presence of an excessive amount of oxygen may retard or actually inhibit polymerization. Carbon dioxide has a retarding effect on the polymerization rate in many systems, and results may be influenced by contamination of samples stored in a dry-ice box.

RATIO OF MONOMER TO WATER

The concentration of the monomer in the emulsion may have a marked influence on the rate of polymerization. For example, the yield obtained by polymerizing a butadiene–methyl methacrylate mixture in sodium oleate emulsion, under otherwise identical conditions and with the ratio of monomers to all components except water the same, increased from 36 to 62 to 85% when the monomer content of the emulsion was increased from 20 to 30 to 45%, respectively. Although more concentrated emulsions may polymerize faster, their greater viscosity results in poor heat transfer, and control of polymerization at a fixed temperature becomes more difficult.

PREPARATION OF EMULSIONS

Uniformity of initial monomer emulsions is important in order to obtain reproducible polymerization cycles and uniform quality of polymer. In small scale laboratory work it is usually sufficient to agitate the polymerizing vessel during polymerization. Frequently it is advantageous to form the emulsifying agent *in situ* (*14*) rather than to use a prepared material. When working with fatty acids, rosins, or long-chain amines, we dissolve the oil-soluble material in the monomer and dissolve the water-soluble alkali or acid in the aqueous phase. A uniform, well-dispersed emulsion is readily obtained when these two solutions are mixed and agitated in the preliminary stages of the polymerization process. Although we have not observed pronounced differences as a result of using a preformed emulsifying agent instead of that formed *in situ*, the micellization of the agent could be different. Variations might be expected, therefore, in certain polymerization systems.

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[1] Deceased May 18, 1946.

METHOD OF ADDITION

Experience has shown that misleading results may be obtained by failure to add everything to the polymerization system in the proper sequence. If the different monomers are mixed for some time before emulsification, there is a possibility of a Diels-Alder type of reaction taking place to a sufficient extent to alter the properties of the product or to reduce the yield. The addition of a catalyst activator to the aqueous solution too long before its use in the polymerization system may result in a retardation rather than an activation of the polymerization rate. In investigating the copolymerization[2] of butadiene and methyl vinyl ketone, it was discovered that the addition of the ketone to the aqueous solution of soap and catalyst a short time before the butadiene was added resulted in the formation of almost no polymer. When the two monomers were added simultaneously to the aqueous solution, a good yield of high grade product was obtained.

EMULSIFYING AGENTS

The primary purpose of the emulsifying agent is to assist in the formation of a stable oil-in-water emulsion which will not break during polymerization but will give a latex capable of being readily broken or coagulated after polymerization is completed. However, it is well known that emulsifying agents not only serve as such, but also affect the rate of polymerization and the quality of the resulting elastomer. Typical emulsifying agents for use in alkaline systems include the alkali metal and ammonium salts of fatty acids, rosin, modified rosins, napththenic acids, alcohol sulfate esters, and various aliphatic and aromatic sulfonic acids. In acidic emulsions the hydrohalides of long-chain amines may be useful. Other nitrogen-containing compounds, such as the quaternary ammonium halides and substituted betaines, have given good results under various conditions.

Mixtures of 75 butadiene–25 styrene were polymerized in the presence of DD mercaptan (Lorol mercaptan from C_{12}–C_{14} alcohols) in potassium persulfate–activated systems containing 4 or 5% of some of the more promising emulsifying agents. The following results indicate that various types of emulsifying agents may be used successfully:

		Polymerization		
Emulsifying Agent, %	pH	Temp., ° C.	Time, hr.	Product Yield[a], %
Fatty alcohol sulfate, 5	3	50	12	70
	6	50	12	90
	>10	50	12	95
Aliphatic (av. C_{16}) sodium sulfonate, 4	>10	40	20	96
Sulfated methyl oleate, 4	>10	40	20	84
Sodium naphthenate, 4	>10	40	20	93
Sodium oleate, 4	>10	40	17	92

[a] Throughout this paper the term "product yield" is used to denote the yield based on original weight of monomeric material employed without correcting for the emulsifying agent or stabilizer included in the finished elastomer.

Satisfactory emulsions are obtained by using some of the commercially available soaps, such as Ivory and Palmolive, as well as sodium oleate. The merits of the Rubber Reserve soap are well known. Nancy wood rosin soap alone may give interesting polymers but is not very satisfactory for persulfate-activated butadiene systems, owing to the slow rate of polymerization. The rate of polymerization may be greatly increased by hydrogenating the rosin or subjecting it to hydrogen exchange.

Combinations of rosin soaps with fatty acid soaps appear to be advantageous when employed in certain preferred polymerization systems. The use of the rosin soap tends to reduce the precoagulation during polymerization, to improve the mill behavior of the polymer, and to result in polymers that are more uniform with respect to tensile properties. The following results, obtained with 75 butadiene–25 styrene mixture, in potassium persulfate–potassium ferricyanide activated systems, indicate that a mixture of 4% oleic acid and 2% Nancy wood rosin gives desirable results:

Oleic Acid[a], %	Nancy Wood Rosin, %	Ratio, Rosin: Total Acid	Total Emulsifying Agent, %	Product Yield at 40°C. for 20 Hr., %
0	4	1.0	4	25
4	0	...	4	93
3	1	0.25	4	9
3	2	0.40	5	90
4	1	0.20	5	95
4	2	0.33	6	97
4	3	0.43	7	93

[a] Commercial red oil was used.

If neither rosin nor fatty acid is desired in the finished product, the sulfonic acid type of emulsifying agent may be preferred. Conditions of coagulation may be such as to convert the sulfonic acid to an innocuous insoluble salt or to leave it in a highly soluble form that can be washed out of the polymer.

Some materials that are relatively ineffective as emulsifying agents in preparing the initial emulsion are quite effective as dispersing agents for preventing flocculation of the emulsion during polymerization. An example is the condensation product of a naphthalene sulfonic acid and formaldehyde (*9, 13*) such as that sold commercially as Daxad 11. The use of such an agent may permit decreasing the percentage of soap required.

CONCENTRATION OF EMULSIFYING AGENT

The rate of polymerization may be markedly influenced by the concentration of the emulsifying agent. For example, monomer conversions of 50–69% have been obtained by polymerizing butadiene for 64 hours at 10° C., using 25% sodium oleate. Increasing the sodium oleate to 50% has given monomer conversions of 62–76%, depending on the catalyst, in 40 hours. By contrast, when 4% soap was used, several hundred hours were required for comparable polymer yields.

The effect of variations in concentration of sodium oleate upon two different butadiene-styrene systems is shown by the following data; in each case 0.75 part excess sodium hydroxide, 1 part Daxad 11, and 1 part potassium persulfate were used:

Butadiene-styrene ratio	70:30	75:25
Potassium ferricyanide, %	0	0.15
Mercaptan, %	Pinene, 1	DD, 0.75
Hours of polymerization	32 at 40° C.	10 at 50° C.
Product yield, %		
4% Na oleate	...	90
6% Na oleate	88	97
8% Na oleate	97	105
10% Na oleate	102	...

EFFECT OF ALKALINITY

The rate of polymerization is also influenced by the pH of the emulsion. The relations between the yield and varying amounts of excess sodium hydroxide for 75 butadiene–25 styrene mixtures polymerized in the presence of varying amounts of potassium persulfate in emulsions containing 4 parts oleic acid, 2 parts rosin, 1 part Daxad 11, 0.15 part potassium ferricyanide, and 1.75 part pinene mercaptan are shown in Figure 1. For each concentration of persulfate, there is a concentration of sodium hydroxide which appears to give the optimum results.

Figure 2 indicates that the rate of polymerization of a 75 butadiene–25 styrene mixture in sulfonated petroleum oil emulsions is influenced by the concentration of the emulsifying agent and the amount of excess caustic in much the same manner as in the fatty acid soap systems; but in these cases the optimum rates are obtained with somewhat lower concentrations of excess caustic. It appears that at least 4% emulsifying agent is required to give a stable emulsion with a suitable polymerization rate. The emulsion contained, in addition to the sulfonated petroleum oil, 1 part Daxad 11, 0.75 part DD mercaptan, 1 part potassium per-

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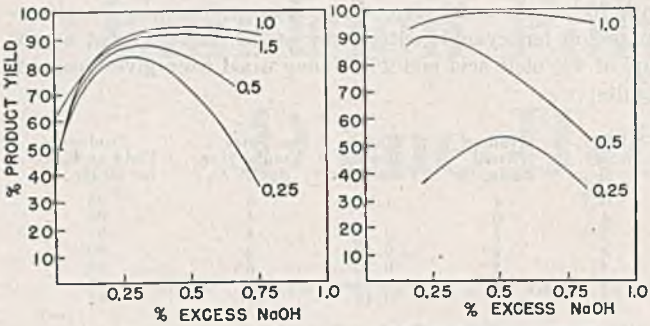
[2] Although the authors believe that the term "interpolymer" better describes a polymer in which x and y monomer units exist in the same molecule, they conform to the customary "copolymer" terminology throughout this paper.



20 hours at 40° C. 13 hours at 50° C.

Figure 1. Effect of Excess Sodium Hydroxide with Varying Persulfate on Polymerization of 75 Butadiene–25 Styrene in Oleate-Rosinate Emulsion (Numbers on Curves Refer to Per Cent Potassium Persulfate)

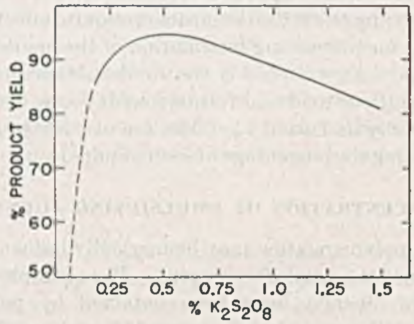


Figure 3. Effect of Persulfate on Polymerization of Butadiene-Styrene in Aliphatic Sulfonate Emulsion for 18 Hours at 40° C.

Butadiene	75	Excess NaOH	0.15
Styrene	25	Daxad 11	1
Water	150	DD mercaptan	0.75
Aliphatic (C_{16}) sulfonate	4	$K_3Fe(CN)_6$	0.15
		$K_2S_2O_8$	x

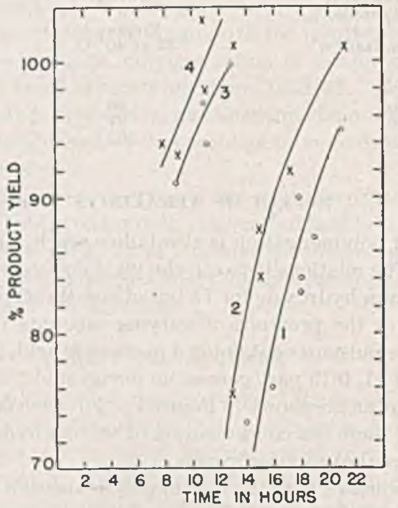


Figure 4. Effect of Potassium Ferricyanide on Polymerization of 75 Butadiene–25 Styrene at 50° C. in Emulsion Containing 5 Parts Palmolive Soap and 0.5 Part DD Mercaptan

Curve No.	1	2	3	4
$K_2S_2O_8$	0.6	1.25	0.6 or 1.25	0.6 or 1.25
$K_3Fe(CN)_6$	..	..	0.15	0.15
Excess NaOH	..	..	..	0.25
Daxad 11	..	..	..	0.25

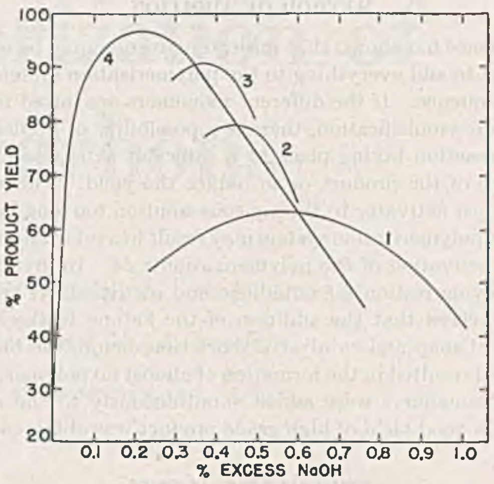


Figure 2. Effect of Excess Sodium Hydroxide on Polymerization of 75 Butadiene–25 Styrene in Sulfonated Petroleum Oil Emulsions for 20 Hours at 40° C. (Numbers on Curves Refer to Per Cent Sulfonated Petroleum Oil)

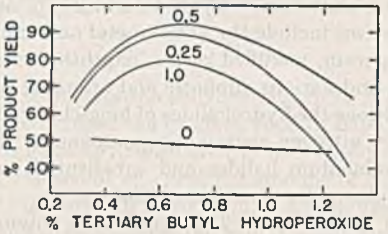


Figure 5. Effect of *tert*-Butyl Hydroperoxide with Varying Ferrocyanide on Polymerization of Butadiene-Styrene in Oleate Emulsion for 16 Hours at 40° C. (Curve Numbers Refer to Per Cent $K_4Fe(CN)_6.3H_2O$)

Butadiene	75
Styrene	25
Water	150
Oleic acid	4
Excess NaOH	0.75
Daxad 11	1
DD mercaptan	1
tert-Butyl hydroperoxide	x
Potassium ferrocyanide	y

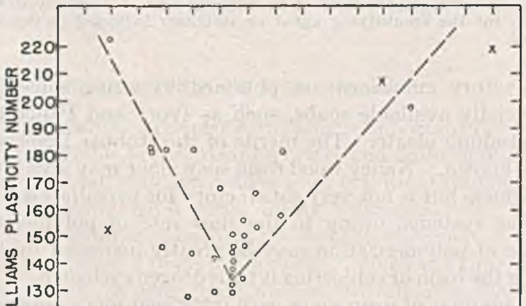


Figure 6. Effect of Chain Length of Mercaptan on Plasticity of Copolymer from 75 Butadiene–25 Styrene Mixture with 0.75 Part Mercaptan (100% Basis), 20 Hours at 40° C.

O = product yield of 85 to 95%
X = product yield of 70 to 85%

sulfate, and 0.15 part potassium ferricyanide. The addition of 2% rosin improves the stability of the emulsion, but, even here, the use of less than 4% sulfonated hydrocarbon results in an excessively slow polymerization cycle.

CATALYSTS

The use of catalysts or polymerization initiators is essential in order to obtain suitable polymerization rates. In practice oxygen-yielding compounds have been found more effective and more adaptable to control than oxygen itself. Although the term "catalyst" has been applied to such compounds, they are not catalysts in the true sense since they are usually consumed. Compounds such as benzoyl peroxide or fatty acid peroxides, which are soluble in the oil phase, can be used as catalysts but in practice have given less favorable results than the water-soluble types. Hydrogen peroxide can be used but salts of per acids such as persulfates and perborates have given more consistently satisfactory results. The choice of catalyst depends upon the other components of the polymerization system. In general, persulfates have been favored in the work covered by this report, but some interesting results with *tert*-butyl hydroperoxide also have been obtained.

There is usually an optimum concentration of catalyst, which may vary with the different systems. The following data, obtained by polymerizing a mixture of butadiene and methyl methacrylate for 16 hours at 60° C. in alkaline–sodium oleate emulsion catalyzed with ammonium persulfate, indicate that 1% functions as a more effective catalyst than either smaller or larger amounts in this particular system:

Ammonium Persulfate, %	Product Yield, %	Ammonium Persulfate, %	Product Yield, %
0	6	1.0	97
0.25	50	1.5	95
0.5	85	2.0	58

Similar variation in polymerization rates with variations of potassium persulfate is shown by a more complicated butadiene-styrene system in Figure 3. It is possible that the lower yield with higher concentrations of persulfate may have been due to a variation in the pH of the emulsion, caused by the decomposition of the persulfate.

CATALYST ACTIVATORS

The acceleration of polymerization by a primary catalyst such as a persulfate may be greatly increased by the use of a secondary catalyst or activator. As will be discussed later, compounds such as the mercaptans, used as modifying agents, may also affect the polymerization rate. For diene hydrocarbons certain iron and copper complex compounds, such as complex metal cyanides, have been found to be especially effective activators.

Typical data follow which illustrate the favorable influence of potassium ferricyanide upon the polymerization rate of a 75 butadiene–25 styrene mixture in a system containing 4 parts oleic acid, 0.75 part excess sodium hydroxide, 0.75 part DD mercaptan, 1 part Daxad 11, and 1 part potassium persulfate:

Potassium Ferricyanide, %	Product Yield at 40° C., %		Potassium Ferricyanide, %	Product Yield at 40° C., %	
	12 hours	16 hours		12 hours	16 hours
0.005	[a]	70	0.1	..	91
0.025	[a]	80	0.15	70	93
0.05	[a]	90	0.2	74	92

[a] Low yield of polymer, too soft and tacky to mill.

Figure 4 shows results obtained by polymerizing 75 butadiene–25 styrene in a 33% emulsion containing 5 parts Palmolive soap and 0.5 part DD mercaptan, with and without excess sodium hydroxide and Daxad 11. The ferricyanide considerably accelerates the polymerization, and in this soap system the addition of 0.15% appears most desirable. Several of these products had acceptable properties even when obtained in essentially 100% product yields.

Potassium ferrocyanide also has a marked effect upon polymerizations activated with *tert*-butyl hydroperoxide (Figure 5). These results indicate that there is an optimum concentration for both potassium ferrocyanide and *tert*-butyl hydroperoxide.

MODIFYING AGENTS

The term "modifying agent" or "regulator" is used to designate compounds which, when present in small amounts during polymerization, markedly increase the plasticity and solubility of the resulting elastomers. They are important tools for improving the processability of the product. Mercaptans (*32*), thiuram disulfides (*3*, *7*), xanthic disulfides (*17*), sulfur (*25*), selenium (*33*), substituted phosphines (*21*), carbon tetrachloride (*2*), and various nitrogen compounds such as hydrazines (*1*), amines (*19*), Schiff bases (*11*), nitroso compounds (*31*), and diazoamino compounds (*4*, *5*, *6*) have been used to modify diene hydrocarbon polymers and copolymers.

Mercaptans as a class are probably the most useful modifying agents, and an elastomer of almost any desired plasticity may be obtained from many different monomers by using the proper concentration of a suitable mercaptan. There appears to be a direct relation between the concentration of the mercaptan and the plasticity of the resulting elastomer. Unfortunately the more plastic products may yield vulcanizates which are inferior in resilience, tensile strength, tear resistance, and other properties. Since the effect of mercaptans of various chain lengths is not identical, a study was made of mercaptans produced from twenty-one different readily available petroleum oils. The data in Table I were obtained by polymerizing mixtures of 75 butadiene–25 styrene in 40% emulsions containing 4 parts oleic acid, 1 part rosin, 0.75 part excess sodium hydroxide, 1 part potassium persulfate, 1 part Daxad 11, 0.15 part potassium ferricyanide, and 0.75 part of the mercaptan (active ingredients). One hundred parts of the elastomers were compounded with 50 parts MPC black, 2 parts stearic acid, 2 parts sulfur, 5 parts zinc oxide, and 1.25 parts 2-mercaptothiazoline.

The Williams plasticity numbers (*29*) of elastomers modified with different samples of mercaptans are plotted against the number of carbon atoms in the mercaptan chain in Figure 6. Although experimental variations and inequalities in yield make it difficult to draw exact conclusions, primary mercaptans containing 11 to 14 carbon atoms appear to be most effective in the persulfate-catalyzed fatty acid soap systems used.

Although aromatic mercaptans were not especially effective as modifying agents, interesting results were obtained with certain cyclic mercaptans, such as pinene mercaptan and menthene mercaptan, and with branched-chain mercaptans, such as Sharples 3B mercaptan (*20*). Table II gives results obtained with a ferricyanide-activated 4% sodium oleate emulsion of a 75 butadiene–25 styrene mixture polymerized at 40° C. In each case the tensile data show the unfavorable influence of an excess of mercaptan.

Table III shows results obtained in comparing DD, menthene, and 3B mercaptan in 36% emulsions containing 5 parts Palmolive soap and 0.6 part potassium persulfate, and polymerized at 50° C.

The mercaptans not only affect the plasticity of the product but also the rate of polymerization. Figure 7 shows data obtained with 40% emulsions containing 4 parts oleic acid, 0.75 part excess sodium hydroxide, 1 part Daxad 11, 1 part potassium persulfate, and 0.15 part potassium ferricyanide. No attempt was made to exclude air from this system, and whether the mercaptan affects induction period or actual polymerization rate remains to be determined.

It was considered that a combination of mercaptans might be even more suitable than a single mercaptan. Thus, it might be possible to combine the greater modifying action of 3B mercap-

TABLE I. EFFECT OF MERCAPTANS MADE FROM HYDROCARBONS ON 75 BUTADIENE–25 STYRENE POLYMERIZATION, WITH 0.75% MERCAPTAN FOR 20 HOURS AT 40° C.

					Stress-Strain Data		
Oil	Av. C Chain	Product Yield, %	Modification	Cure, min. at 142° C.	Stress at 300%, lb./sq. in.	Tensile strength, lb./sq. in.	Elongation at break, %
Dependip	7.6	81	Fair	60	1360	3150	510
Octane	8	85	Fair	45	1410	4120	570
HFVM & P naphtha	9.5	80	Fair	60	1700	3270	450
Oleum spirits	9.8	85	Fair	45	1080	3010	570
Tydol No. 1	10.9	85	Good	45	1070	3420	620
Deobase	10.9	89	Very good	45	1140	2900	540
Perfection kerosene	11	83	Good	60	1480	3270	500
Fortnite LTB	11.1	90	Good	45	1450	2930	465
No. 30 white oil	11.7	94	Very good	45	1160	2760	525
Bayol D	11.8	92	Very good	60	1420	2440	430
Tydol No. 2	12	85	Good	45	1020	3280	620
No. 9 refined	12.1	90	Good	45	1280	3380	540
Control (DDM)	12.5	94	Very good	45	1250	3210	560
Pure No. 1	12.8	93	Very good	45	1220	3410	560
Penn No. 1	13.1	95	Very good	60	1510	3320	500
Penn No. 2	13.3	92	Good	45	2050	3840	440
Penn No. 3	14.1	92	Fair	60	1880	3010	400
No. 40 white	16	92	Fair	45	1330	3590	495
Penn No. 4	18.1	82	Poor	45	2060	3780	435
No. 50 white	19	78	Poor	30	1740	3860	480
No. 70 white	22.5	69	Poor	30	2470	2710	315

tan with the accelerating action of DD mercaptan. The results obtained (Figure 8) indicate that the single and mixed mercaptans give distinct sets of nearly parallel curves; although the mixed mercaptans have a greater influence on plasticity at low yields, the single mercaptans are more effective in increasing the plasticity at higher yields. It is possible that the acceleration of polymerization with mixed mercaptans accounts for these results. If the rate of diffusion of the modifier to the point where polymerization is in progress is involved, acceleration of polymerization might explain the anomaly of less modifier being more effective under certain conditions.

A study of the mechanism of the action of modifying agents offers a promising field for academic research. Some of these modifying agents may function by terminating polymer chain growth or introducing easily rupturable linkages and, thereby, result in products of lower molecular weight. Other modifying agents may act by preventing cross linking or by interfering with cyclization. The utility of a given compound as a modifying agent depends upon the nature of the monomer, the emulsifying agent, the pH of the emulsion, or the method of catalysis.

TEMPERATURE OF POLYMERIZATION

The rate of polymerization can be increased by raising the temperature, but our general experience has shown that the quality of the elastomer is improved by polymerizing at lower temperatures. In some cases freeze resistance is increased by raising the temperature of polymerization, but processability, tensile strength, and elasticity are generally improved by polymerization at lower temperatures.

STABILIZERS

Elastomers made from diene hydrocarbons must be protected from oxidation during milling and processing. For this reason it is advisable to add an antioxidant, preferably in the form of an aqueous dispersion, to the latex when the optimum yield is reached (*27*). Such a dispersion may be prepared from any antioxidant by grinding with a suitable dispersing agent or emulsifying a solution of the antioxidant in an inert solvent. The antioxidants may serve to terminate polymerization, but in certain cases other agents or inhibitors are also added.

COAGULATION

A suitable coagulation process should be complete, yield a readily washable coagulum, and have no adverse effect on the properties of the product. Coagulation of most of the emulsions discussed in this report may be brought about by adding salts of bi- or trivalent metals such as barium, magnesium, or aluminum, or by the addition of sodium chloride brine or acidified brine, or by cooling or heating. An acidic coagulant is advantageous for coagulation of soap latices since it converts the soap to free fatty acid or rosin and a highly soluble salt. When practical, cooling or heating are preferred methods of coagulation because they involve no contamination of the finished product with coagulant. For example, neoprene latices containing sodium rosinate and Daxad 11 are acidified with sufficient acetic acid to precipitate the rosin and are then coagulated by freezing on a rotating drum. The resulting film is washed with water to remove sodium acetate. In this laboratory an acidic sodium chloride brine is commonly used to coagulate butadiene latices made with fatty acid or rosin soaps.

YIELD

Every manufacturer of elastomers knows that the properties of his product are greatly affected by the yield at which the product is isolated. However, it is frequently possible, by the proper use of modifiers and by polymerizing at sufficiently low temperature, to polymerize to a yield of 90% or better and still obtain a good-processing polymer which yields suitable vulcanizates. The maximum yield obtainable without adversely affecting the

TABLE II. COMPARISON OF PINENE AND DD MERCAPTANS

				Stress-Strain Data[a]		
% Mercaptan	Polymerization Time, Hr.	Product Yield, %	Williams Plasticity-Recovery	Stress at 300%, lb./sq. in.	Tensile strength, lb./sq. in.	Elongation break, %
None	24	60	337–161	2550	3580	380
None	49	93	369–138	...	1845	190
0.25 DD	24	88	271–180	2640	3465	350
0.75 DD	20	95	134–173	1420	3180	500
1.5 DD	20	96	82–5	995	2215	540
1.0 pinene	22	92	230–220	1620	3610	500
2.0 pinene	20	93	156–145	1280	3210	530
4.0 pinene	20	98	107–100	850	2215	380

[a] On 2-MT (2-mercaptothiazoline) tread stocks cured 45 minutes at 142° C.

TABLE III. COMPARISON OF DD, MENTHENE, AND 3B MERCAPTANS

				Stress-Strain Data[a]		
% Mercaptan	Polymerization Time, Hr.	Product Yield, %	Williams Plasticity-Recovery	Stress at 300%, lb./sq. in.	Tensile strength, lb./sq. in.	Elongation at break, %
0.5 DD	15	86	106–24	1510	3130	490
0.5 DD	18	90	135–107	1670	3580	490
0.5 DD	21	95	144–116	1760	3090	430
0.3 menthene	19	76	102–25	1420	2980	500
0.3 menthene	21	93	130–104	2185	2840	350
0.4 menthene	19	84	90–12	1450	2640	450
0.1 3B	19	56	133–144	1645	3380	470
0.2 3B	22	71	96–11	1620	2900	440
0.3 3B	19	74	60–9	1450	2840	490
0.3 3B	22	78	65–9	1645	3065	460

[a] On tread stocks cured 45 minutes at 142° C.

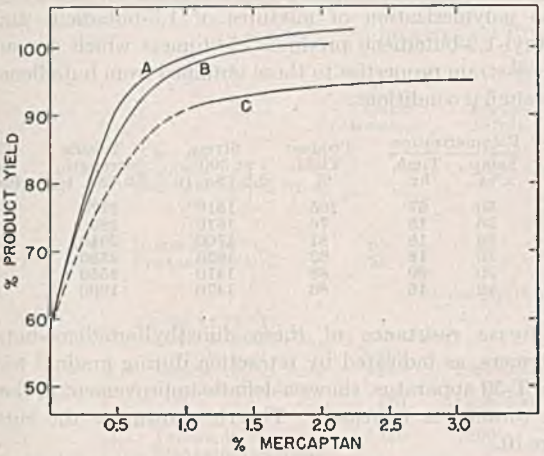


Figure 7. Effect of Mercaptan Concentration on Polymerization of 75 Butadiene–25 Styrene in Oleate Emulsion for 20 Hours at 40° C.

A, DD mercaptan; *B*, No. 30 white oil mercaptan; *C*, pinene mercaptan

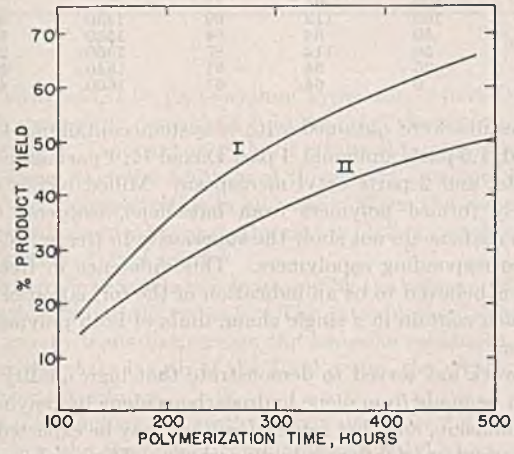


Figure 9. Polymerization Rate of Butadiene in Oleate Emulsion at 10° C. in Presence of Octyl Mercaptan and Ammonium Persulfate

I. 1% ammonium persulfate, 2% octyl mercaptan
II. 0.5% ammonium persulfate, 1% octyl mercaptan

product is influenced not only by the character of the modifying agents added to the system, but also by the nature and amount of impurities in the polymerizables, since impurities are frequently negative modifiers.

LABORATORY PROCEDURE

Glass equipment appears to be most satisfactory for use in laboratory polymerization. With materials having boiling points appreciably above the temperature of polymerization, it is possible to carry out the emulsion polymerization at atmospheric pressure. Since butadiene boils at −5° C., it is necessary in this case to use closed systems. It has been found satisfactory to use thick-walled Pyrex tubes (approximately 3 × 40 cm.) enclosed in holders made from perforated metal tubes and rotated end to end (35 r.p.m.) in a water bath at the desired temperature. These tubes are closed with neoprene stoppers which have been treated with caustic solution to remove extractable material. In filling the tubes, the water and water-soluble ingredients are placed in the tube, and the mixture is frozen by placing the tube in an acetone–solid carbon dioxide bath. Liquid butadiene and butadiene-soluble materials are then weighed into the tube, and the tubes are sealed and warmed to the desired temperature.

After the aqueous phase has been thawed, the tube can be shaken rapidly, if necessary, to form the emulsion, but usually simple rotation in the water bath is sufficient. If, upon removal from the water bath, the tube is suspected of containing appreciable amounts of butadiene, it is cooled to about 0° C. before being opened. After coagulation, the polymers are washed on a 6 × 2 inch (15.2 × 5.1 cm.) wash mill with one corrugated roll. The washed elastomer is dried first on a corrugated mill and finally on a smooth 6 × 2 inch mill with differential speed rolls.

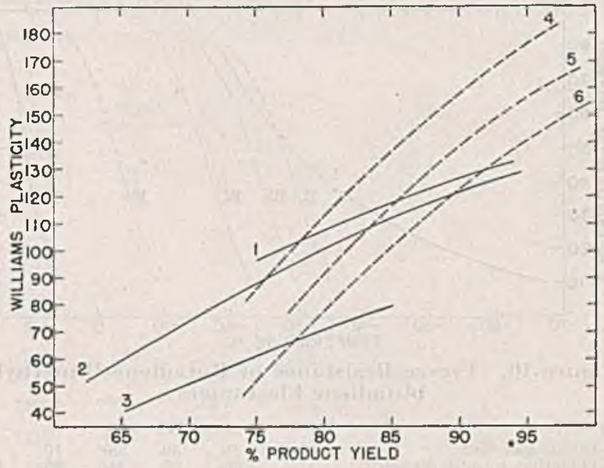


Figure 8. Effect of Yield on Plasticity of Compounds Modified with Combinations of Mercaptans

Curve No.	1	2	3	4	5	6
DD, %	..	0.5	..	0.05	0.05	0.05
Mentnene, %	0.3	..	..	0.3	..	0.4
3B, %	..	..	0.3	..	0.3	..

The samples are compounded on these small mills and cured at conventional temperatures and pressures in small presses. The apparatus used in determining the tensile properties of these samples was described by Williams and Sturgis (*30*).

Since elastomers containing butadiene are notoriously inferior in gum stocks, black stocks were used in compounding. The usual cure was 30 minutes at 153° C., and the formula generally employed was:

Elastomer	100	Sulfur	2
Phenyl-β-naphthylamine	2	Mercaptobenzothiazole	1
MPC black	50	Zinc oxide	5
Stearic acid	2		

In some recent work more active accelerators, such as 2-mercaptothiazoline, were employed. With some samples tensile strength measurements were made at temperatures ranging from −40° to +100° C.

Resistance to swelling in solvents is usually determined by weighing the sample in air and in water at room temperature before and after emersion in the solvent.

Several more practical methods for the determination of freeze resistance have been developed since this work was started, but valuable preliminary information was obtained by using a modification of the T-50 method described by Gibbons, Gerke, and Tingey (*8*). In this modification the temperature at which each 10% retraction occurred is reported; that is, a T-10 of −40° C. means that a sample stretched 240% of its original length when frozen at −70° C. and then released to allow free retraction, retracted 10% of the elongation when warmed to −40° C. The T-20 is the temperature at which it retracted 20%, etc.

The hardness (Shore durometer Type A) and the Schopper rebound were measured with a pile of three slabs.

Elastomers which gave interesting results in those preliminary tests were evaluated further by conventional rubber testing methods.

ELASTOMERS FROM BUTADIENES

The sodium-catalyzed polymerization of 1,3-butadiene was used extensively in formulating the numbered Bunas in Germany and SKA and SKB in Russia (*26*). Less attention has been given to the emulsion polymerization of butadiene alone, and it is generally assumed that the presence of another polymerizable compound is essential in order to prevent excessive cross linkage or to give the preferred 1,4 addition and obtain the best products.

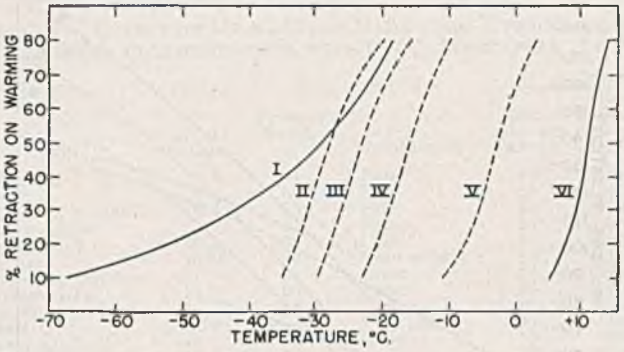


Figure 10. Freeze Resistance of Butadiene-Dimethylbutadiene Elastomers

Curve No.	I	II	III	IV	V	VI
1,3-Butadiene, %	100	40	30	20	10	...
2,3-Dimethyl-1,3-butadiene, %	...	60	70	80	90	100

The present commercial processes do involve the use of another polymerizable compound with the butadiene, but it is possible to improve the elastomers obtained from butadiene alone by suitable emulsion technique. However, to obtain high-quality butadiene polymers in emulsion, it is necessary to polymerize at lower temperatures than are commonly used commercially. The following data show the results of tests on straight butadiene polymers made in a 4% sodium oleate emulsion containing persulfate and octyl mercaptan, and polymerized at 10° C.:

Ammonium Persulfate, %	Octyl Mercaptan, %	Product Yield, %	Stress at 300%, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %
1	2	38	820	1500	420
		48	630	2940	640
		66	850	2180	460
		80	...	1450	250
0.5	1	30	480	1900	620
		45	820	2090	460
		52	1130	1600	350

In both systems the product isolated at an intermediate yield is superior to that at either the highest or the lowest yield. As Figure 9 shows, the polymerization rate is far slower than that used in commercial systems, but it is possible to modify the system so as to obtain faster polymerization rates. For example, a 92% yield was obtained in 64 hours at 10° C. by using a system containing 25 parts oleic acid, 0.5 part excess sodium hydroxide, 1 part Daxad 11, 0.5 part sodium persulfate, 1 part DD mercaptan, 4 parts methanol, 0.1 part potassium ferrocyanide, and 200 parts water per 100 parts butadiene. The product, compounded in a typical channel black stock, gave a vulcanizate having a tensile strength of 2500 pounds per square inch and an elongation at break of 650%. This shows that high yields of good quality butadiene polymers are possible.

Isoprene gave reasonably good polymers, although in general they were inferior to those from butadiene. A 90% yield of isoprene polymer was obtained at 30° C. and it gave vulcanizates with a tensile strength of 1950 pounds per square inch at 480% elongation. Practical road tests indicate that, in spite of these comparatively poor tensile properties, a tread of polyisoprene would give more than half as much service as a Grade A rubber tread.

2,3-Dimethyl-1,3-butadiene gives better milling elastomers than either butadiene or isoprene, but loggy vulcanizates which have a greater tendency to freeze. They have good tensile strength, as indicated by the following data obtained with polymers formed in an alkaline oleate emulsion containing persulfate and cured 30 minutes at 153° C.:

Polymerization		Product Yield, %	Stress at 300%, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %
Temp., ° C.	Time, hr.				
100	4	50	1410	2720	460
60	65	100	1900	2900	390
50	17	72	1810	3030	420
30	90	72	2040	2660	350

The polymerization of mixtures of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene produces elastomers which are superior in stress-strain properties to those obtained from butadiene alone under similar conditions:

Butadiene, %	Polymerization		Product Yield, %	Stress at 300%, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %
	Temp., ° C.	Time, hr.				
10	50	67	105	1810	2770	390
10	30	18	76	1610	2800	430
20	30	18	81	1700	2040	430
30	30	18	82	1920	2580	350
60	30	90	88	1410	2550	430
60	50	16	86	1470	1900	350

The freeze resistance of these dimethylbutadiene-butadiene copolymers, as indicated by retraction during gradual warming in the T-50 apparatus, shows a definite improvement as the butadiene content is increased. This is shown by the curves of Figure 10.

Even more freeze-resistant elastomers can be obtained by polymerizing mixtures of isoprene and butadiene (Figure 11). Tensile data follow on elastomers cured 30 minutes at 153° C.:

Butadiene, %	Isoprene, %	Polymerization Time at 35° C., Hr.	Product Yield, %	Tensile Strength, Lb./Sq. In.	Elongation at Break, %
0	100	64	35	...	...
0	100	112	69	1330	410
50	50	64	54	1580	540
50	50	112	87	1300	230
75	25	64	61	1840	490
100	0	64	67	1600	430

These results were obtained with a system containing 4 parts oleic acid, 1.5 parts ammonia, 1 part Daxad 11, 1 part ammonium persulfate, and 2 parts octyl mercaptan. Milled blends of the separately formed polymers from butadiene, isoprene, or dimethylbutadiene do not show the superiority in freeze resistance of the corresponding copolymers. This difference in freeze resistance is believed to be an indication of the formation of polymers which contain in a single chain, units of both polymerizing monomers.

This work has served to demonstrate that high quality polymers can be made from diene hydrocarbons alone by polymerization in emulsion, and that some advantage may be expected from copolymerization of different hydrocarbons. The emulsion polymerization of these diene hydrocarbons is worthy of more detailed investigation, and the development of the proper system may result in an elastomer superior to GR-S for general use.

COPOLYMERS OF BUTADIENE AND VINYL COMPOUNDS

Although good elastomers can be made from butadiene alone, thus far it has been easier to make a good quality product from mixtures of butadiene with other polymerizable compounds. The first work was that of Tschunkur, Meisenburg, and Bock using styrene and vinyl naphthalene (*16*, *28*). Many other types of compounds copolymerizable with butadiene were studied later by various investigators, but it is not possible to give here a complete bibliography of the extensive literature on the subject. In general, the second polymerizable components are vinyl compounds which contain an activating group such as a second vinyl, a nitrile (*12*), a carboxyl (*10*), or a phenyl group. Activation may also be accomplished by unsymmetrical substitution of two or more halogen atoms on a double-bonded carbon (*23*). Many of these vinyl compounds have been investigated, but only a few have given sufficiently attractive products or are sufficiently available commercially to be considered for the manufacture of synthetic rubbers. Table IV summarizes the properties of butadiene copolymers with vinyl compounds having different activating groups.

In this series of tests the second monomer was used on an equimolar rather than an equal weight basis, the ratio being 4.3 moles of butadiene per mole of the second vinyl compound. The mixed monomers were polymerized in an emulsion containing 5

Table IV. Properties of Butadiene Copolymers with Various Monomers

(Structure is $CH_2{=}CRR_1$)

	No Second Monomer	Acrylonitrile	Methacrylonitrile	Methyl Methacrylate	Butyl Methacrylate	Methyl α-Chloracrylate	Styrene	α-Methylstyrene
R group		H	CH_3	CH_3	CH_3	Cl	H	CH_3
R_1 group		CN	CN	CO_2CH_3	$CO_2C_4H_9$	CO_2CH_3	C_6H_5	C_6H_5
2nd monomer, % by wt.		18.6	22.4	30	38	34	30.8	33.6
Polymerization Data								
Hours at 30° C.	65	65	40	65	48	50	88	90
Product yield, %	55	88	100	93	90	87	83	85
Stress-Strain Data (Cured 30 Min. at 141° C.)								
Tested at 25° C.								
Stress at 300%, lb./sq. in.	900	...	1380	740	620	1900	650	350
Tensile, lb./sq. in.	2320	2000-2500	2970	2720	2900	2290	3220	2410
Elongation at break, %	470	400-600	450	600	650	340	650	800
Tested at 70° C.								
Tensile, lb./sq. in.	850	1160	1030	1330	1470	650	2010	1700
Elongation at break, %	250	150	260	470	590	200	620	860
Kerosene Absorption (48 Hr. at 100° C.)								
Vol. increase, %	>200	42	62	135	203	64	150	195
Freeze Resistance								
T-10, ° C.	−65	−40	−33	−46	−55	−12	−49	−47
T-50, ° C.	−34	−30	−23	−37	−46	0	−41	−38
T-80, ° C.	−21	−23	−11	−26	−36	+6	−32	−29

parts oleic acid, 1.06 parts sodium hydroxide, 1 part Daxad 11, 1 part ammonium persulfate, 0.5 part octyl mercaptan, and 116 parts water. Comparison with the results obtained on butadiene alone shows that the addition of the second monomer increases the rate of polymerization in all cases. When the second monomer contains a nitrile group, the rate is further increased by the introduction of alkyl groups.

The kerosene resistance is increased by the presence of chlorine or, especially, nitrile radicals. The introduction of additional alkyl groups tends to decrease the kerosene resistance, and the greater the chain length of the alkyl group, the greater the loss in kerosene resistance.

The introduction of a methyl group decreases the freeze resistance, but the elastomers containing the butyl group are more freeze resistant than those containing the methyl group.

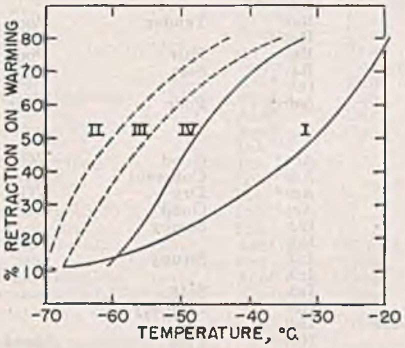


Figure 11. Freeze Resistance of Butadiene-Isoprene Elastomers

Curve No.	I	II	III	IV
1,3-Butadiene, %	100	75	50	...
Isoprene, %	...	25	50	100

The compounding formula was as follows: copolymer 100, phenyl-β-naphthylamine 2, stearic acid 2, zinc oxide 5, MPC black 50, sulfur 2, and mercaptobenzothiazole 1.

Table V summarizes data pertaining to the polymerization of mixtures of butadiene with a number of other polymerizable compounds. In testing a new compound, the general procedure was to form a 40% emulsion of a mixture of 70 parts butadiene and 30 parts of second component in an alkaline sodium oleate system with a suitable catalyst, usually a persulfate, and to agitate the emulsion at 30° or 40° C. for 65 hours. The emulsion was then treated with an antioxidant and coagulated. The coagulum was washed on a mill with one corrugated roll and milled to constant weight. In some cases, indicated by *f*, an acid system was used with *C*-cetylbetaine as emulsifying agent. Many of these experiments were carried out before the present modifiers or catalyst activators were developed. The products, therefore, do not necessarily represent the best that can be obtained from the particular compounds.

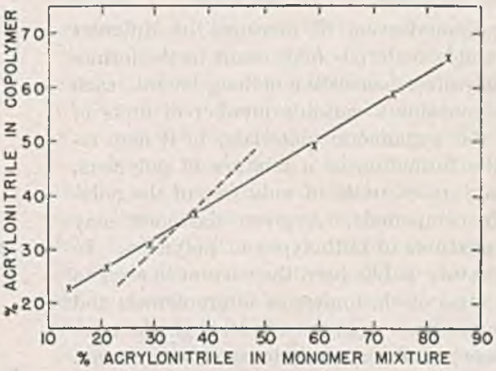


Figure 12. Relation between Composition of Monomer Mixture and Copolymer for Butadiene-Acrylonitrile

The second monomer is considered to have inhibited polymerization when the product yield was 25% or less of that which would have been obtained from the same amount of butadiene alone. Product yields 75–110% of that to be expected from the butadiene are considered normal; lower yields indicate retardation, and higher yields acceleration. In all cases where polymerization was accelerated, copolymers are believed to have been formed. When possible, this was confirmed by determination of a characteristic element such as chlorine or nitrogen. Some combinations with normal or even retarded polymerization rates gave products which contain appreciable amounts of a second monomer.

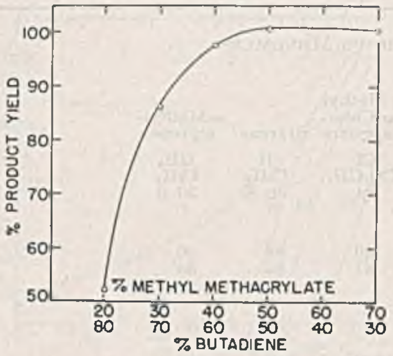


Figure 13. Effect of Monomer Ratio on Yield of Elastomer for Butadiene–Methyl Methacrylate in Ammonium Oleate Emulsion

These results indicate that minor changes in the structure of the second monomer can have a pronounced effect upon its ability to form an interpolymer with butadiene, possibly as a result of differences in the firmness of the electron bondage. For example, high yields of elastomer were obtained from mixtures of butadiene and 2-nitro-2-methylpropylmethacrylate; mixtures of butadiene and 2-nitrobutyl methacrylate failed to yield significant amounts of elastomer in either acid or alkaline systems. A similar influence of structure on ease of formation of polymers is found in the case of crotonic anilide and methacrylic anilide. Mixtures of crotonic anilide ($CH_3—CH=CHCONHC_6H_5$) and butadiene gave only small amounts of cheesy product in either acid or alkaline emulsions; butadiene and methacrylic anilide [$CH_2=C(CH_3)CONHC_6H_5$] gave high yields of elastomer.

STRUCTURE OF COPOLYMERS

The polymerization of mixtures of different polymerizable materials may result in the formation of elastomers consisting of long chains, each of which contains a variable number of units of each of the monomeric materials; or it may result in the formation of a mixture of polymers, each made up of units of only one of the polymerizable compounds. A given elastomer may contain mixtures of both types of polymers. In this laboratory it has been the custom to refer to the first class of elastomers as interpolymers and to the second as copolymers, although the term copolymers is used commonly to cover both classes.

It is often difficult to determine precisely which type of polymer is present. In some cases it is possible to determine the presence of a particular type by visual examination, physical separation, and analysis. In other cases simple extraction with solvents and analysis may serve to show the presence of different types of products. Comparison of the physical properties of the products formed by polymerization of mixtures with those formed by mill blends offers some indication of the presence of true interpolymers. Freeze resistance is believed to be a significant means of determining the difference between true interpolymers and mixtures. In certain cases determination of the index of refraction gives valuable information.

Table V. Elastomers from Butadiene with Vinyl Compounds

Second Monomer	Polymerization Rate[a]	Mill Appearance[b]	Tensile Strength[c]	Elongation[d]
Acyclic monoenes				
1,1-Dichloroethylene	Acc[e]	Fair	Good	Good
1-Bromo-1-chloroethylene	Norm[e]	Good	Poor	VG
1-Fluoro-1-chloroethylene	Inh	Soft	...	...
cis-1,2-Dichloroethylene	Ret	Tough	Poor	Fair
trans-1,2-Dichloroethylene	Ret	Tough	Fair	Good
1,1,2-Trichloroethylene	Norm[e]	Tough	Poor	Poor
1,1,2-Trifluoro-2-chloroethylene	Ret[e]	Coherent	Fair	Fair
1,1,2,2-Tetrachloroethylene	Ret	Tough	Poor	Fair
2-Chloro-1-propene	Ret	Thready	Fair	VG
3-Chloro-1-propene	Ret	Coherent	Fair	VG
2-Methyl-3-chloro-1-propene	Ret	Soft	...	...
1,1-Dichloro-2-methyl-1-propene	Norm[e]	Flaky	Fair	Fair
1,1,3-Trichloro-2-methyl-1-propene	Ret	Sticky	...	...
2,4,4-Trimethyl-2-pentene	Norm	Poor	Poor	Poor
Acyclic dienes				
1-Methyl-1,3-pentadiene	Norm	Good	Poor	VG
2-Methyl-1,3-butadiene	Norm	Good	Fair	VG
2,3-Dimethyl-1,3-butadiene	Acc[e]	Good	Good	Good
1-Chloro-1,3-butadiene	Ret[e]	Crumbly	...	...
2-Chloro-1,3-butadiene	Acc[e]	Fair	Fair	Fair
2-Fluoro-1,3-butadiene	Acc[e]	Poor	Poor	Fair
1-Chloro-2-methyl-1,3-butadiene	Inh	....	...	...
2-Chloro-3-methyl-1,3-butadiene	Acc[e]	Flaky	Fair	Poor
3-Chloro-2,4-heptadiene	Norm	Fair	Poor	VG
2,3-Dichloro-1,3-butadiene	Inh	....	...	...
1,2,4-Trichloro-1,3-butadiene	Acc[e]	Good	Poor	Poor
1,1,2,3,4-Pentachlor-1,3-butadiene[f]	Ret	....	Poor	Poor
2-Methyl-1,3-pentadiene	Acc[e]	Good	Fair	Good
3-Chloro-2,5-dimethyl-1,5-hexadiene	Inh	....	...	...
1,3-Dichloro-2,4-hexadiene	Inh	....	...	...
3-Chloro-1,3,4,5-hexatetraene	Inh	....	...	...
5,6-Dichlorohexa-1-en-3-yne	Norm[e]	Good	...	...
3,5,6-Trichloro-1,3-hexadiene	Acc[e]	Good	Fair	Fair
2,5-Dimethyl-1,3,5-hexatriene	Inh	Soft	Poor	Fair
Acyclic hydroxy compounds				
Allyl alcohol	Inh	....	...	...
2-Chloro-2-propen-1-ol	Inh	Slime	...	...
1-Hydroxy-3-chloro-2,4-hexadiene	Inh	....	...	...
Dimethylvinylethynylcarbinol	Acc[e]	VG	VG	Good
2-Ethoxy-1-butene	Inh	....	...	...
3-Methoxy-2-chloro-1-propene	Ret[e]	Crumbly	Good	VG
3-Methoxy-2-methyl-1,1-dichloro-1-propene	Inh	....	...	...
1-Divinyl ether	Ret	Tender	Poor	Poor
2-Chloroallyl ether	Ret[e]	Fair	Poor	Poor
Isobutyl vinyl ether[f]	Ret	Soft	Poor	Good
2-Methyl amyl vinyl ether[f]	Ret	....	Poor	Fair
Divinyl sulfide	Inh	....	...	...
1-Mercapto-3-chloro-2,4-hexadiene	Inh	....	...	...
Tetramethallyl silicate[f]	Norm	Poor	Poor	Poor
Methyl glycol vinyl ether[f]	Inh	Poor	Poor	Poor
Diethyldiethoxyethylene[f]	Inh	....	...	...
2,3-Diethylthio-1,3-butadiene	Inh	....	...	...
Oxo compounds				
Chloroacetone[f]	Inh	....	...	...
Crotonaldehyde	Inh	....	...	...
α-Chlorocrotonaldehyde	Inh	....	...	...
1-Buten-3-one (methyl vinyl ketone)	Acc[e]	Good	VG	VG
2-Chloro-1-butan-3-one	Norm[e]	Crumbly	Poor	Poor
Mesityl oxide	Inh	....	...	...
Phorone	Ret	Tender	Poor	Poor
Divinylformal	Ret	....	Poor	Fair
1,1-Diethoxy-2-propene	Ret	Fair	Poor	VG
Dichlorovinyl ethyl ether[f]	Ret	Soft	Poor	Fair
Biacetyl	Inh	....	...	...
Hexyl ketone dimer[f]	Norm	Poor	Poor	Poor
Monocarboxylic acids				
Acrylonitrile	Acc[e]	Good	VG	Good
Methacrylonitrile	Acc[e]	Coherent	Good	Good
α-Chloroacrylonitrile	Acc[e]	Dry	VG	Poor
α,β-Dichloroacrylonitrile	Acc[e]	Good	Good	Poor
3-Cyano-1-propene[f]	Inh	Sirupy	...	...
1-Cyano-2-butene	Inh	....	...	...
2-Cyano-1-chloro-1-propene[f]	Inh	Sirupy	...	...
2-Cyano-3-chloro-1-propene[f]	Inh	....	...	...
1-Cyano-3-chloro-1-propene	Inh	Soft	...	...
1-Cyano-2-methyl-1-propene	Inh	Powdery	...	...
2-Cyano-4-methyl-1,3-pentadiene	Inh	....	...	...
1-Cyano-1,3-butadiene	Norm	Poor	Good	Fair
2-Cyano-1,3-butadiene[f]	Acc	Poor	Poor	Poor
1-Acetoxy-1,3-butadiene[f]	Inh	....	...	...
2-Acetoxy-1,3-butadiene	Ret	Gummy	...	...
1-Acetoxy-3-chloro-2,4-hexadiene	Acc[e]	Good	Fair	Good
1,1-Dichloro-2-methyl-3-acetoxy-1-propene	Ret	Crumbly	Fair	Good
Vinyl formate	Inh	....	...	...
Vinyl acetate	Inh	....	...	...
Vinyl chloroacetate[f]	Inh	....	...	...
Methyl methacrylate	Acc[e]	Good	VG	VG
Ethyl methacrylate	Acc[e]	Good	Good	Fair
n-Propyl methacrylate	Acc[e]	Good	Good	Good
n-Butyl methacrylate	Acc[c]	Good	Good	Good
Butyl methacrylate	Acc[e]	Good	Good	Good
n-Octyl methacrylate	Acc[e]	Tender	Poor	Poor
Vinyl methacrylate	Acc[e]	Good	Poor	Poor
Allyl methacrylate	Acc[c]	Good	Poor	Poor
Methallyl methacrylate	Acc[e]	Dry	Poor	Poor
3-Chloro-2-butenyl methacrylate	Norm[e]	Good	Poor	Poor
2-Nitropropyl methacrylate	Inh	....	...	...

Table V. Elastomers from Butadiene with Vinyl Compounds (*Cont'd*)

Second Monomer	Polymerization Rate[a]	Mill Appearance[b]	Tensile Strength[c]	Elongation[d]
Monocarboxylic acids (*Cont'd*)				
2-Nitro-2-methyl propyl methacrylate[f]	Acc[e]	Good	VG	VG
2-Nitrobutyl methacrylate	Inh	....	...	...
Ethylene glycol monomethacrylate	Inh	....	...	...
Methoxy methyl methacrylate	Acc[e]	Good	Fair	Fair
Ethyl thiomethacrylate[f]	Acc[e]	Good	Poor	VG
Polycarboxylic acids				
Dimethyl fumarate[f]	Acc[e]	Good	Good	VG
Diisobutyl fumarate	Acc[e]	Tacky	Poor	Good
Diallyl fumarate	Acc[e]	Crumbly	Poor	Poor
Dimethallyl fumarate	Acc[e]	Crumbly	...	...
Di(3-chloro-2-butenyl) fumarate	Acc[e]	Flaky	Poor	Poor
1,2-Dicyanoethylene	Acc[e]	Crumbly	Good	Poor
2-Methyl-2-nitropropyl fumarate[f]	Acc[e]	Fair	Good	Good
Dimethyl maleate[f]	Ret	Soft	...	...
Dimethallyl maleate	Acc[e]	Crumbly	...	...
Diethyl methylene maleate[f]	Ret	Good	Fair	VG
Diisobutyl maleate	Acc[e]	Fair	Poor	Poor
Ethyl cyanoacetate	Inh	....	...	...
α-Cyanosorbic acid[f]	Ret	Resinous	...	...
Methyl α-cyanosorbate[f]	Inh	....	...	...
2-Methyl-2-nitropropyl maleate[f]	Acc[e]	....	Fair	Poor
Di-2-nitrobutyl fumarate[f]	Inh	....	...	...
Hydroxy carboxylic acids				
Diallyl carbonate[f]	Norm	Poor	Poor	Poor
Dimethallyl carbonate[f]	Ret	....	Poor	Poor
Acrolein cyanohydrin acetate	Inh	....	...	...
3-Cyano-3-acetoxy-1-butene[f]	Ret	Good	Poor	VG
Cyanomethyl methacrylate	Acc[e]	Crumbly	Good	Fair
β-Cyanoethyl methacrylate[f]	Acc[e]	Poor	Poor	Poor
Methacryl isothiocyanate[f]	Inh	....	...	...
Methacrylurea	Acc[e]	Crumbly	Fair	Poor
Diethoxymethylurea[f]	Norm	Poor	Poor	Poor
Vinyl thiolacetate	Ret[e]	Good	Fair	Good
Dimethyllyl methallyloxy succinate[f]	Ret	Poor	Poor	Poor
Amines				
N-Allyl maleic half-amide[f]	Inh	....	...	...
Monomethacrylurea	Norm[e]	Waxy	Good	Poor
N-Dimethylcrotonamide	Ret[e]	Good	...	...
Dimethallylamine[f]	Acc	Poor	Poor	Good
Methacryl dimethylamide	Inh	Soft	...	...
N-Methyl maleic monoamide	Inh	....	...	...
N-Butyl maleic monoamide	Ret	Soft	...	...
N-Methyl methacrylamide[f]	Norm	Poor	Poor	Poor
N-Stearyl methacrylamide[f]	Acc[e]	Poor	Poor	Poor
Methallyl isothiocyanate	Inh	....	...	...
Dimethylamine hexylmethacrylamide	Inh	....	...	...
N-(β-Dimethyl aminoethyl) methacrylamide	Acc[e]	Poor	Poor	Poor
Dimethylaminoethyl methacrylate[f]	Acc[e]	Good	Poor	Poor
Diethylaminoethyl methacrylate[f]	Acc[e]	....	Fair	Poor
2-Cyanoisopropyl methacrylamide[f]	Inh	....	...	...
2-Propene phosphonic bisdimethylamide	Acc	Flaky	Poor	Poor
Isocyclic compounds				
Methylenecyclohexane	Ret	Good	Poor	Good
β-Pinene	Norm	Tender	Poor	Good
Dipentene	Norm	Fair	Poor	Poor
Cyclopentadiene[f]	Norm	Poor	Poor	Poor
Styrene	Acc[e]	Fair	VG	VG
p-Methylstyrene	Norm[e]	Coherent	VG	VG
α-Methylstyrene	Acc[e]	Fair	VG	VG
p-Methyl-α-methylstyrene	Acc[e]	Fair	VG	VG
α-Chlorostyrene	Acc[e]	Dry	Poor	Good
2,5-Dichlorostyrene	Acc[e]	Good	VG	VG
β-Nitrostyrene[f]	Inh	....	...	...
3-Methyl-β-nitrostyrene[f]	Inh	....	...	...
3-β-Dinitrostyrene[f]	Inh	....	...	...
m-Nitrostyrene[f]	Inh	....	...	...
m-Chloro-β-nitrostyrene[f]	Inh	....	...	...
β-Nitro-β-methylstyrene	Inh	....	...	...
1-Phenyl-1,3-butadiene[f]	Acc[e]	Crumbly	...	...
Dicyclopentadiene	Ret	Good	Fair	VG
2,3-Diphenyl-1,3-butadiene	Acc[e]	Good	Good	VG
2,3-Di(*p*-fluorophenyl)-1,3-butadiene	Norm[e]	Good	VG	VG
Isocyclic hydroxy compounds				
α-Ethoxystyrene	Inh	....	...	...
Cinnamyl alcohol	Inh	....	...	...
p-Methoxy-β-nitrostyrene	Inh	....	...	...
Cyclohexyl methacrylate	Acc[a]	Good	Good	Good
Pentachlorophenyl methacrylate	Inh	....	...	...
Isocyclic oxo compounds				
β-Carvone	Inh	Sticky	...	...
1-Phenyl-1-buten-3-one[f]	Acc[e]	Good	VG	Good
1,3-Diphenyl-1-propen-3-one[f]	Acc[e]	Good	Good	Fair
1-Phenyl-5-chloro-1-penten-3-one	Inh	....	...	...
1,5-Diphenyl-1,4-pentadien-3-one	Acc[e]	Fair	Good	Good
1-Phenyl-1,3-hexadien-5-one	Inh	....	...	...
1-Phenyl-5-methyl-1,4-hexadien-3-one	Acc[e]	Good	Fair	Fair
Cinnamic aldehyde–methylamine	Inh	....	...	...
1-(*p*-Nitrophenyl)-1-buten-3-one[f]	Inh	....	...	...
1,4-Diphenyl-2-butene-1,4-dione	Acc[e]	Crumbly	Fair	Fair

(*Continued on page 220*)

The presence of an element, such as nitrogen or chlorine, which can readily be determined quantitatively is frequently helpful in studying copolymers. For example, a butadiene-acrylonitrile copolymer was dissolved in benzene (5% cement) and, at 40 C., diluted with 58 grams ethyl alcohol per 100 grams cement. The mixture was cooled to 28° C. and, upon standing, separated into two layers. The solvents were removed by evaporation, the product of higher molecular weight was redissolved, and the treatment repeated. The original elastomer was separated into four fractions of different solubilities. The data obtained with these fractions indicate there is comparatively little difference in the chemical composition of the various fractions, i.e., the product is essentially a true interpolymer. The least soluble fraction does contain slightly less nitrogen than the most soluble fraction. The viscosities of cements made from these fractions, as determined in a Gardner-Holdt bubble tube, indicate a wide difference in molecular weight:

Relative Solubility	% of Original	Nitrogen Content, %	Bubble-Tube Viscosity of 9.5% Benzene Cements, Sec.
	100	7.31%	9
1	23	7.30	2
2	23	7.24	3.7
3	18	7.34	12
4	36	6.99	300

Results obtained by polymerizing, in both acid and alkaline systems, a number of different mixtures of butadiene and acrylonitrile indicate that the composition of the copolymer is chiefly dependent upon the composition of the monomer mixture even if the polymerization rates vary widely. These data (Figure 12) indicate a linear relation between the compositions of the monomer mixture and the resulting copolymer. According to these results, a monomer mixture containing a little over 35% acrylonitrile should give a quantitative yield of elastomer of the same composition as indicated by the insection of the dotted line for a uniform copolymerization and the experimentally determined relation. Copolymers made from higher butadiene-acrylonitrile ratios contain a higher acrylonitrile content than the monomer mixtures; those made from low butadiene-acrylonitrile ratios contain a lesser portion of the nitrile. While this generalization holds for this particular combination of monomers, it is not necessarily applicable to all other combinations. In fact, with some mixtures one monomer may polymerize to yield a product containing little or none of the second material.

PROPERTIES OF CERTAIN COPOLYMERS

The proportion of the second monomer in the starting mixture markedly affects both the rate of polymerization and the properties of the resulting polymer. Improvements in certain properties obtained by a selected ratio of monomers may be accompanied by deficiencies in other properties. For example, a higher retention of tensile strength at elevated temperatures may coexist with poorer freeze resistance (Table VIII). Certain of the second monomers listed in

Table V. Elastomers from Butadiene with Vinyl Compounds (*Cont'd*)

Second Monomer	Polymerization Rate[a]	Mill Appearance[b]	Tensile Strength[c]	Elongation[d]
Isocyclic carboxylic acids				
α-Cyanostyrene	Ret	Waxy-brittle	...	...
β-Cyanostyrene	Acc[e]	....	Fair	Fair
1-Cyano-4-phenyl-1,3-butadiene	Norm	....	Poor	Fair
1-Cyano-1,4-diphenyl-1,3-butadiene	Ret	Waxy-brittle	...	...
Vinyl benzoate[f]	Inh	....	...	...
Ethylene glycol dicinnamate	Acc[e]	Noncoherent	...	...
Methyl-4-nitrocinnamate	Ret	Noncoherent	...	...
Methyl α-cyano-β-phenyl acrylate	Acc[e]	....	Poor	Poor
1-Phenyl-4-cyano-4-carboethoxy-1,3-butadiene	Acc[e]	Good	Fair	Good
Methyl-*o*-cyanocinnamate				
59° isomer	Norm	Good	Poor	Fair
92° isomer	Acc[e]	Good	Good	Good
Isocyclic amines				
Aminostyrene[f]	Inh	Powder	...	...
Crotonanilide	Inh	Cheesy	...	...
Methacryl anilide	Acc[e]	Flaky	Good	VG
Methacryl *p*-nitroanilide	Inh	....	...	...
Methacryl-*m*-toluidide	Ret[e]	Hard	Good	VG
o-Cyanocinnamic anilide, *trans* [f] (m.p. 186–187° C.)	Norm[e]	Fair	Poor	Poor
o-Cyanocinnamic anilide, *cis* [f] (m.p. 130–135° C.)	Ret[e]	Fair	Poor	Poor
-Cyanocinnamic anilide *m*-nitroanilide	Inh	....	...	...
Methacryl *p*-hydroxyanilide	Inh	....	...	...
Methacryl *p*-aniside	Inh	....	...	...
Heterocyclic compounds				
2-Vinylpyridine	Acc	Good	VG	VG
5-Ethyl-2-vinylpyridine	Acc	Good	VG	VG
β(α-Furyl) acrylic acid	Inh	....	...	...
Furyl acrylic acid	Inh	....	...	...
Methyl β-furyl acrylate	Acc[e]	Good	Good	Good
Allyl β-furyl acrylate	Acc[e]	Dry	Poor	Poor
Furfuryl methacrylate	Acc[e]	Good	...	...
β-Furyl acrylonitrile[f]	Inh	....	...	...
Ethyl α-cyano-β-furyl acrylate	Inh	....	...	...
Furoic anilide	Norm[e]	Poor	...	...
β-Nitrofurylethylene	Inh	....	...	...
1-Furyl-1-buten-3-one	Acc[e]	Good	Good	Good
1-Furyl-5-methyl-1,4-hexadien-3-one	Inh	....	...	...
1-Furyl-3-phenyl-1-propen-3-one	Acc[e]	Good	Good	Good
Chlorovinyl ethylene oxide	Inh	....	...	...
Ethylene sulfide	Inh	Powder	...	...
Propylene sulfide	Inh	Plastic	...	...
Indole	Inh	....	...	...
2-Methylindole	Inh	....	...	...
N-Methyl maleicimide	Inh	....	...	...
N-Butyl maleicimide[f]	Ret	Soft	...	...
N-Cyclohexyl maleicimide	Ret[e]	Good	Fair	VG
N-Methyl citroconicimide	Ret[e]	Good	...	...
N-Allyl maleicamide	Inh	Powder	...	...
N-Vinyl succinimide	Inh	....	...	...
Terpene peroxide	Inh	....	...	...

[a] Acc = accelerated; Norm = normal; Ret = retarded; Inh = inhibited.

[b] Good means the band on the mill was smooth and unbroken; Fair, the band was somewhat broken and rough; Poor, the band was difficult to maintain. Certain of the poor-milling polymers are described more specifically.

[c] Poor, less than 1500 lb./sq. in.; Fair, 1500–2000 lb.; Good, 2000–3000 lb.; Very Good, above 3000 lb.

[d] Poor, less than 250%; Fair, 250–350%; Good, 350–450%; Very Good, above 450%.

[e] Product contains appreciable amounts of second monomer.

[f] Polymerized in acid emulsions.

Table V, such as methyl and butyl methacrylate (*24*), methyl vinyl ketone (*15*), dimethylvinylethynylcarbinol (*22*), in combination with butadiene and isoprene, have been studied in more detail, and some of the results are described in the following sections. The copolymers were compounded according to the basic formula: copolymer 100, phenyl-β-naphthylamine 2, stearic acid 2, zinc oxide 5, MPC black 50, sulfur 2, mercaptobenzothiazole 1.

Methacrylate Copolymers. When mixtures of butadiene and methyl methacrylate were polymerized in an ammonium oleate emulsion containing 0.8 part excess ammonia and 1 part ammonium persulfate, the polymer yield obtained in 40 hours at 30° C. was found to increase considerably with increase in methyl methacrylate–butadiene ratio (Figure 13). The variation in properties with monomer ratio is shown by the data of Table VI.

In a practical road test a tire made from a 70 butadiene–30 methyl methacrylate elastomer was only slightly inferior to a high grade rubber control. These polymers made with methyl methacrylate compare favorably with those made with styrene in vulcanizate properties, and are actually superior in processability and oil resistance.

Data obtained in determining properties, such as freeze resistance, kerosene absorption, Schopper rebound and Shore durometer hardness, of vulcanizates of elastomers formed from mixtures of butadiene or isoprene with methyl methacrylate or butyl methacrylate are plotted in Figures 14 to 18. Butyl methacrylate is superior to methyl methacrylate in imparting freeze resistance and resiliency, but methyl methacrylate tends to give harder, more oil-resistant vulcanizates. The T-10 results indicate that the tendency of the polymer to become brittle at very low temperatures increases with increasing methyl methacrylate content. The T-50 and T-80 results indicate that the presence of small amounts of methyl methacrylate actually improved the retention of "snap" at intermediate temperatures. Butadiene is superior to isoprene in imparting freeze resistance, oil resistance, and resiliency.

Methyl Vinyl Ketone Copolymers. Mixtures of butadiene and methyl vinyl ketone can be polymerized to give good yields of copolymers whose vulcanizates exhibit to an unusual degree a combination of kerosene and freeze resistance (Table VII). In fact, for a given freeze resistance they are superior to butadiene-acrylonitrile polymers in kerosene resistance. These particular elastomers were made by polymerizing at 30° C. in a myristylamine $[CH_3(CH_2)_{12}CH_2NH_2]$–hydrochloric acid system catalyzed with ammonium persulfate and containing no modifier; good elastomers have also been made in oleate, or preferably Lorol sulfate, systems. Methyl vinyl ketone is a strong lachrymator, and it is difficult to obtain a vulcanizate of its diene copolymers free from the characteristic odor.

Dimethylvinylethynylcarbinol Interpolymers. $(CH_3)_2COH—C\equiv C—CH=CH_2$ gives excellent elastomers when interpolymerized with butadiene. Typical data (Table VIII) were obtained with a system containing 4 parts oleic acid, 1 part Daxad 11, 0.5 part sodium hydroxide in excess of that required to neutralize the oleic acid, 1 part potassium persulfate, 0.05 part potassium ferricyanide, and 1 part DD mercaptan. The data show that good copolymers are obtained with 15 to 30 parts of the carbinol. It is believed to be significant that the heat build-up reaches a minimum when 20–30 parts of carbinol are used. The 70 butadiene–30 carbinol copolymer is especially interesting; at approximately the same state of cure (judged by modulus) as the 10 and 15% carbinol copolymers, the tear resistance, heat build-up, and tensile strength at 70° C. reach an optimum.

The possibility of using three or more monomers in forming an elastomer is intriguing and susceptible of an infinite number of

Table VI. Properties of Butadiene–Methyl Methacrylate Elastomers

(Cure, 30 minutes at 153° C.)

% Methyl Methacrylate	Stress at 300%, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elongation at Break, %	Kerosene Absorption[a], Vol. %
20	1625	3100	420	208
30	1975	3400	400	217
40	2100	4350	440	110
50	...	2525	290	105
70	...	1400	210	48

[a] Increase in volume in 48 hours at 100° C.

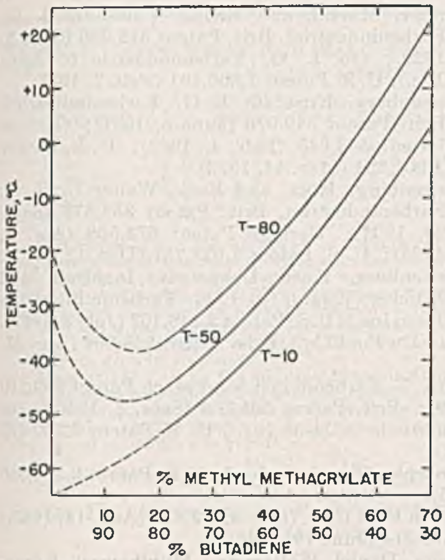


Figure 14. Freeze Resistance of Butadiene–Methyl Methacrylate Elastomers as Determined by T-50 Method

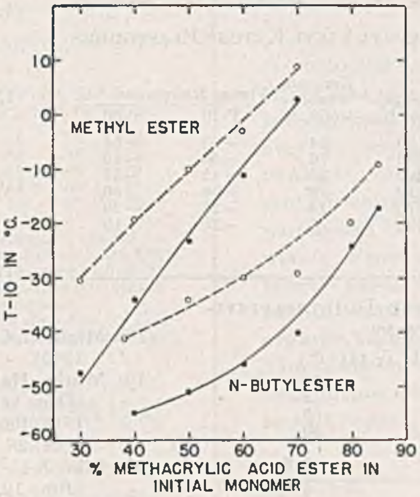


Figure 15. Effect of Methacrylic Acid Esters Mixed with Butadiene and Isoprene on Freeze Resistance (T-10 Value) of Vulcanized Copolymers

——— Butadiene copolymer
- - - - Isoprene copolymer

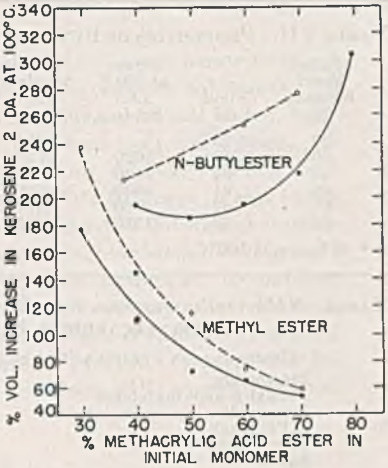


Figure 16. Effect of Methacrylic Acid Esters Mixed with Butadiene and Isoprene on Kerosene Absorption of Vulcanized Copolymers (Cured 30 Minutes at 153° C.)

——— Butadiene copolymer
- - - - Isoprene copolymer

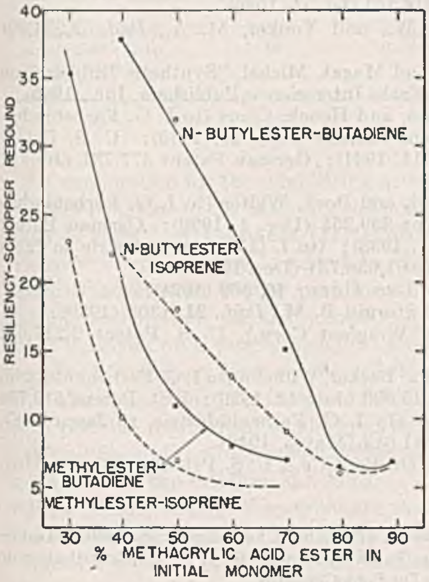


Figure 17. Effect of Methacrylic Acid Esters Mixed with Butadiene and Isoprene on Resilience of Vulcanized Copolymers (Cured 30 Minutes at 153° C.)

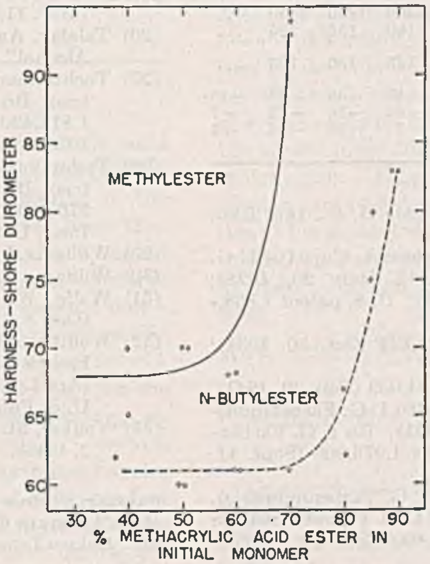


Figure 18. Effect of Methacrylic Acid Esters Mixed with Butadiene on Hardness of Vulcanized Copolymers (Cured 30 Minutes at 153° C.)

variations. The replacement of part of the styrene in the GR-S formula with dimethylvinylethynylcarbinol was investigated in some detail, and mixtures of 75 butadiene–20 styrene–5 dimethylvinylethynylcarbinol gave (*18*) elastomers superior to GR-S in millability, tensile properties, and low heat build-up under flexing, but not superior to those made from butadiene with 20 or 30 parts of the carbinol and no styrene.

CONCLUSION

In any study of polymerization, careful consideration must be given to factors such as type and concentration of emulsifying agent, concentration of monomer, temperature, catalyst, and certain added chemicals which may have a marked effect upon the results obtained.

It is possible to make elastomers of considerable utility from mixtures of butadiene and many other polymerizable compounds. Several of these are superior to those made from butadiene and styrene in particular respects; but considering availability and cost of raw materials, this work has not uncovered any butadiene copolymers which would have been preferred over those made with styrene or acrylonitrile in the period of national emergency. The possibility of obtaining high grade elastomers from the diene hydrocarbons alone appears to justify further investigation.

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LITERATURE CITED

(1) Bachle, Otto (to I. G. Farbenindustrie), German Patent 702,209 (Feb. 1, 1941).
(2) Bock, Walter, and Tschunkur, Eduard (to I. G. Farbenindustrie), Brit. Patent 349,499 (May 26, 1931); German Patent 532,271 (Aug. 22, 1931); U. S. Patent 1,898,522 (Feb. 21, 1933).
(3) Browning, G. L., Jr. (to B. F. Goodrich Co.), U. S. Patent 2,385,190 (Sept. 18, 1945).
(4) Bysow, B. W. (to Resinotrest), Brit. Patent 314,933 (July 5, 1929); German Patent 521,903 (Mar. 31, 1936).
(5) Dogadkin, B. A., Beresan, K. B., and Lapuk, M. G., Russian Patent 46,354 (Mar. 31, 1936).
(6) Fryling, C. F. (to B. F. Goodrich Co.), U. S. Patent 2,313,233 (Mar. 9, 1943).
(7) *Ibid.*, 2,376,350 (May 22, 1945).

TABLE VII. PROPERTIES OF BUTADIENE–METHYL VINYL KETONE ELASTOMERS

Methyl Vinyl Ketone, %	Yield, %	Stress at 300%, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Elongation, %	Kerosene Absorption[a], %	Freeze Resistance, ° C.	
						T-10	T-50
20	93	...	1210	120	94	−63	−54
30	80	1020	2720	520	76	−50	−40
40	91	1640	3080	420	35	−42	−37
50	91	2890	3050	310	23	−36	−30
60	82	1780	3450	470	14	−28	−20
80	32	1210	2890	520	5	−20	−10

[a] 48 hours at 100°C.

TABLE VIII. PROPERTIES OF BUTADIENE–DIMETHYLVINYLETHYNYLCARBINOL ELASTOMERS

COMPOUNDING FORMULA (CURED 30 MIN. AT 141° C.)

Elastomers	100
Phenyl-β-naphthylamine	2
Zinc oxide	5
MPC black	50
Stearic acid	2
Sulfur	1.5
Heliozone	1.5
Process oil	3
Benzothiazyl-2-monocyclohexylsulfonamide	1.3

Dimethylvinylethynylcarbinol, parts	10	15	20	30	50
Tested at 25° C.					
Stress at 300%, lb./sq. in.	1050	900	1525	1100	1390
Tensile strength, lb./sq. in.	2275	2875	3000	4400	3220
Elongation at break, %	465	580	460	655	480
Tear resistance, lb.	175	145	165	290	...
Shore durometer hardness	59	57	59	58	...
Heat build-up in 20 min. on Goodrich flexometer (1/8-in. stroke)	52	53	44	44	...
Resiliency (Yerzley)	53	49	56	54	...
Tested at 70° C.					
Tensile strength, lb./sq. in.	1025	1400	1850	2450	...
Tear resistance, lb.	140	180	135	285	...
Kerosene absorption, % vol. increase in 48 hr. at 100° C.	180	155	130	103	...
Freeze resistance, ° C.					
T-10	−62	−57	−46	−29	−16
T-50	−43	−42	−36	−22	−7
T-80	−32	−31	−28	−14	−1

(8) Gibbons, W. A., Gerke, R. H., and Tingey, H. C., IND. ENG. CHEM., ANAL. ED., 5 279 (1933).

(9) Gunther, Fritz, Hopff, Heinrich, and Schuster, Curt (to I. G. Farbenindustrie), Brit. Patent 294,412 (July 26, 1928); German Patent 519,483 (Feb. 28, 1931); U. S. patent 1,838,826 (Dec. 29, 1931).

(10) I. G. Farbenindustrie, Brit. Patent 360,822 (Oct. 30, 1931); German Patent 667,163 (Nov. 5, 1938).

(11) I. G. Farbenindustrie, German Patent 704,039 (Feb. 20, 1941).

(12) Konrad, Erich, and Tschunkur, Eduard (to I. G. Farbenindustrie) Brit. Patent 360,821 (Oct. 30, 1931); (to I. G. Farbenindustrie to Jasco Inc.), U. S. Patent 1,973,000 (Sept. 11, 1934).

(13) Luther, Martin, and Heuck, Claus (to I. G. Farbenindustrie), Brit. Patent 312,201 (May 21, 1930); U. S. Patent 1,864,078 (June 21, 1932); German Patent 558,890 (Sept. 19, 1932).

(14) Luther, Martin, and Heuck, Claus (to I. G. Farbenindustrie), Brit. Patent 318,296 (Sept. 2, 1929); (to I. G. Farbenindustrie to Jasco Inc.), U. S. Patent 1,896,491 (Feb. 7, 1933).

(15) Meisenburg, Kurt (to I. G. Farbenindustrie), Brit. Patent 349,976 (June 5, 1931); German Patent 543,343 (Feb. 4, 1932); U. S. Patent 1,901,354 (Mar. 14, 1933).

(16) Meisenburg, Kurt, and Bock, Walter (to I. G. Farbenindustrie), Brit. Patent 358,877 (Sept. 29, 1931); German Patent 573,568 (Apr. 3, 1933); U. S. Patent 1,938,751 (Dec. 12, 1933).

(17) Meisenburg, Kurt, Dennstedt, Ingofroh, and Zaucker, Ewald (to I. G. Farbenindustrie to Jasco Inc.), U. S. Patent 2,248,107 (July 8, 1941).

(18) Mighton, C. J. (to Du Pont Co.), Brit. Patent 568,964 (Apr. 27, 1945).

(19) Murke, Hans (to I. G. Farbenindustrie), French Patent 850,210 (Dec. 11, 1939); Brit. Patent 525,733 (Sept. 3, 1940); (to I. G. Farbenindustrie to Jasco Inc.), U. S. Patent 2,260,475 (Oct. 28, 1941).

(20) Olin, J. F. (to Sharples Chemicals Inc.), U. S. Patent 2,378,030 (June 12, 1945).

(21) Parker, J. L. (to Du Pont Co.), *Ibid.*, 2,382,812 (Aug. 14, 1945); Brit. Patent 578,214 (June 19, 1946).

(22) Sandhaas, Wilhelm, Daniel, Walter, and Muhlhausen, Kornelius (to I. G. Farbenindustrie), U. S. Patent 2,200,705 (May 14, 1940).

(23) Sebrell, L. B. (to Wingfoot Corp.), *Ibid.*, 2,215,379 (Sept. 17, 1940); Brit. Patent 533,142 (Feb. 6, 1941).

(24) Starkweather, H. W., and Collins, A. M. (to Du Pont Co.), U. S. Patent 2,218,362 Oct. 15, 1940).

(25) Starkweather, H. W., and Youker, M. A., *Ibid.*, 2,234,204 (Mar. 11, 1941).

(26) Talalay, Anselm, and Magat, Michel, "Synthetic Rubber from Alcohol", New York, Interscience Publishers, Inc., 1945.

(27) Tochtermann, Hans, and Heuck, Claus (to I. G. Farbenindustrie), Brit. Patent 329,969 (May 27, 1930); U. S. Patent 1,814,420 (July 14, 1931); German Patent 577,731 (June 3, 1933).

(28) Tschunkur, Eduard, and Bock, Walter (to I. G. Farbenindustrie), Brit. Patent 339,255 (Dec. 1, 1930); German Patent 570,980 (Feb. 27, 1933); (to I. G. Farbenindustrie to Jasco Inc.), U. S. Patent 1,938,731 (Dec. 12, 1933).

(29) Williams, Ira, IND. ENG. CHEM., 16, 362 (1924).

(30) Williams, Ira, and Sturgis, B. M., *Ibid.*, 31, 1303 (1939).

(31) Wolfe, W. D. (to Wingfoot Corp.), U. S. Patent 2,217,631 (Oct. 8, 1940).

(32) Wollthan, Heinz, and Becker, Wilhelm (to I. G. Farbenindustrie) French Patent 843,903 (July 12, 1939); Brit. Patent 519,730 (April 4, 1940); (to I. G. Farbenindustrie, to Jasco Inc.), U. S. Patent 2,281,613 (May 5, 1942).

(33) Youker, M. A. (to Du Pont Co.), U. S. Patent 2,333,403 (Nov. 2, 1943).

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Action of Acrylonitrile on Viscose

EFFECT ON THE NORMAL AGING PROCESS

J. P. HOLLIHAN AND SANFORD A. MOSS, JR.

American Viscose Corporation, Marcus Hook, Pa.

DURING the aging of viscose, the cellulose xanthate becomes steadily more precipitable; this behavior is probably due largely to the gradual loss of the solubilizing xanthate groups (*2*, *9*). Some authors, however, contend that the effect is primarily physical or colloidal (*6*, *9*). Whatever the mechanism, the effect is of great practical importance inasmuch as viscose solutions are always aged to a definite degree of precipitability before being spun. This optimum spinning age is generally determined by standard tests involving a salting out of the cellulose xanthate, the results being expressed as salt index, Hottenroth number, etc. A number of substances are known which, when added to viscose, substantially affect the rate of aging (*9*). The effect of these compounds, however, is entirely a retardation of the normal rate of aging, and no immediate increase or change in the salt index is observed when they are added. In contrast, acrylonitrile and certain related compounds (*4*) have a marked solubilizing action and cause an immediate rise in salt test, as indicated by the data of Tables I and II.

TABLE I. SALT INDEX AND BALL FALL OF ACRYLONITRILE-TREATED VISCOSES

Acrylonitrile Added, %	Salt Index[a], %				Ball Fall[b], Sec.			
	5 hr.[c]	20 hr.	42 hr.	68 hr.	5 hr.[c]	20 hr.	42 hr.	68 hr.
None	4.1	2.2	1.4	0.7	57	68	71	77
0.25	5.0	3.4	2.4	1.5	49	63	66	73
0.50	6.5	4.4	3.1	2.1	50	61	66	73
1.0	8.7	5.9	4.0	2.7	48	58	63	71
2.0[d]	11.8	8.0	5.8	4.3	37	53	57	70

[a] Salt index is the concentration of sodium chloride solution needed to coagulate a small quantity of viscose under standard conditions. On the scale used here, 14.0 would represent a freshly prepared viscose, which is difficultly precipitable, and 2.0 would represent one that is easily precipitable and has aged considerably past the optimum spinning condition.

[b] Ball fall is the time required for a steel ball, 1/8 inch in diameter, to fall through 8 inches of viscose at 18° C. The decrease indicated here represents a moderate drop in viscosity.

[c] Time at 18° C. after the addition of acrylonitrile.

[d] This sample developed a green opacity almost immediately; microscopic examination showed it to be due to the presence of insoluble droplets of some oily material. At 23° C. this insoluble phase disappeared within a few hours. The odor of ammonia was noted.

TABLE II. APPROXIMATE RATE OF ACRYLONITRILE-VISCOSE REACTION

Material Added	Time after Addition, Min.	Remarks
Acrylonitrile, 2.8%	3	Green color starting to develop
	4	Salt index about 9, rising
	25	Salt index 14.5
	56	Salt index 14.3; green opacity is pronounced, and there is some odor of ammonia
Acrylonitrile, 2.8%, emulsified with sodium oleate	2	Definite green color developing
	19	Salt index 13.7

An explanation for the solubilizing action of acrylonitrile could possibly be given on the basis of a colloidal protective mechanism. Thus Scherer and Leonards (*11*) explain the lowering of the viscosity when pyridine is added to viscose on the basis of a selective adsorption of the pyridine. Alternatively, a second possible explanation for the solubilizing action of acrylonitrile could be given on a purely chemical basis, if we assume that a reaction takes place between the cellulose and the acrylonitrile with the formation of a more soluble cellulosic derivative. A third possible mechanism would involve interaction between the acrylonitrile and the by-product sulfur, the net result being a re-xanthation of the cellulose xanthate. (Viscose solution contains sodium sulfide, sodium thiocarbonate, sodium perthiocarbonate, and related compounds. This group is spoken of as by-product sulfur and arises in part during the xanthation of the alkali cellulose. Additional by-product sulfur is also formed during the aging process, since the sulfur released by the decomposition of the cellulose xanthate reacts with the "free" sodium hydroxide to form these compounds. For practical purposes the by-product sulfur may be considered to be composed entirely of sodium sulfide and sodium thiocarbonate.)

As a first attack on the problem, the sulfur relations shown in Table III were determined. The total and by-product sulfur decrease some 12 and 45%, respectively, whereas the xanthate sulfur increases some 25%. These data point at once to a purely chemical mechanism for the solubilizing, since it is known that the salt index increases with increasing xanthate sulfur content. Specifically, it is clear from these data that a part of the by-product sulfur has reacted with the acrylonitrile and has been transformed into xanthate sulfur or into some sulfur-containing derivative similar in solubilizing action to the xanthate group. Further, from the decrease in total sulfur it is clear that some volatile sulfur compound must have been formed and subsequently lost to the atmosphere. As a first assumption it seems reasonable to suppose that this volatile substance is carbon disulfide, particularly since it is known that, when carbon disulfide is added to viscose, a further xanthation of the cellulose xanthate is readily effected (*3*, *9*, *10*, *12*).

A number of substances are known which affect the rate of aging of viscose solutions. No immediate change or increase in salt index, however, is ever observed when they are added. In contrast, acrylonitrile and certain related compounds cause an immediate increase in salt index, which can be explained by the following mechanism: When acrylonitrile is added to viscose, it reacts rapidly with the principal by-product sulfur constituents; the latter are converted into organic sulfides, and carbon disulfide is released. The carbon disulfide evolved causes further xanthation of the cellulose with a resultant rise in salt index.

The next step in the study was the elimination of effects which might be due to the presence of cellulose. This was accomplished by reacting the acrylonitrile with an artificial by-product solution prepared by shaking carbon disulfide with sodium hydroxide. Such a solution apparently contains the sulfur entirely as sodium thiocarbonate (*13*) and does not contain the sodium sulfide, polysulfide, and the like which are normally present in viscose. However, since viscose by-product sulfur is largely sodium thiocarbonate, the artificial by-product solution is a reasonable simulation of the conditions actually encountered in viscose. When acrylonitrile is added to this artificial solution, the same sequence of events occur as with viscose. In this case, however, the droplets which form during the opaque stage can be separated by centrifuging. They were found to be nonvolatile and quite viscous, and to have a strong sulfurous odor. Since the properties of the separated droplets were similar to those of an organic sulfide, the following equations were proposed to account both for their formation and for their subsequent disappearance with time:

$$2CH_2{=}CHCN + Na_2CS_3 + 2H_2O \longrightarrow 2NaOH + (CNCH_2CH_2)_2S + CS_2 \quad (1)$$

$$(CNCH_2CH_2)_2S + 2NaOH + 2H_2O \longrightarrow 2NH_3 + (NaOOCCH_2CH_2)_2S \quad (2)$$

This mechanism suffices to explain all of the phenomena previously noted. The rise in salt index would be due to rexanthation of the cellulose xanthate by the carbon disulfide evolved in reaction 1. The green opacity would correspond to the formation of droplets of water-insoluble thionitrile, as in reaction 1, and their disappearance would correspond to the hydrolysis of the nitrile to the water-soluble β,β'-sodium thiodiproprionate, as in reaction 2.

TABLE III. SULFUR RELATIONS IN ACRYLONITRILE-TREATED VISCOSES

Viscose	% Sulfur[a]		
	Total	By-product	Xanthate
Control	2.39	1.33	1.06
2% acrylonitrile	2.08	0.74	1.34
Control	2.28	1.34	0.95
2% acrylonitrile	2.03	0.71	1.32

[a] These analyses were carried out 8 hours after the addition of acrylonitrile.

To test the mechanism further, reaction products in quantities large enough to identify were prepared by reacting acrylonitrile with sodium sulfide, sodium thiocarbonate, and sodium hydroxide. The general appearance and properties of the reaction products left little doubt but that a thionitrile is formed in the first two cases. This reaction, incidentally, affords an easy method for the preparation of these organic sulfides in aqueous solution. (It will be noted that the monosulfide is the cyano analog of mustard gas.) Although it was not possible to determine from these data whether the thionitrile is present as the monosulfide or the disulfide, further experimentation (described later in the paper) showed that the thionitrile is always present essentially in the monosulfide form, as required by Equation 1.

As a further test of the mechanism, a direct determination was made for any carbon disulfide which might be evolved (Equation 1). The diethylamine method (*5, 7*) was used, which is extremely sensitive for carbon disulfide. The general procedure followed was to pass a stream of air, which had been carefully cleaned of hydrogen sulfide and carbon disulfide, through artificial by-product sulfur solution until all of the carbon disulfide which is normally present in the solution had been swept out. Acrylonitrile is then added, and the air stream is tested on continued sweeping for the presence of carbon disulfide. It was found possible to demonstrate by this procedure that large quantities of carbon disulfide are evolved on the addition of the acrylonitrile.

EXPERIMENTAL PROCEDURE

Reaction products were prepared by reacting acrylonitrile with (*a*) artificial by-product sulfur solution, (*b*) 10% sodium sulfide solution, and (*c*) 6% sodium hydroxide solution. The artificial by-product solution, *a*, is essentially sodium thiocarbonate and was selected to afford a test of Equation 1. The reaction with sodium sulfide, *b*, was included since viscose contains considerable sodium sulfide in addition to sodium thiocarbonate. The reaction with sodium hydroxide, *c*, was included to permit a comparison of the sulfur-containing reaction products from *a* and *b* with those of the ether, $CNCH_2CH_2OCH_2CH_2CN$, which might be expected to form to some extent when acrylonitrile is added to the alkaline viscose (*1*).

REACTION WITH BY-PRODUCT SULFUR SOLUTION. Three hundred milliliters of 6.0% sodium hydroxide were shaken with 25 ml. of carbon disulfide and a few drops of sulfonated castor oil for 4 hours. The mixture was centrifuged, and 50 ml. of acrylonitrile were added to 200 ml. of the clear solution. The red color changed to a yellowish green in a few minutes. The reaction products and the unreacted acrylonitrile were extracted with ethyl ether. Anhydrous sodium sulfate was added to the ether solution, and after filtration the solution was vacuum-distilled. The oily fraction distilled over at 10–15 mm. pressure; the temperature was not determined but was estimated to be about 130° C. About 10 ml. of a yellow oil were obtained. It was immiscible with water and fairly viscous, and had an unpleasant odor resembling hydrogen sulfide.

REACTION WITH SODIUM SULFIDE. Three hundred milliliters of 10% sodium sulfide solution were shaken with 50 ml. of acrylonitrile for several hours. The mixture was extracted with ethyl ether, and the extract treated as in step *a*. The distillation characteristics and physical appearance of the product were identical with *a*. About 5 ml. of product were obtained.

REACTION WITH SODIUM HYDROXIDE. The preparation of the product was carried out as in step *b*. The product is a fairly viscous oil and is water clear, but becomes slightly yellow near the end of the distillation. The distillation behavior is the same as in step *a*. About 3 ml. of product were obtained.

COMPARISON OF PRODUCTS FROM *a*, *b*, AND *c*. The general appearance of the products from *a* and *b* were similar and quite different from that of *c*. The refractive indices of the products from *a* and *c* at 23° C. were 1.4903 and 1.4389, respectively. Recrystallizations from water were not carried out, but the product from step *a* was comparable in general properties to the monosulfide, $(CNCH_2CH_2)_2S$, as described by Nekrasov (*8*). The nitrogen content of the product from *a* was found to be 19.8%. Since the theoretical nitrogen content of the monosulfide is 20.0% and the disulfide 16.3%, the reaction product appears to be the monosulfide.

ANALYSIS FOR CARBON DISULFIDE. The by-product sulfur solution used in these analyses was prepared by shaking 6.0% sodium hydroxide solution with an excess of carbon disulfide at 23° C. for 12 hours, followed by an extraction with petroleum ether. In carrying out the analyses, a moderately strong stream of cleaned air is bubbled through 10 ml. of the by-product solution, followed by passage through 20 ml. of diethylamine test reagent. The procedure used for cleaning the air and the details of the reaction train are those of Hunter (*5*). Samples were withdrawn from the diethylamine test solution and diluted 1 to 10, and the transmission was observed in the Evelyn colorimeter. The method is extremely sensitive, and considerable difficulty was encountered at first in obtaining a satisfactory blank. Satisfactory results were later obtained with the construction of an all-glass apparatus.

As illustrative data, in one run the by-product solution gave an initial transmission reading of 76.5 (zero point, 100). After 30 minutes of sweeping, the transmission had risen to 98.0. The solution was allowed to remain undisturbed for one hour before being rechecked; 98.0 was again obtained. One milliliter of acrylonitrile was then added, and the air stream tested as soon as possible (which in this case is after the 10-minute sweeping required to make any one determination). A transmission reading of 74.5 was obtained. After 30 minutes of additional sweeping, a reading of 76.5 was obtained; and after 30 more minutes of sweeping, 77.0. Hence it is clear that fairly large quantities of carbon disulfide are developed.

SUMMARY

When acrylonitrile is added to viscose, it reacts rapidly with the principal by-product sulfur constituents; they are converted into identical organic sulfides, and carbon disulfide is released as shown:

$$2CH_2{=}CHCN + Na_2S + 2H_2O \longrightarrow 2NaOH + (CNCH_2CH_2)_2S \qquad (I)$$

$$2CH_2{=}CHCN + Na_2CS_3 + 2H_2O \longrightarrow 2NaOH + (CNCH_2CH_2)_2S + CS_2 \qquad (II)$$

The insoluble thionitrile is suspended in the viscose in the form of droplets, which disappear in a matter of hours due to the following hydrolysis:

$$(CNCH_2CH_2)_2S + 2NaOH + 2H_2O \longrightarrow 2NH_3 + (NaOOCCH_2CH_2)_2S \qquad (III)$$

The carbon disulfide evolved in reaction II causes a further xanthation of the cellulose xanthate in the viscose, and the salt index is immediately raised.

LITERATURE CITED

(1) Bruson, H. A., and Riener, T. W., *J. Am. Chem. Soc.*, 65, 23–7 (1943).
(2) DeWyss, George, IND. ENG. CHEM., 17, 1043–5 (1925).
(3) Geiger, Ernst, *Helv. Chim. Acta*, 13, 281–303 (1930).
(4) Hollihan, J. P., and Moss, S. A., Jr., U. S. Patent Application 549,290.
(5) Hunter, A. W., *J. Ind. Hyg. Toxicol.*, 22, No. 6, 231–4 (1940).
(6) Leuchs, K., *Chem.-Ztg.*, 47, 801 (1923).
(7) McKee, R. W., *J. Ind. Hyg. Toxicol.*, 23, No. 4, 151 (1941).
(8) Nekrasov, V. V., *J. Russ. Phys. Chem. Soc.*, 59, 921–4 (1927).
(9) Ott, Emil, "Cellulose and Cellulose Derivatives", New York, Interscience Publishers, Inc., 1943.
(10) *Russian Organic Chem. Ind.*, 3, No. 12, 693 (1937).
(11) Scherer, P. C., Jr., and Leonards, J. R., *Rayon Textile Monthly*, 23, 607–9 (1942).
(12) Vitale, Tomasso, *Giorn. chim. ind. applicata*, 13, 476–9 (1931).
(13) Weeldenburg, J. G., *Rec. trav. chim.*, 47, 496–512 (1928).

Tocopherols as Antioxidants for Vitamin A in Fish Liver Oils

L. O. BUXTON

National Oil Products Company, Inc., Harrison, N. J.

Pure β- and γ-tocopherols, alone and in association with vegetable oil lecithin, were studied for the inhibition of vitamin A destruction and peroxidation in soup-fin shark liver and halibut liver oils. Both forms of tocopherols were found to be effective antioxidants for retarding peroxidation, a characteristic not possessed by α-tocopherol. γ-Tocopherol was more effective for inhibiting peroxidation in the oils studied than was β-tocopherol, especially during the later stages of vitamin A destruction. β- and γ-tocopherol at a 0.10% concentration markedly increased the stability of vitamin A in the various oils examined. Lecithin at a 1.0% level enhanced the effectiveness of both tocopherols for inhibiting vitamin A destruction and peroxidation. No difference was observed between the antioxidant characteristics of pure natural γ-tocopherol and those of pure synthetic γ-tocopherol.

THE inherent resistance of natural glyceride oils to oxidative changes is due primarily to the presence in the oils of varying quantities of substances commonly termed antioxidants. Many natural oils, particularly fish liver oils, are notoriously easy prey to oxidative changes, regardless of the fact that they also contain some natural antioxidants. Fish liver oils are our most valuable source of vitamin A; because of the lability of vitamin A to oxidative changes, it is important that oxidation be inhibited to the fullest degree.

Evidence to date has established that tocopherols and allied substances in association with phosphatidic materials are largely responsible for the stability exhibited by natural vegetable oils. Olcott and Emmerson (*6*) were the first to show that the tocopherols are increasingly effective as antioxidants in lard in the order alpha, beta, and gamma. The gamma form was found to have about three times the antioxygenic index of α-tocopherol, and the activity of β-tocopherol was intermediate between the other two. Esters of the tocopherols were ineffective as antioxidants. Olcott and Mattill (*7*) showed that the antioxidants or inhibitols present in the lipid fractions of vegetables and in vegetable oils are so similar to vitamin E (tocopherols) that it was impossible to fractionate them.

In a paper on the use of natural as well as synthetic α-tocopherol as an antioxidant in cottonseed oil, Swift, Rose, and Jamieson (*11*) demonstrated that the α-tocopherols function most effectively at lower levels of concentration. These authors also showed that a cephalin fraction from cottonseed oil greatly enhanced the antioxygenic activity of α-tocopherol. Certain acids also increase the antioxygenic activity of tocopherols and of the corresponding quinones in autoxidizing fats (*5*). Published data on the antioxidant activity of phosphatides in oils as a whole is conflicting. It has been the author's experience that, when relatively pure phosphatides alone are added to antioxidant-free fish liver oils, they have no antioxidant activity for inhibiting either peroxide formation or vitamin A destruction, even at concentrations as high as 5%. When relatively pure phosphatides are added to crude fish liver oils, they may or may not exhibit an antioxidant effect, depending upon whether the crude oils contain natural antioxidant principles which may act synergistically with the added phosphatides to enchance the stability of the oils. Golumbic (*4*) reported that the antioxygenic *o*-quinones present in vegetable fats but not in animal fats retarded peroxide accumulation in the former type of oils after the complete disappearance of the tocopherols. Riemenschneider (*8*) showed that various vegetable oils added to lard in amounts of 1 to 10% appreciably increase its stability and that the increase is related to the tocopherol content of the oils.

Robeson and Baxter (*9*) isolated α-tocopherol from Mangona shark liver oil and from soup-fin shark liver oil by distillation and concluded that the α-tocopherol found in the soup-fin shark liver oil was about 0.04%. The Mangona shark liver oil was found to contain about 0.01% and was the major antioxidant present in the oil. Bird (*2*) concluded that the natural antioxidants in fish oils probably involve several types of compounds. Using halibut liver oil, he showed that exhaustive extraction with 80% methanol removed only part of the antioxidants, whereas with water or dilute aqueous alkali, complete extraction or destruction of the antioxidant fraction occurred. It was also reported that α-tocopherol at high concentrations is an effective antioxidant for vitamin A.

In another report from these laboratories (*3*) it was shown that the natural antioxidants present in various types of fish liver oils were either completely removed or destroyed when the oils were treated with activated carbon in the presence of a solvent for the oil. The present investigation reports the effect of the pure α-, β-, and γ-tocopherol isomers, alone and in combination with vegetable oil lecithin, on vitamin A destruction and peroxidation in soup-fin shark and halibut liver oils. It was postulated that such studies on the relation between the destruction of vitamin A and the rate and extent of peroxidation, with and without the added tocopherols or tocopherols plus lecithin, should bring to light any similarity between the action of the latter type of antioxidants and those naturally occurring in the crude fish liver oils. Furthermore, to date the literature is lacking in information on the effectiveness of α-, β-, and γ-tocopherols as antioxidants for vitamin A as it exists naturally in fish liver oils. This work is not concerned with the merits of tocopherols or tocopherols plus lecithin as antioxidants for the alcohol form of vitamin A.

MATERIALS

CRUDE OILS. The samples of crude soup-fin shark and halibut liver oils used in this work were of known origin and of the highest quality. They were filtered before using and were dry and free from foreign matter. It was established by numerous stability studies, under analogous storage conditions on other comparable lots of soup-fin shark and halibut liver oils, that the oils used in this investigation behaved in a manner quite representative of this type of oil, both as to the rate and extent of peroxidation and the rate of vitamin A destruction. The crude oils used can be considered as being relatively stable, in so far as fish liver oils are concerned. Their analysis is given in Table I.

CARBON-TREATED OILS. The samples of crude soup-fin shark and halibut liver oils were treated with 20% (based on oil weight) of activated carbon (Nuchar XXX), using cyclohexane as the solvent (20% solution of oil in solvent) by the process reported previously (*3*). The cyclohexane used was a special grade sold by The Barrett Company and was devoid of unsaturates, as determined spectrophotometrically. The carbon-treated oil samples were

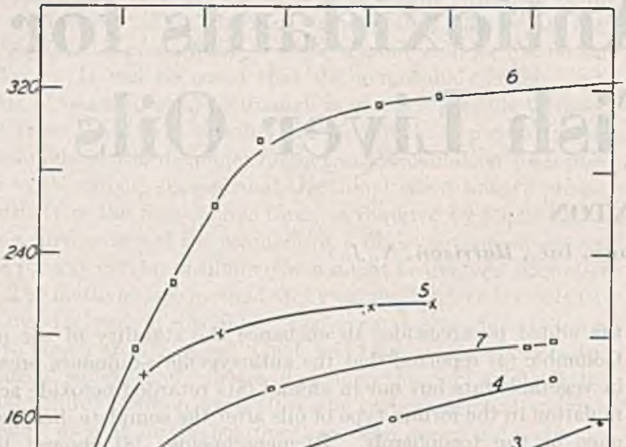


FIGURE 1

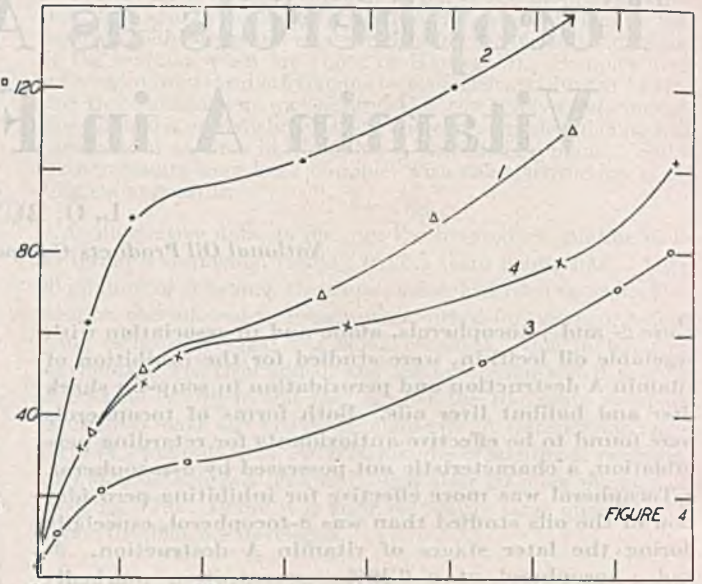


FIGURE 4

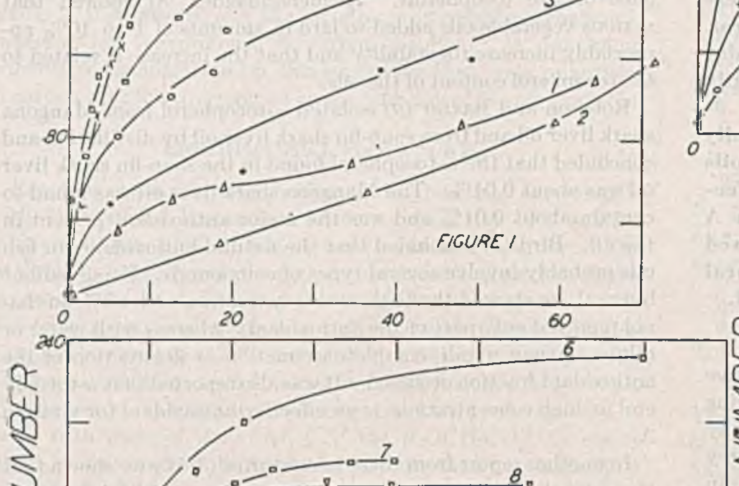


FIGURE 2

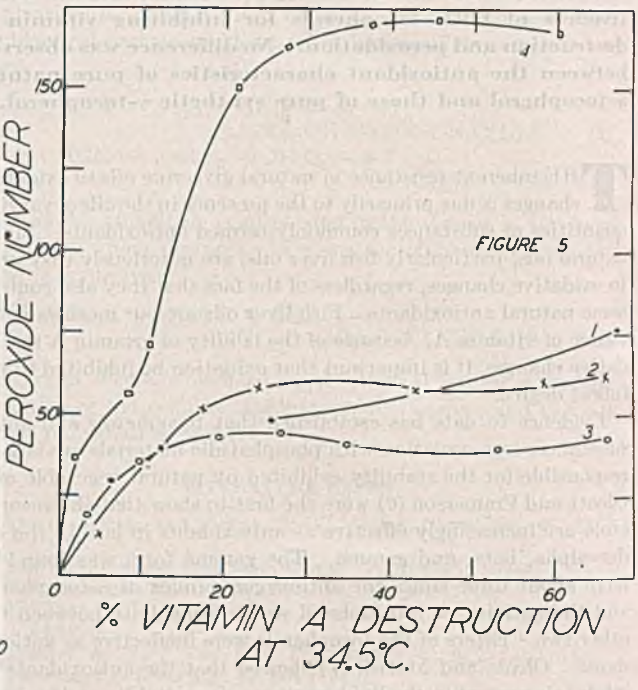


FIGURE 5

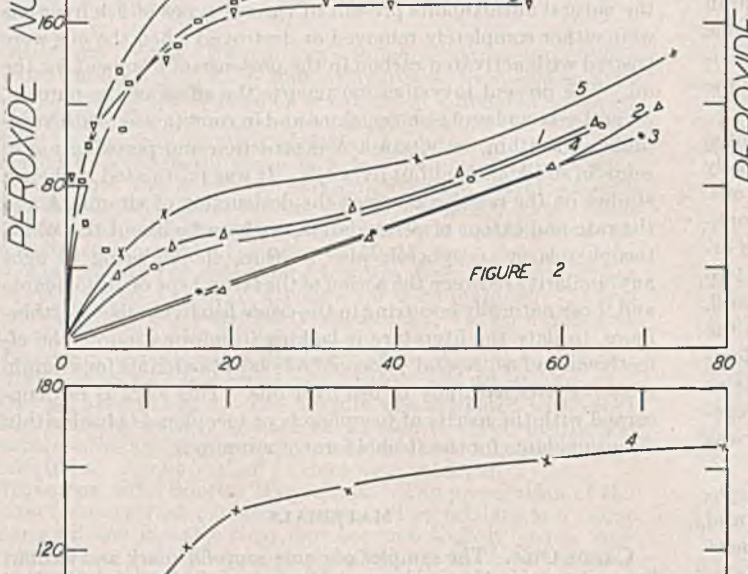


FIGURE 3

Figures 1 and 6

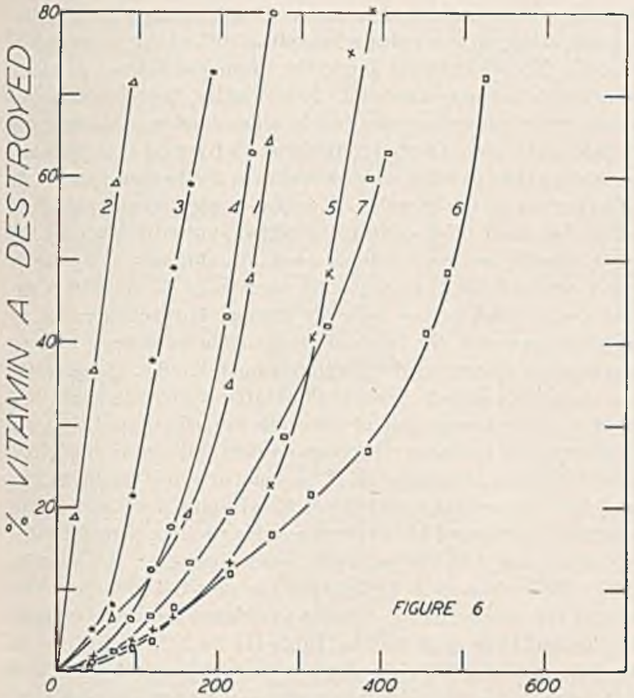
Curve 1.	**Crude soup-fin shark liver oil C**
Curve 2.	**Carbon-treated shark liver oil C**
Curve 3.	**Same as 2, + 0.10% synthetic α-tocopherol**
Curve 4.	**Same + 0.25% synthetic α-tocopherol**
Curve 5.	**Same + 0.50% synthetic α-tocopherol**
Curve 6.	**Same + 1.00% synthetic α-tocopherol**
Curve 7.	**Same + 1.25% Vegol (40%)**

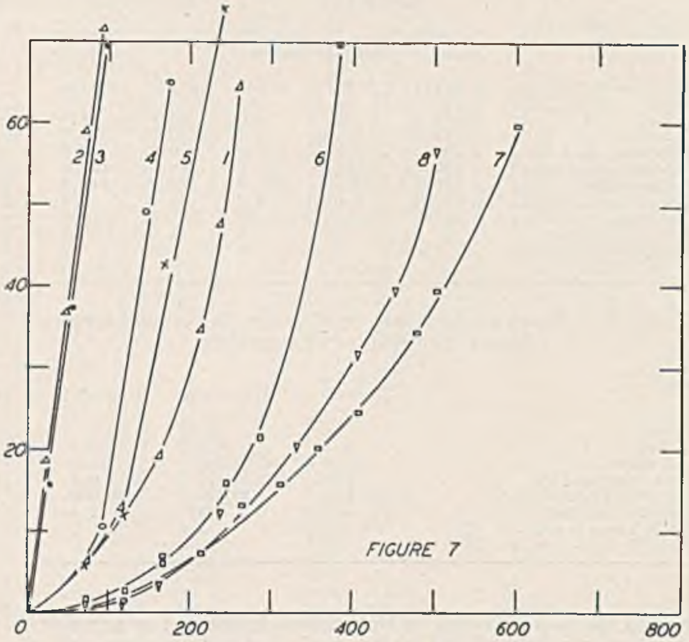
Figures 2 and 7

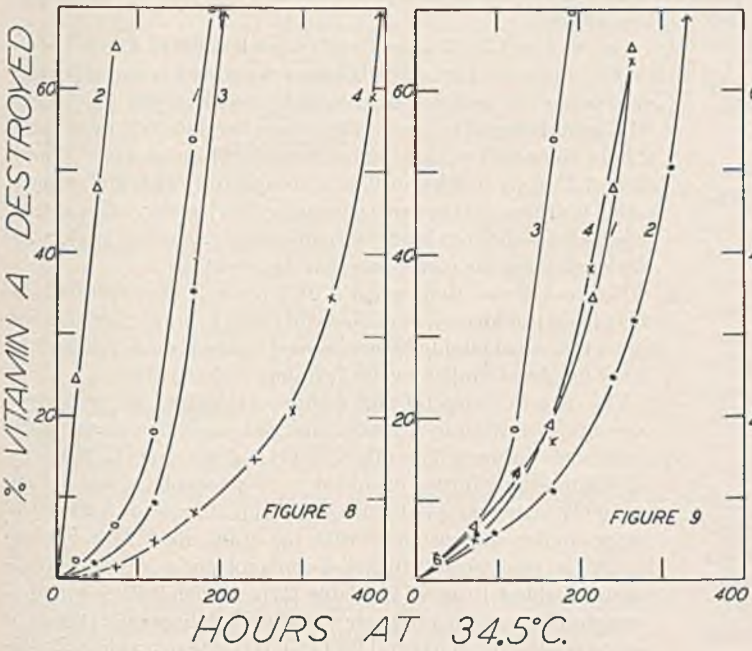
Curve 1.	**Crude soup-fin shark liver oil C**
Curve 2.	**Carbon-treated shark liver oil C**
Curve 3.	**Same as 2, + 1% lecithin**
Curve 4.	**Same + 0.50% lecithin and 0.05% synthetic α-tocopherol**
Curve 5.	**Same + 0.50% lecithin and 0.10% synthetic α-tocopherol**
Curve 6.	**Same + 0.50% lecithin and 0.50% synthetic α-tocopherol**
Curve 7.	**Same + 5.0% lecithin and 0.50% synthetic α-tocopherol**
Curve 8.	**Same + 0.50% lecithin and 1.25% Vegol (40%)**

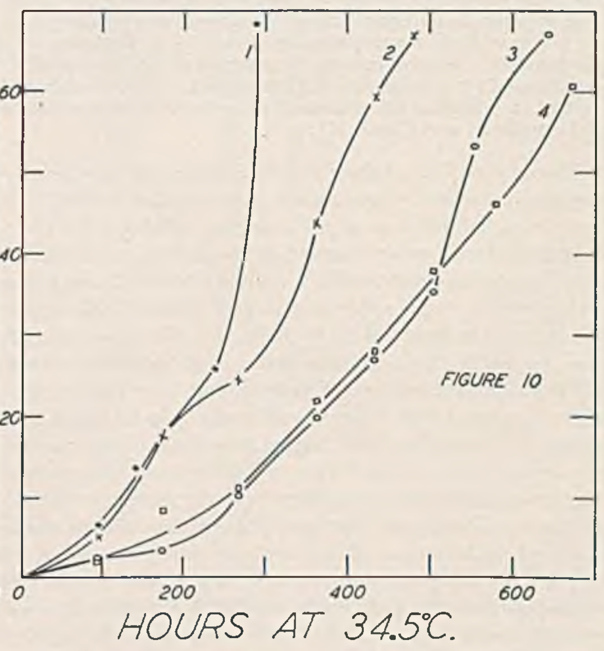
Figures 3 and 8

Curve 1.	**Crude halibut liver oil A**
Curve 2.	**Carbon-treated halibut liver oil A**
Curve 3.	**Same as 2, + 0.10% synthetic α-tocopherol**
Curve 4.	**Same + 0.50% synthetic α-tocopherol**









Figures 4 and 9

Curve 1. Crude soup-fin shark liver oil C
Curve 2. Same as 1, + 0.10% synthetic α-tocopherol
Curve 3. Crude halibut liver oil A
Curve 4. Same + 0.1% synthetic α-tocopherol

Figures 5 and 10

Curve 1. Crude soup-fin shark liver oil B
Curve 2. Same as 1, + 0.1% natural γ-tocopherol
Curve 3. Same + 0.1% natural γ-tocopherol and 1.0% lecithin
Curve 4. Same as 3, + 0.5% natural γ-tocopherol

used immediately after preparation or stored in completely filled, closed vials at −18° C. until the peroxide and vitamin A stability tests were conducted. From a vast accumulation of unpublished data on such carbon-treated oils, it can be assumed that the only difference between the crude and the carbon-treated oils, in so far as this investigation is concerned, is that the latter were devoid of natural antioxidants. Partial analytical data on the carbon-treated oils are given in Table II.

TOCOPHEROLS. The synthetic α-, β-, and γ-tocopherols used were obtained from Merck & Company. The Vegol (40% grade) and the pure natural α- and γ-tocopherols used were secured from Distillation Products, Inc. The E value of the Vegol sample at 2965 Å. in cyclohexane was 40.4. The tocopherol isomers were used without further purification and can be considered pure specimens, since the extinction coefficients checked favorably with reported values on similar types of materials.

LECITHIN. The commercial lecithin product called Yelkin BSS, obtained from the American Lecithin Company, Inc., was used without further treatment. This product is considered a refined grade of lecithin. Many different types of lecithin or phosphatide preparations were investigated in the course of this study; the differences were slight and merely a matter of degree.

The samples of crude and carbon-treated shark liver and halibut liver oil, with and without the added tocopherols or tocopherols plus lecithin, were studied for percentage vitamin A destruction and peroxidation by the method outlined previously (*10*). Placed in thoroughly cleaned open vials of uniform size, 2-mm. samples of the various oils were stored in a constant temperature oven maintained at 34.5° ± 0.5° C. At definite intervals, as graphically recorded in Figures 6 to 15 and in Table III, three vials of the same oil were separately tested for peroxide number and vitamin A. The average values of the individual determinations are re-

TABLE I. ANALYSIS OF CRUDE SOUP-FIN SHARK AND HALIBUT LIVER OILS

	Soup-Fin Shark A	Soup-Fin Shark B	Soup-Fin Shark C	Halibut A	Halibut B
Sp. gr. at 60° F.	0.912	0.927	0.930	0.931	0.925
Color					
Red	4.1	3.7	4.0	2.1	3.6
Yellow	18.0	23.0	36.0	30.0	70.0
Free fatty acid, %	0.65	0.35	0.2	0.3	0.6
Saponification value	177.0	174.5	181.7	170.5	173.0
Iodine value	139.4	157.9	175.9	139.0	142.5
Unsaponified matter, %	5.75	6.61	4.3	11.0	8.4
Vitamin A, units/gram	71,500	122,000	105,000	94,200	60,000
Peroxide number	0	0	5.3	1.2	2.5
Phosphorus, p.p.m.	138	37	29	10	7

TABLE II. PARTIAL ANALYSIS OF CARBON-TREATED SOUP-FIN SHARK AND HALIBUT LIVER OILS

	Soup-Fin Shark C	Halibut A	Halibut B
Color			
Red	0.4	0.3	0.4
Yellow	10.0	10.0	10.0
Free fatty acid, %	0.2	0.25	0.5
Vitamin A, units/gram	103,000	93,500	60,000
Peroxide number	4.0	1.1	2.4
Phosphorus, p.p.m.	0	0	0

corded in Table III and in the various figures. The peroxide numbers were established by the method already reported (*10*). The vitamin A determinations were made in a spectrophotometric grade of 99% isopropanol by means of a Beckman spectrophotometer. The oil constants reported in Tables I and II were ascertained by official A.O.A.C. methods. The phosphorus content of the oils was determined by the microcolorimetric method of Berenblum and Chain (*1*).

The data in Table I show that two of the soup-fin shark liver oil samples possessed considerably higher iodine values than the samples of halibut liver oil. The iodine value of a fish liver oil is only a relatively minor element of the picture, however, in so far as peroxidation and vitamin A stability of the oil are concerned. Other factors, such as the content and types of antioxidants and synergists, the types of fatty acids, and the glycerol configuration, appear to play a major role in governing the resistance of an oil to oxidative changes. Crude halibut liver oils, even though more saturated than most lots of crude soup-fin shark liver oils, are generally less stable in regard to vitamin A destruction than the latter type of oils. This is undoubtedly due mainly to a higher concentration or to more potent vitamin A antioxidants in the soup-fin shark liver oils. Many unpublished data accumulated in the course of this work establish that crude soup-fin shark liver oils possess appreciably higher phosphorus contents (phosphatides) than do crude halibut liver oils. This may account for some of the stability differences, since the greater quantity of phosphatides would act synergistically with other natural antioxidants present in the soup-fin liver oils to further enhance their stability. The rate and extent of peroxide formation is, however, greater in the soup-fin shark liver oils. This behavior is unquestionably due, in part at least, to the greater degree and type of unsaturation present in the soup-fin shark liver oils. A comparison of curves 1 and 3 of Figure 14 illustrates this point.

The individual peroxide and percentage of vitamin A destruction values obtained on the crude and carbon-treated fish liver oils exposed to air at 34.5° C., with and without the added tocopherols or tocopherols plus lecithin, are presented graphically in Figures 1 to 5 and in Table III.

RELATION OF VITAMIN A DESTRUCTION TO PEROXIDATION

Curves 1 and 2 of Figures 1 and 3 show the relation between the destruction of vitamin A and the rate and extent of peroxidation in the blank samples of crude and carbon-treated soup-fin shark C and halibut liver oil A, respectively. Here again, as reported previously, in fish liver oils treated with 20% carbon (*3*), the percentage of vitamin A decrease is directly proportional to the peroxide value, up to a point where 60 to 70% of the vitamin A is oxidized. This behavior is due to the absence of active vitamin A antioxidants in the treated oils. Numerically, the peroxide number at a given percentage of vitamin A destruction in the samples of crude and carbon-treated soup-fin shark liver oil C is considerably higher than in comparable samples of the halibut liver oil A.

The curves on the samples of carbon-treated soup-fin shark C and halibut liver oil A containing added synthetic α-tocopherol and synthetic α-tocopherol plus lecithin (Figures 1, 2, and 3) clearly establish that, at the same percentage of vitamin A destruction, a much higher peroxide number is reached in the α-tocopherol samples, the increase in peroxide number at a given percentage of vitamin A destruction being related to the quantity of α-tocopherol added. This is illustrated by curves 1 and 4 of Figure 1, in the comparison of the crude soup-fin shark liver oil C and a sample of the same oil carbon-treated and containing 0.25% added synthetic α-tocopherol. This comparison is made because these two oils exhibit about the same vitamin A stability. For example, at a value of 19% vitamin A destruction, peroxide numbers of 58 and 133, respectively, were observed. At approximately 64% vitamin A destruction the peroxide numbers were 110 and 180, respectively. Similar results are recorded in Figure 3 on halibut liver oil A and in Table III on halibut liver oil B. The data in Table III show further that, in crude halibut liver oil B, pure synthetic and pure natural α-tocopherol exhibit identical effects.

Curves 5 and 7 in Figure 1 and curves 6 and 8 in Figure 2 show that a similar relation exists between peroxidation and vitamin A destruction in samples of carbon-treated soup-fin shark liver oil C containing added synthetic α-tocopherol (0.50% by weight); this is compared with a mixed tocopherol concentrate (Vegol, 40%, 1.25% by weight, or 0.50% tocopherol), with and without added lecithin. At the same percentage of vitamin A destruction, however, a somewhat lower peroxide value was noted in the samples containing the mixed tocopherol concentrate.

Figure 4 shows that, when 0.10% by weight of synthetic α-tocopherol is added to crude soup-fin shark liver oil C and halibut liver oil A, considerably higher peroxide numbers are reached than in the blanks at similar levels of vitamin A destruction.

The data in Table III and Figure 5 establish that, at a given percentage of vitamin A destruction, the peroxide number of the crude soup-fin shark liver oils A and B and the crude halibut liver oil B containing 0.10% of added β- or γ-tocopherol are not appreciably higher, and in the majority of instances are lower, than under similar circumstances with the crude oils. This was certainly the case when 0.10% γ-tocopherol was added to carbon-treated halibut liver oil B (Table III). When 0.50% β- and γ-tocopherol were added to crude soup-fin shark liver oil B (Figure 5) and to crude halibut liver oil B (Table III), the peroxide values increased rapidly to a high maximum and then leveled off, essentially as observed with α-tocopherol (Figure 1). At different percentages of vitamin A destruction in the various oils in Table III, lower peroxide values were observed using γ- as compared to β-tocopherol. In all instances when β- and γ-tocopherols were used, alone or with lecithin, the peroxide values were lower at a given loss of vitamin A than under comparable conditions with α-tocopherol.

Lecithin at a 1.0% concentration in the sample of carbon-treated soup-fin shark liver oil C (curves 2 and 3, Figure 2) had no effect on the relation between peroxidation and vitamin A destruction. However, when 0.50% lecithin was used in combination with synthetic α-tocopherol in this same oil, a lower peroxide number was observed at various stages of vitamin A destruction. In crude halibut liver oil B (Table III), with and without 0.1% added synthetic or natural α-tocopherol, lecithin at a 1% concentration lowered appreciably the peroxide number at a given percentage of vitamin A destruction. Similar results were obtained with carbon-treated halibut liver oil B containing 0.1%

Table III. Stability of Fish Liver Oils

Antioxidant	Days at 34.5° C.	0	1	2	3	4	6	7	11	13	15	18	21	24	28	32
Soup-Fin Shark Liver Oil A																
None	Peroxide No.	0	..	..	17.4	..	..	32.1	46.4	..	51.9	52.1	58.8	64.6	...	...
	% vit. A destr.	...	..	..	3.4	..	..	8.9	17.8	..	28.4	38.3	57.3	78.4	...	...
1% Lecithin	Peroxide No.	0	..	..	..	8.7	..	21.1	35.8	..	42.1	44.1	39.9	44.3	45.3	...
	% vit. A destr.	...	..	..	..	0	..	4.4	9.8	..	18.8	28.5	38.5	50.3	73.3	...
0.1% syn. β-tocopherol	Peroxide No.	0	..	..	..	24.4	..	40.5	54.7	..	59.6	61.7	61.5	60.7	60.7	...
	% vit. A destr.	...	..	..	..	6.0	..	7.3	18.1	..	26.8	37.2	45.4	52.2	65.3	...
1% lecithin	Peroxide No.	0	..	..	..	9.4	..	21.1	43.0	..	50.0	53.7	52.3	51.2	52.1	48.6
0.1% syn. β-tocopherol	% vit. A destr.	...	..	..	..	3.5	..	7.2	11.1	..	18.3	24.8	30.9	41.0	51.7	65.7
0.1% syn. γ-tocopherol	Peroxide No.	0	..	..	..	19.4	..	33.3	48.7	..	60.4	60.7	58.8	51.3	57.8	...
	% vit. A destr.	...	..	..	..	5.2	..	6.1	11.5	..	20.8	30.7	37.1	49.3	64.4	...
1% lecithin	Peroxide No.	0	..	..	..	5.0	..	18.3	35.9	..	51.4	54.2	55.1	53.6	48.3	43.3
0.1% syn. γ-tocopherol	% vit. A destr.	...	..	..	..	0	..	0.8	6.7	..	13.1	20.9	26.8	33.8	49.2	61.1
0.1% nat. γ-tocopherol	Peroxide No.	0	..	..	..	17.4	..	34.3	52.1	..	62.1	63.7	60.9	56.9	60.3	..
	% vit. A destr.	...	..	..	..	1.2	..	4.8	12.5	..	20.2	28.4	37.3	47.5	62.3	...
1% lecithin	Peroxide No.	0	..	..	..	3.8	..	15.2	35.1	..	50.1	54.9	56.5	51.0	...	...
0.1% nat. γ-tocopherol	% vit. A destr.	...	..	..	..	0	..	2.4	7.9	..	12.5	19.4	26.6	34.0	...	...
Halibut Liver Oil B																
None	Peroxide No.	2.5	..	12.4	16.3	19.8	51.5	63.1	...	..	...	...	...	...	...	...
	% vit. A destr.	...	..	4.4	8.7	16.2	53.3	66.3	...	..	...	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	15.4	..	28.8	51.4	..	...	...	...	...	...	...
	% vit. A destr.	...	..	..	..	10.2	..	72.3	82.7	..	...	...	...	...	...	...
0.1% syn. β-tocopherol	Peroxide No.	2.5	..	..	..	33.1	..	44.2	54.2	61.3	68.0	...	...	...	...	...
	% vit. A destr.	...	..	..	..	12.2	..	21.6	38.7	53.2	65.4	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	19.7	..	28.6	33.1	..	36.3	33.9	...	...	...	...
0.1% syn. β-tocopherol	% vit. A destr.	...	..	..	..	7.5	..	15.1	26.7	..	39.8	52.4	...	...	...	...
0.5% syn. β-tocopherol	Peroxide No.	1.9	..	..	..	13.5	..	57.0	73.2	..	175.0	193.5	217.0	229.0	211.0	216.0
	% vit. A destr.	...	..	..	..	0	..	13.5	13.9	..	23.6	32.6	39.0	49.0	59.8	...
0.1% nat. γ-tocopherol	Peroxide No.	2.5	..	..	..	22.9	..	32.6	45.2	..	57.5	58.8	...	...	...	...
	% vit. A destr.	...	..	..	..	8.7	..	17.5	35.0	..	42.7	65.6	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	16.6	..	20.8	28.4	..	31.4	35.0	...	...	...	...
0.1% nat. γ-tocopherol	% vit. A destr.	...	..	..	..	6.8	..	12.2	21.8	..	36.6	52.5	...	...	...	...
0.5% nat. γ-tocopherol	Peroxide No.	1.9	..	..	..	6.2	..	25.4	42.2	..	110.0	122.6	150.0	158.0	159.0	176.0
	% vit. A destr.	...	..	..	..	2.2	..	7.9	8.7	..	14.3	19.0	31.8	35.4	42.0	59.5
0.5% nat. γ-tocopherol	Peroxide No.	2.1	..	..	..	3.0	..	11.1	13.5	..	54.0	63.7	76.0	87.8	89.9	95.3
1% lecithin	% vit. A destr.	...	..	..	..	2.2	..	6.9	2.1	..	3.7	6.0	11.5	11.0	14.2	20.3
0.1% syn. α-tocopherol	Peroxide No.	2.5	..	..	..	37.5	..	50.1	77.6	..	132.8	172.0	...	...	...	...
	% vit. A destr.	...	..	..	..	7.8	..	14.2	38.7	..	86.7	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	21.9	..	33.1	45.4	..	52.0	72.6	...	...	...	...
0.1% syn. α-tocopherol	% vit. A destr.	...	..	..	..	4.6	..	9.8	18.2	..	40.6	78.0	...	...	...	...
0.1% nat. α-tocopherol	Peroxide No.	2.5	..	..	..	37.7	..	58.9	71.7	..	123.1	163.5	...	...	...	...
	% vit. A destr.	...	..	..	..	6.7	..	13.5	35.1	..	85.5	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	19.1	..	37.7	48.9	..	50.5	64.4	...	...	...	...
0.1% nat. α-tocopherol	% vit. A destr.	...	..	..	..	5.0	..	10.0	18.4	..	38.6	62.5	...	...	...	...
Carbon-Treated Halibut Liver Oil B																
None	Peroxide No.	2.4	22.6	44.3	63.8	...	..	..	...	..	...	...	...	...	...	...
	% vit. A destr.	...	22.9	45.4	65.0	..	..	..	...	..	...	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	17.9	32.3	44.9	..	..	..	...	..	...	...	...	...	...	...
	% vit. A destr.	...	19.6	48.5	72.9	..	..	..	...	..	...	...	...	...	...	...
0.1% syn. β-tocopherol	Peroxide No.	2.5	..	..	..	12.4	..	46.8	67.3	..	97.3	...	...	...	...	...
	% vit. A destr.	...	..	..	..	10.5	..	25.1	55.4	..	78.7	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	6.7	..	27.1	33.2	..	37.8	50.9	...	...	...	...
0.1% syn. β-tocopherol	% vit. A destr.	...	..	..	..	8.1	..	22.9	33.7	..	58.8	78.4	...	...	...	...
0.1% nat. γ-tocopherol	Peroxide No.	2.5	..	..	..	26.1	..	36.8	51.1	..	26.0	38.1	...	...	...	...
	% vit. A destr.	...	..	..	..	8.2	..	11.6	42.7	..	65.1	81.7	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	11.3	..	18.4	23.7	..	29.6	11.2	...	...	...	...
0.1% nat. γ-tocopherol	% vit. A destr.	...	..	..	..	4.2	..	9.0	22.5	..	45.5	54.6	...	...	...	...
0.1% nat. α-tocopherol	Peroxide No.	2.5	..	..	..	20.1	..	61.4	125.5	..	...	...	...	...	...	...
	% vit. A destr.	...	..	..	..	3.5	..	20.0	82.7	..	...	...	...	...	...	...
1% lecithin	Peroxide No.	2.5	..	..	..	14.1	..	41.1	47.2	..	72.4	...	...	...	...	...
0.1% nat. α-tocopherol	% vit. A destr.	...	..	..	..	2.7	..	11.2	27.5	..	85.4	...	...	...	...	...

natural α-tocopherol and 1% lecithin. Lecithin also had a lowering effect, but to a greater degree than when α-tocopherol was used, on the peroxide number in the oils containing added β- and γ-tocopherol at different percentages of vitamin A loss (Figure 5 and Table III). At a 5.0% concentration (curves 6 and 7, Figure 2), lecithin, when tested in association with 0.5% added synthetic α-tocopherol in carbon-treated soup-fin shark liver oil, also lowered the peroxide number at the same percentage of vitamin A destruction, especially after about 10% of the vitamin A was destroyed.

EFFECT OF STORAGE ON VITAMIN A DESTRUCTION

The main object for adding antioxidants to vitamin A materials such as fish liver oils is to inhibit vitamin A destruction to the fullest practical extent. Figures 6–10 and Table III summarize the data on the percentage of vitamin A destroyed during storage at 34.5° C. of the various samples studied. The percentage of vitamin A destroyed in the carbon-treated oils is directly proportional to time up to the point where 60–70% of the potency is destroyed; this indicates the absence of active antioxidants. The crude soup-fin shark liver and the halibut liver oils were considerably more stable than the same oils after carbon treatment. The former were more stable than the crude halibut liver oils. All the oils containing the added α-, β-, and γ-tocopherols or these tocopherols plus lecithin exhibited greater vitamin A stability than comparable blanks. No appreciable difference (Table III) was noted between the stabilizing effect of the synthetic and natural forms of α- and γ-tocopherol, with and without 1% added lecithin, at a 0.1% concentration in crude halibut liver oil B and in crude soup-fin shark liver oil A. In all the oils examined containing added α-, β-, or γ-tocopherol in a concentration of 0.10% and greater, the tocopherols were effective antioxidants for vitamin A. Under the condition employed, the gamma form was only slightly more effective than the beta form for inhibiting vitamin A destruction. Both forms are slightly more potent antioxidants than the alpha form for vitamin A in fish liver oils.

Lecithin enhanced the antioxidant effectiveness of the pure tocopherols and of the mixed tocopherol concentrate in preventing vitamin A loss. This is particularly noticeable in the oils containing the lower percentage (0.10%) concentration of the pure tocopherols and also during the early stages of vitamin A destruction. Lecithin at 5% had a greater enhancing effect than 0.5% lecithin on 0.50% synthetic α-tocopherol in the carbon-treated soup-fin shark liver C oil (curves 6 and 7, Figure 6). Additional unpublished data on the use of lecithin in combination with the different tocopherol isomers indicate that the enhancing or syn-

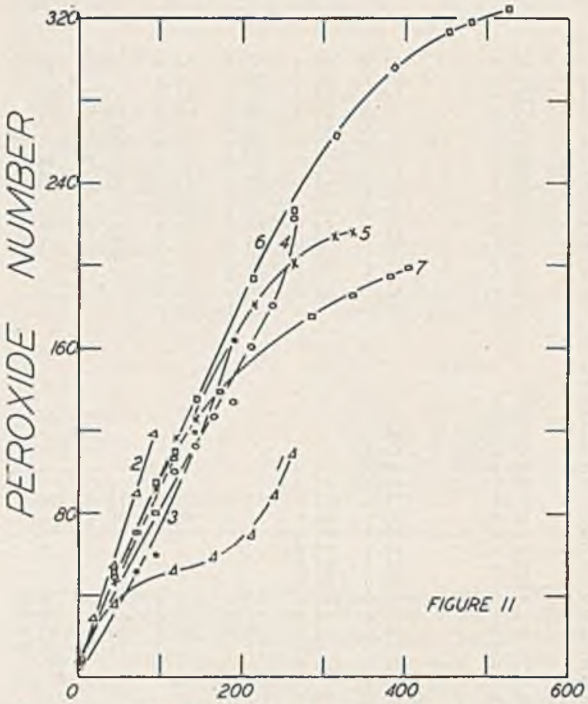
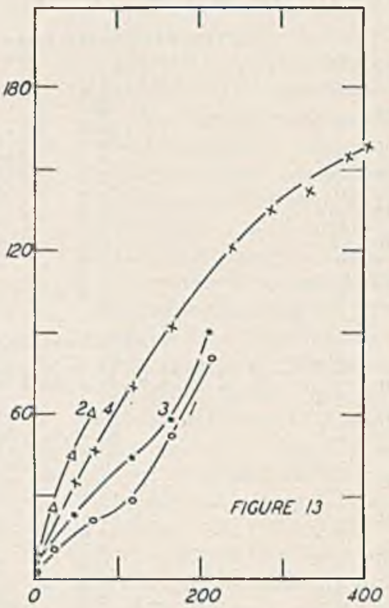
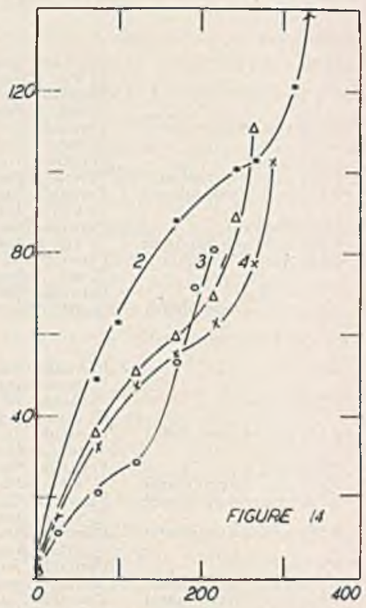


Figure 11

Curve 1. Crude soup-fin shark liver oil C
Curve 2. Carbon-treated shark liver oil C
Curve 3. Same as 2, + 0.10% synthetic α-tocopherol
Curve 4. Same + 0.25% synthetic α-tocopherol
Curve 5. Same + 0.50% synthetic α-tocopherol
Curve 6. Same + 1.00% synthetic α-tocopherol
Curve 7. Same + 1.25% Vegol (40%)





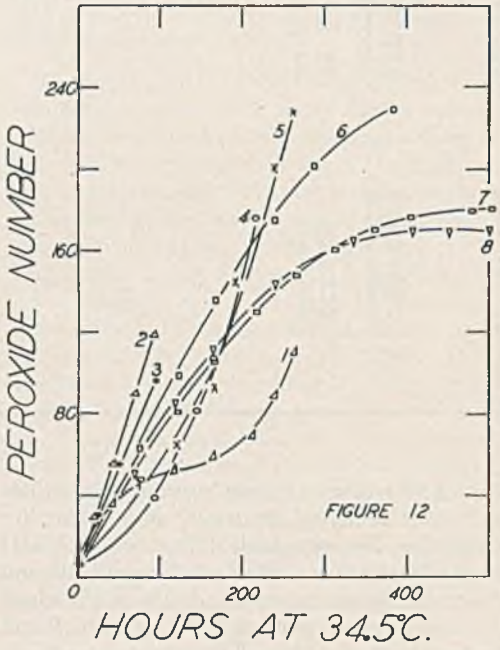


Figure 12

Curve 1. Crude soup-fin shark liver oil C
Curve 2. Carbon-treated shark liver oil C
Curve 3. Same as 2, + 1% lecithin
Curve 4. Same + 0.50% lecithin and 0.05% synthetic α-tocopherol
Curve 5. Same + 0.50% lecithin and 0.10% synthetic α-tocopherol
Curve 6. Same + 0.50% lecithin and 0.50% synthetic α-tocopherol
Curve 7. Same + 5.0% lecithin and 0.50% synthetic α-tocopherol
Curve 8. Same + 0.50% lecithin and 1.25% Vegol (40%)

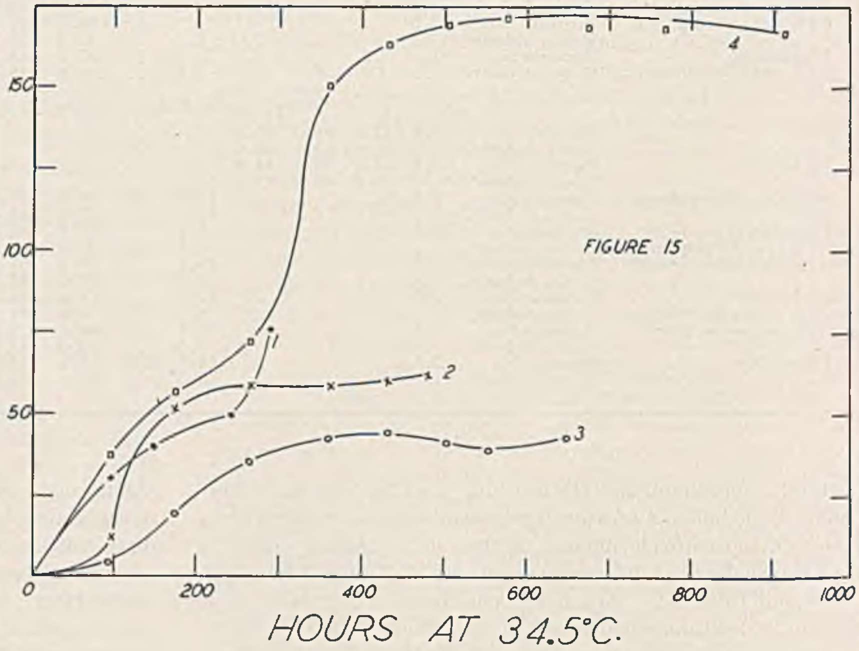


Figure 13

Curve 1. Crude halibut liver oil A
Curve 2. Carbon-treated halibut liver oil A
Curve 3. Same as 2, + 0.10% synthetic α-tocopherol
Curve 4. Same + 0.50% synthetic α-tocopherol

Figure 14

Curve 1. Crude soup-fin shark liver oil C
Curve 2. Same as 1, + 0.10% synthetic α-tocopherol
Curve 3. Crude halibut liver oil A
Curve 4. Same as 3, + 0.1% synthetic α-tocopherol

Figure 15

Curve 1. Crude soup-fin shark liver oil B
Curve 2. Same as 1, + 0.1% natural γ-tocopherol
Curve 3. Same + 0.1% natural γ-tocopherol and 1.0% lecithin
Curve 4. Same + 0.5% natural γ-tocopherol

ergistic effect of lecithin is not proportional to its concentration and also depends upon the type of fish liver oil used. Lecithin alone exhibits no protective action for the vitamin A at a 1.0% concentration in the carbon-treated soup-fin shark liver oil C (curves 2 and 3, Figure 6) and in the crude and carbon-treated halibut liver oil B (Table III). However, at a 1.0% concentration in crude soup-fin shark liver oil A, lecithin increased the vitamin A stability of crude soup-fin shark liver oil A, 50.3% for the lecithin-containing oil as compared to 78.4% vitamin A loss for the blank oil after 24 days of storage. These results indicate that this particular oil probably contains an appreciable amount of a natural antioxidant which is capable of acting synergistically with lecithin. If the oil does contain such an antioxidant, it is not predominantly α-tocopherol, because of the slow rate and type of peroxidation displayed. The analysis of crude soup-fin shark liver oil A (Table I) shows that it contains appreciably more phosphorus than the other oils studied. When 0.50% γ-tocopherol and 1.0% lecithin were added to crude halibut liver oil B, the percentage loss of vitamin A after 32 days was 20.3 as compared to 66.3% for the original oil after 7 days (Table III). All the oils containing added lecithin and either α-, β-, or γ-tocopherol exhibited greater vitamin A stability than analogous blanks containing only the tocopherols.

A comparison of curves 1 and 4 in Figure 6 shows that vitamin A in the sample of carbon-treated shark liver oil containing 0.25% of added synthetic α-tocopherol still decreased slightly faster than in the untreated crude oil. Curves 1 and 3 of Figure 8 indicate that the addition of 0.1% synthetic α-tocopherol to carbon-treated halibut liver oil A stabilizes the vitamin A in the oil to about the same degree as it does in the crude oil. When 0.1% natural α-tocopherol is added to carbon-treated halibut liver oil B, it stabilizes the oil to a greater degree than the crude oil (Table III). α-Tocopherol is a more effective antioxidant for vitamin A in the carbon-treated halibut liver oil A than in the carbon-treated soup-fin shark liver oil C. A concentration of 0.10% of β- and γ-tocopherol in carbon-treated halibut liver oil B (Table III) stabilized the oil appreciably more than when 0.10% of α-tocopherol was used and to a greater degree than the crude oil. Generally speaking, tocopherols alone or with lecithin are more effective as antioxidants for inhibiting vitamin A destruction and peroxidation in oils of low unsaturation than in oils of high iodine value.

RATE AND EXTENT OF PEROXIDATION

Figures 11 to 15 and Table III contain data on the rate of peroxidation. It has generally been thought that, in order to prevent vitamin A losses due to oxidation, peroxidation had to be inhibited nearly completely. The present data show that, when relatively high percentages (0.25% and up) of either α-, β-, or γ-tocopherol are added to soup-fin shark or halibut liver oils, relatively high peroxide values (100 and up) can be tolerated with only minor losses of vitamin A (around 10% and less). In nearly all crude fish liver oils and certainly in carbon-treated fish liver oils stored under the conditions of this study, when the peroxide value reaches a numerical figure of around 70 or 80 substantially all of the vitamin A content of the oils has been destroyed. Both β- and γ-tocopherol at a 0.10% concentration are more efficacious antioxidants of the peroxide-inhibiting type for fish liver oils than α-tocopherol. The results on γ-tocopherol establish that it is more effective than β-tocopherol for inhibiting peroxidation. At a 0.50% concentration in the oils studied, β- and γ-tocopherol failed to inhibit peroxidation even though they stabilized effectively the vitamin A contents of the oils. The three tocopherol forms were more potent in controlling peroxidation in the halibut liver oils than in the soup-fin shark liver oils. During the latter stages of vitamin A destruction, in the fish liver oils containing 0.10% of added γ-tocopherol alone and in combination with lecithin, some irregularities in peroxide values were observed (Table III). A somewhat similar behavior was observed in soup-fin shark liver oil A containing 0.10% of added β-tocopherol alone and with lecithin. In these instances the peroxidation proceeded smoothly until the peroxide value reached a rather low maximum —around 30 to 60 depending on the particular oil—and then it either remains more or less static or decreases. This same behavior was observed in unpublished work on certain types of solvent extract fractions from shark liver oils particularly. No such peroxidation behavior was observed with α-tocopherol under analogous circumstances.

Lecithin at 0.50% concentration exhibited a slight depressing effect on the peroxidation in carbon-treated soup-fin shark liver oil C containing added α-tocopherol. In crude and carbon-treated halibut liver oil B (Table III) with and without added α-, β-, or γ-tocopherol, lecithin at a 1.0% concentration decreased the peroxidation rate appreciably. Lecithin also considerably lowered the peroxidation rate of crude soup-fin shark liver oil A. In the oils containing added α-tocopherol alone, peroxides accumulated faster than in the respective crude oils. No similarity was observed between the rate and extent of peroxidation in the lots of crude and carbon-treated soup-fin shark and halibut liver oils and in the same oils containing added α-, β-, or γ-tocopherol alone or with lecithin.

SUMMARY

Stability studies of vitamin A in soup-fin shark and halibut liver oils, with and without added synthetic and natural α- and γ-tocopherol and synthetic β-tocopherol alone and plus lecithin, establish that the tocopherols are effective vitamin A antioxidants at relatively high concentrations. However, at the same concentration the tocopherols, either alone or associated with lecithin, are not effective antioxidants for inhibiting peroxidation in such oils. Lecithin alone at 1.0% concentration in crude halibut liver, carbon-treated halibut liver, and soup-fin shark liver oils exhibited little or no activity for inhibiting vitamin A destruction. Under similar conditions and when associated with the pure tocopherols, lecithin had a depressing effect on the rate of peroxidation in such oils. The effectiveness of the pure tocopherols as antioxidants for vitamin A was enhanced by using them in association with lecithin. In all instances much higher peroxide numbers were observed in oils containing synthetic or natural added α-tocopherol than in those without them at the same percentage of vitamin A destruction. Pure β- and γ-tocopherol at a 0.10% concentration in the oils studied decreased slightly the rate of peroxidation; however, at a level of 0.50% the peroxidation rate was increased the same amount as when α-tocopherol was used. No appreciable difference could be noted in the oils examined between the antioxidant effectiveness of the pure synthetic and the natural forms of α- and γ-tocopherol in inhibiting peroxidation and vitamin A destruction. When 0.1% synthetic α-tocopherol was added to samples of crude soup-fin shark and halibut liver oil, the rate of vitamin A destruction was decreased; however, the rate of peroxidation was markedly increased. Pure α-, β-, and γ-tocopherols, alone or in combination with lecithin at relatively high concentrations, do not act as antioxidants in preventing peroxidation in crude or carbon-treated soup-fin shark or halibut liver oils, whereas they are effective antioxidants for vitamin A in such peroxide-containing oils. The relations observed between peroxide formation and vitamin A destruction in crude and carbon-treated soup-fin shark and halibut liver oils, with and without α-, β-, and γ-tocopherols, indicate that the antioxidative behavior of the crude fish liver oils examined is not due predominantly to any tocopherols which may be present.

ACKNOWLEDGMENT

The author expresses his thanks to H. J. Konen, now at Schenley Distillers, Inc., to Jane A. Nagle for many helpful suggestions and assistance in accumulating the data presented in this paper, and to Merck & Company, Inc., and Distillation Products, Inc., for the samples of pure tocopherols used in the course of this investigation.

LITERATURE CITED

(1) Berenblum, I., and Chain, E., *Biochem. J.*, 32, 295 (1938).
(2) Bird, O. D., Publication 299, Univ. Microfilms, Ann Arbor, Mich., 1941.
(3) Buxton, L. O., IND. ENG. CHEM., 34, 1486 (1942).
(4) Golumbic, C., *Oil & Soap*, 20, 105 (1943).
(5) Golumbic, C., and Mattill, H. A., *J. Am. Chem. Soc.*, 63, 1279 (1941).
(6) Olcott, H. S., and Emmerson, O.H., *Ibid.*, 59, 1008 (1937).
(7) Olcott, H. S., and Mattill, H. A., *Ibid.*, 58, 1627 (1936).
(8) Riemenschneider, R. W., Turer, J., and Ault, W. C., *Oil & Soap*, 21, 90 (1944).
(9) Robeson C. E., and Baxter, J. G., *J. Am. Chem. Soc.*, 65, 940 (1943).
(10) Simons, E. J., Buxton, L. O., and Colman, H. B., IND. ENG. CHEM., 32, 706 (1940).
(11) Swift, C. E., Rose, W. G., and Jamieson, G. S., *Oil & Soap*, 19, 176 (1942).

PRESENTED in part before the Division of Biological Chemistry at the 109th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

BATCH DISTILLATION NOMOGRAPH

MELVIN NORD

Nord and Company, Inc., Keyport, N. J.

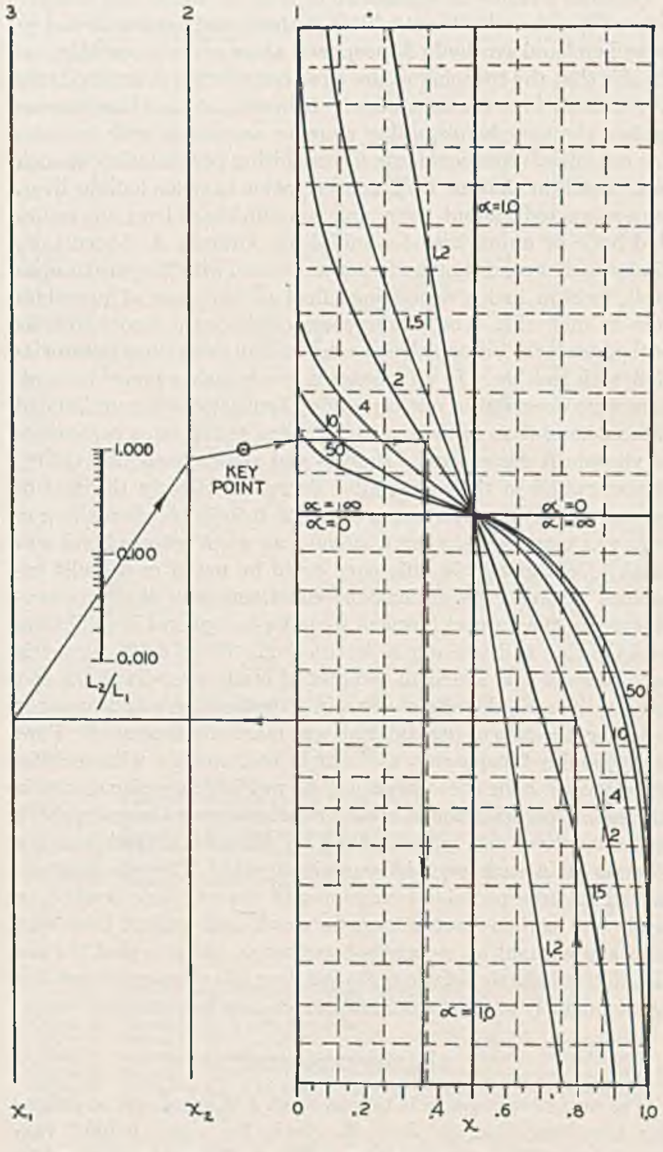


Figure 1. Simple Batch Distillation Nomograph

IN THE theory of simple batch distillation of binary solutions the following, known as Rayleigh's equation, occurs:

$$\ln \frac{L_1}{L_2} = \frac{1}{\alpha - 1}\left(\ln \frac{x_1}{x_2} + \alpha \ln \frac{1 - x_2}{1 - x_1}\right) \tag{1}$$

where L_1 and L_2 are the number of moles (or pounds) of original charge and residue, respectively, x_1 and x_2 are the mole fractions (or weight fractions) of light component in the original charge and the residue, and α is the relative volatility of the light component, which is assumed to be constant over the concentration range considered[1]. In order to solve Equation 1 for x_1 or x_2, trial-and-error solution is necessary.

It is possible, however, to construct a nomograph which will solve Equation 1 without trial and error. Rayleigh's equation may be rewritten as follows:

$$\frac{L_1}{L_2} = \left[\frac{x_1}{x_2}\left(\frac{1 - x_2}{1 - x_1}\right)^{\alpha}\right]^{1/(\alpha - 1)} \tag{2}$$

or

$$\frac{L_2}{L_1} = \frac{\left[\dfrac{(1 - x_1)^{\alpha/(\alpha - 1)}}{x_1^{1/(\alpha - 1)}}\right]}{\left[\dfrac{(1 - x_2)^{\alpha/(\alpha - 1)}}{x_2^{1/(\alpha - 1)}}\right]} \tag{3}$$

If

$$f(x) = \left[\frac{(1 - x)^{\alpha/(\alpha - 1)}}{x^{1/(\alpha - 1)}}\right] \tag{4}$$

$$\frac{L_2}{L_1} = \frac{f(x_1)}{f(x_2)} \tag{5}$$

Therefore, from a graph of $\ln f(x)$ against x, for lines of constant α, one can subtract $\ln f(x_2)$ from $\ln f(x_1)$ nomographically to find the ratio L_2/L_1, or the fraction of the initial charge which remains in the still. This is demonstrated in Figure 1.

As an example of the use of the nomograph, assume $x_1 = 0.80$, $\alpha = 2.0$, and $L_2/L_1 = 0.044$; then x_2 is found as follows: At 0.80 on the x scale, go vertically up to $\alpha = 2.0$, then horizontally over to the scale marked x_1, scale 3. Connect the point on the x_1 scale with point 0.044 on the L_2/L_1 scale and continue to scale 2, marked x_2. Then draw a line from this point through the key point and continue to scale 1, then horizontally to $\alpha = 2.0$ and vertically down to the x scale. The result is 0.36, which is the desired value of x_2. This path is indicated by directed lines on the nomograph. The nomograph can be used in the reverse manner to find x_1, or it may be used to find L_2/L_1 when x_1 and x_2 are known.

If more precise results are desired than can be obtained with a nomograph of moderate size, the values obtained in this way may be regarded as the first approximation in a trial-and-error solution. If it is desired to take into account variations in α, the nomograph may be applied over small enough intervals of concentration so that constant values of α may be used over each interval.

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[1] Perry, J. H., Chemical Engineers' Handbook, 2nd ed., p. 1383 (1941).

January's HEADLINES...

Events of Interest to Chemists, Chemical Engineers, and Executives∼∼*Reviewed by the Editors*

¶ January 1. Special subcommittee of House Interstate and Foreign Commerce Committee recommends comprehensive program of exploration, conservation, and research to stretch U. S. supplies of petroleum.∼∼A. L. Viles, president Rubber Manufacturers' Association, says for first time annual rubber consumption topped million-ton mark, with consumption 54% above 1940. ∼∼George R. Gibbons, senior vice president Aluminum Co. of America, says our economic capacity for producing new aluminum is four times that in highest prewar year.∼∼G. G. Suits, vice president of GE and director of company's research laboratory, in science forum broadcast says heat from atomic energy piles may be used to manufacture important new chemical products.

¶ January 2. Civilian Production Administration, Division of Office of Temporary Controls, says controls over imports of tin will continue because of lack of imports.∼∼Airline Foods Corp. opens centralized laboratory in N. Y. to broaden its activities in food research[1].∼∼J. Heng Lin, medical director American Bureau for Medical Aid to China, announces first penicillin plant in China opened Jan. 1.∼∼Standard Oil (N. J.) forms new petroleum research organization, Esso Development Co., in Great Britain[1].∼∼Government files antitrust suit against Standard Oil of California and its wholly-owned subsidiary, Standard Stations.∼∼Standard Oil (N. J.) forms Enjay Co. to sell and distribute products handled by chemical products department of Stanco Distributors, Inc., and Standard Alcohol Co.[2]∼∼Large drug manufacturers favor legislation requiring pretesting of streptomycin for purity and potency.∼∼CPA says rubber manufacturers are no longer required to obtain permission to consume natural rubber, butyl, and GR-S.∼∼Anglo-American Oil announces formation of petroleum research organization to expand work of its British Laboratories.

¶ January 3. Bernard M. Baruch gives "victory dinner" in N. Y. to commemorate adoption Dec. 30, 1946, of U. S. proposals by UN Atomic Energy Commission∼∼USAEC discloses appointment to commission of three expert industrial relations consultants, Lloyd K. Garrison, N. Y. attorney, former chairman and prior thereto general counsel of now extinct War Labor Board; George H. Taylor, also former WLB chairman and now professor of industrial relations at Wharton School of Finance and Commerce, University of Pennsylvania; and David A. Morse, Assistant Secretary of Labor and former general counsel of National Labor Relations Board.∼∼Du Pont's application to build $4,200,000 factory for manufacture of x-ray film at Parlin, N. J., approved[3].∼∼McCarthy Chemical Co. announces plans for construction of $3,000,000 chemical plant, 55 miles east of Houston, Tex.[4]∼∼War Assets Administration recommends to Congress that Big and Little Inch pipelines be sold for transportation of petroleum or natural gas or a combination of both.∼∼Representative Mundt introduces bill in House to curb industrial and municipal pollution of nation's streams.

¶ January 4. Baruch and five aides on UNAEC resign saying their task is completed, but Baruch urges U. S. to continue to make bombs, at least until ratification of treaty.

¶ January 5. Naugatuck Chemical Division, U. S. Rubber, obtains synthetic rubber project from Reconstruction Finance Corp. to process synthetic latex at Los Angeles[1].∼∼Monsanto Chemical announces formation in Seattle of western division to supervise its expanding operations on Pacific Coast[4].∼∼Brig. Gen. Robert Wood Johnson asks for appointment of commission of five civilians to plan dispersion and protection underground of national defense industries for age of atomic warfare[5].∼∼Chemical Division, CPA, says potash supplies for April and May 1947 will be 25% less than for similar period last year.

¶ January 6. J. W. Crosby, president Thiokol Corp., says company plans diversification in 1947 into allied fields, particularly organic sulfur chemistry.∼∼Possibility that American Institute of Chemists become a professional division of ACS explored.

¶ January 7. Carthage Hydrocol, Inc., awards contract for construction of $16,000,000 plant for manufacture of synthetic petroleum products and chemicals from natural gas at Brownsville, Tex.[3]∼∼Synthetic Organic Chemical Manufacturers' Assoc. files protest with Committee for Reciprocity Information against further tariff concessions on chemical imports this year.

¶ January 8. Alden H. Emery, Secretary ACS, at dinner of N. Y. Chapter Alpha Chi Sigma, says survey of service performed during war by all physical scientists and engineers is being made.

¶ January 9. Pacific Fleet Headquarters announces *Prinz Eugen* sank in Kwajalein harbor Dec. 16 after having survived both atomic bomb bursts.∼∼Andrei A. Gromyko, pushing his plan for commission on general disarmaments in UN Security Council, says U. S. is delaying UN progress on disarmament by insisting plan for atomic control be agreed upon first.∼∼Shell Pipe Line Co. announces plans for a $1,250,000 six-inch pipeline from its Sheridan recycling plant to its Deer Park refinery.

¶ January 10. President Truman nominates Warren R. Austin as U. S. representative on UNAEC and recommends liquidation of Rubber Development Corp.∼∼R. R. Williams, director of research, Research Corp., receives Perkin Medal for outstanding chemical achievement at joint dinner meeting American Section Society of Chemical Industry, ACS, American Institute of Chemical Engineers, and Electrochemical Society in New York[6]. ∼∼J. R. Oppenheimer, University of California, and wartime director Los Alamos, N. Mex., atomic energy laboratory, elected chairman General Advisory Committee of Scientists for AEC.

¶ January 11. Republican leaders pick Senator Hickenlooper, of Iowa, to head Senate-House Committee on Atomic Energy[7].

¶ January 12. Glidden Co., International Minerals and Metals Corp., and Phelps Dodge Refining Corp. organize Zinc Chemical Co. for production of zinc chemicals with plant in Baltimore[3]. ∼∼WAA offers sulfa surpluses for sale in both powder and tablet form.∼∼John R. Steelman, assistant to President Truman, says Congress will be asked for permanent legislation to protect and maintain synthetic rubber industry.

¶ January 13. Warren R. Austin and Bernard M. Baruch confer, and announcement is made U. S. will continue to insist on basic principles of Baruch plan for international atomic control, including abolition of veto on punishment.

¶ January 14. John L. Collyer, president B. F. Goodrich, urges prompt action by Congress to establish national program to maintain war-born synthetic rubber plants in stand-by operation.

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[1] *Chem. Eng. News*, **25**, 174 (Jan. 20, 1947).
[2] *Ibid.*, 104 (Jan. 13, 1947).
[3] *Ibid.*, 244 (Jan. 27, 1947).
[4] *Ibid.*, 172 (Jan. 20, 1947).
[5] *Ibid.*, 280 (Jan. 27, 1947).
[6] *Ibid.*, 160 (Jan. 20, 1947).
[7] *Ibid.*, 213 (Jan. 27, 1947).

¶ JANUARY 15. Office of International Trade says benzol, phenol, and phenolformaldehyde resins go on consolidated license procedure for export to group K countries Jan. 22[8].∼∼International Emergency Food Council lifts allocations on argols and tartaric acid.∼∼Mathieson Alkali acquires Lake Charles, La., government ammonia plant, WAA announces[9].∼∼OIT removes export controls on rosin and its intermediates.∼∼President sends to Senate following nominations for USAEC: David E. Lilienthal, Robert F. Bacher, Sumner T. Pike, Lewis L. Strauss, and Wilson W. Waymack, and Carroll L. Wilson, general manager.

¶ JANUARY 16. Representative Celler introduces bill in Congress to create a national science foundation to coordinate Government's scientific programs and train young scientists.

¶ JANUARY 17. WAA offers for sale 163-acre site near Lake Charles, La., suitable for chemical plant.∼∼GOP steering committee refers tariff and reciprocal trade agreement policy to Senate Finance Committee.∼∼General Eisenhower warns Americans against atomic apathy.∼∼Senate confirms Warren R. Austin as U. S. representative on UNAEC.

¶ JANUARY 20. UN Security Council approves U. S. request that consideration of international atomic control be postponed until Feb. 4.∼∼WAA offers for sale or lease a $1,100,000 aluminum powder plant in Glassmere, Pa.∼∼Dow Chemical buys government-owned styrene plant in Velasco, Tex., for $35,155,000[8].∼∼Legislation is introduced in House of Representatives to continue exclusive public purchase of rubber until permanent rubber policy is established.∼∼Department of Agriculture announces dehydrated guava juice powder, rich in pectin, vitamin C, and fruit flavor, has been developed by scientists at Hawaiian Experiment Station.

¶ JANUARY 21. UN Economic and Employment Commission acts on U. S. motion and sets aside plans for study of industrial uses of atomic energy.∼∼Representative Arends (Ill.) offers resolution for congressional study of nation's rubber policy to encourage domestic production and stock-piling for national defense.

¶ JANUARY 22. Government begins antitrust suit against GE and other defendants on charges of conspiracy to control manufacture and pricing of hard metal compositions.∼∼Office of Technical Services publishes sale list of the first 270 atomic energy papers cleared from security standpoint by AEC.∼∼Attorney General Clark announces creation of small business unit in Justice Department's antitrust division to "assist small business and promote free competitive system of private enterprise".∼∼Senate Committee proposes aid for light-metals industry.∼∼WAA lists three wartime chemicals manufacturing installations formally declared surplus by owning agencies—Monsanto, Texas City; Q. O. Chemical Co., Newark, N. J.; and Midwest Solvents Co., Atchison, Kans.∼∼Identical bills are introduced in House and Senate to authorize construction of $8,000,000 research laboratory for Army Quartermaster Corps at Boston.∼∼Standard Chemical Co. announces plans to build chlorine-caustic soda plant at Sarnia, Ont.

¶ JANUARY 23. J. B. Conant, president Harvard University, urges two-year colleges with federal-state aid to meet education demand between high school and present college training.

¶ JANUARY 24. Gustav Egloff, at technical conference, Northwestern University's technological institute, conducted by Chicago Section, ACS, reports important untapped sources of uranium oxide in Sweden.∼∼Senator Hickenlooper promises Congress will keep close watch on activities of USAEC.∼∼Monsanto announces plans for extension of Texas City plant and construction of additional units at other Texas points.∼∼OIT ends export curbs on fertilizer materials to Philippines and North and South America.∼∼Glyco Products leases government Chemical Warfare Service plant at Natrium, W. Va.

¶ JANUARY 25. Warren R. Austin at dinner of N. Y. State Bar Association in N. Y., says U. S. opposes any change in veto rights of great powers on Security Council but points out two provisions in charter binding all signers to punish peace violators.∼∼Benjamin Graham, financial economist of N. Y., says national productivity-over-all industrial output for each man-hour of labor was 18% higher in 1946 than in 1940.∼∼M. H. Trytten, director Office of Scientific Personnel, warns that large-scale training programs of armed forces in colleges threatens nation's supply of potential scientists.∼∼Henry T. Wensel, chief scientific branch of research group, War Department General Staff, and Ralph E. Lapp, scientific adviser of scientific branch, say cheap atomic power will not be available before 1960.∼∼USAEC names Frank J. Wilson, retired chief U. S. secret service, as consultant on measures to prevent "leaks".

¶ JANUARY 26. Esso Laboratories develop new synthetic resin from petroleum for application to iron, brass, bronze, aluminum and highly polished metal in addition to wood and steel.∼∼R. P. Russell, president Standard Oil Development Co., N. Y., is designated to receive Cadman Memorial Medal of Institute of Petroleum, London, for outstanding research in petroleum science.

¶ JANUARY 27. H. E. Smith, president U. S. Rubber, says company has acquired interest in North British Rubber Co., Edinburgh, Scotland.∼∼Former Secretary of War Stimson, in *Harper's Magazine* for February, says President's decision to use atomic bomb had whole-hearted support of seven of country's top scientists in order to avoid heavy bloodshed.∼∼U. S. Rubber and United Rubber workers, CIO, sign first nationwide employer-employee contract adopted in American rubber industry. About 30,000 workers in 16 plants from R. I. to Calif. are affected.∼∼President Truman, in letter to Karl T. Thompson, president MIT, says final decision to use atomic bomb against Japan "had to be made by the President after a complete survey of the whole situation had been made".∼∼Senate passes and sends to White House measure permitting alcohol plants to continue sugar production for a period ending April 30, 1948.∼∼Dow Chemical announces $20,000,000 expansion of Freeport, Tex., plant.

¶ JANUARY 28. David E. Lilienthal tells Senate members of USAEC that present security methods must give way to better system if U. S. is to guard its atomic secrets.∼∼Secretary of Navy issues directive putting Office of Naval Research under Assistant Secretary of Navy for Air.

¶ JANUARY 29. Lewis W. Chubb, director Westinghouse Research Laboratories, East Pittsburgh, receives John Fritz Medal for notable scientific achievement in 1946.∼∼Sharples Chemicals and Continental Oil form Sharples Continental Corp. to manufacture synthetic organic chemicals from petroleum raw materials.∼∼Production experts leave for Germany to find ways of getting more penicillin to American-occupied zone, War Department officials say.∼∼Diamond Alkali will lease army's CWS chlorine plant at Pine Bluff, Ark., Fred W. Fraley, vice president in charge of sales, says.∼∼L. E. Johnson, area engineer for AEC, says construction of $20,000,000 Knolls atomic power laboratory near Schenectady will start this spring.

¶ JANUARY 30. Warren R. Austin begins series of conferences with members of Security Council to end deadlock on atom.∼∼Vannevar Bush, chairman joint research and development board of Army and Navy, receives Hoover Medal for 1946 for outstanding research.∼∼James McCormack, formerly of Plans and Operations Division, War Department General Staff, appointed director of Division of Military Applications, AEC.

¶ JANUARY 31. Senate Oil Investigating Committee urges "bold steps" to promote synthetic fuel production.∼∼USAEC reports to Congress on possibility of applying nuclear energy to propulsion of aircraft and of other peacetime uses.∼∼WAA offers California plant for production of guayule rubber for sale.

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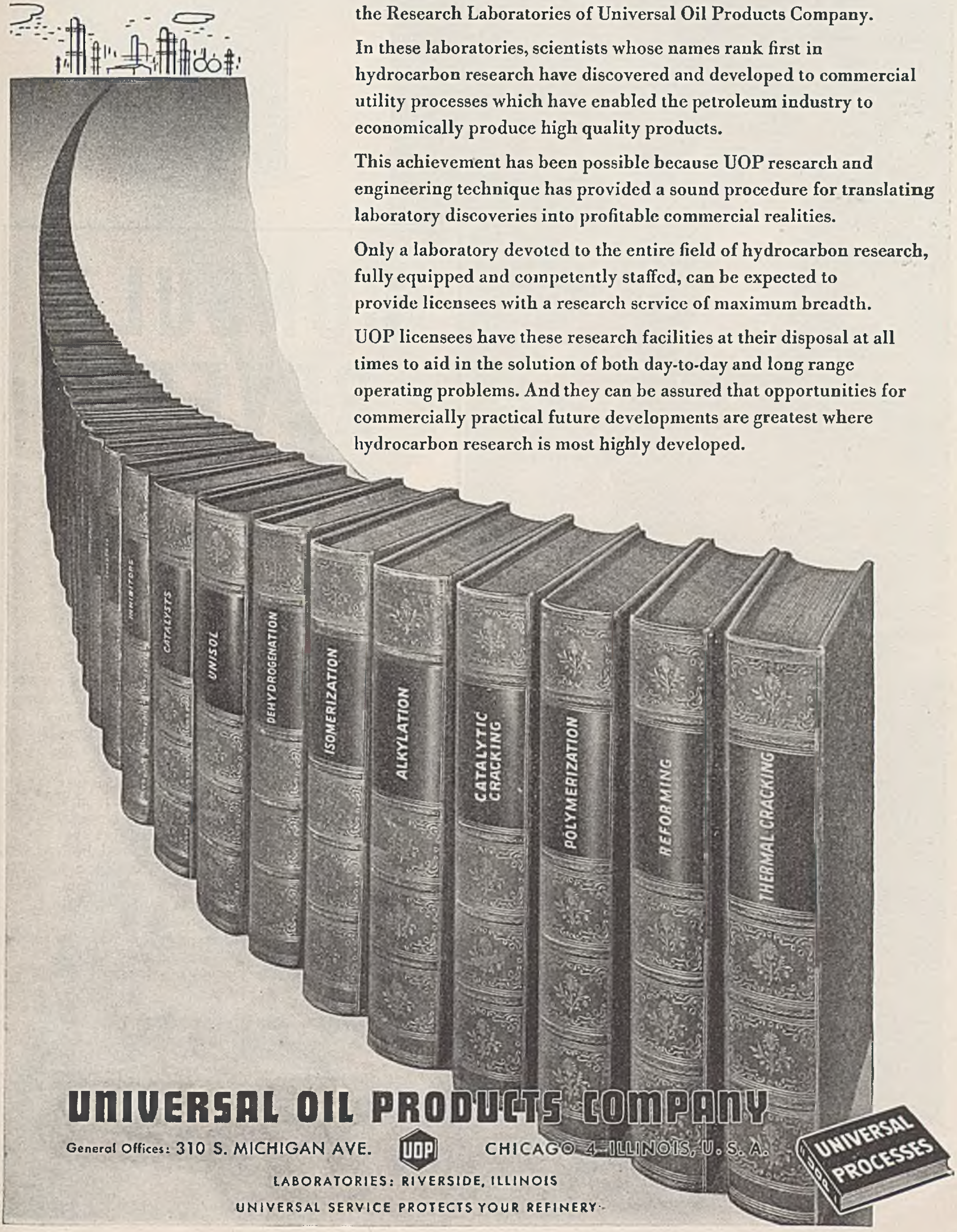
[8] *Chem. Eng. News* 25, 314 (Feb 3, 1947).
[9] *Ibid*, 317 (Feb. 3, 1947).


INHIBITORS
CATALYSTS
UNISOL
DEHYDROGENATION
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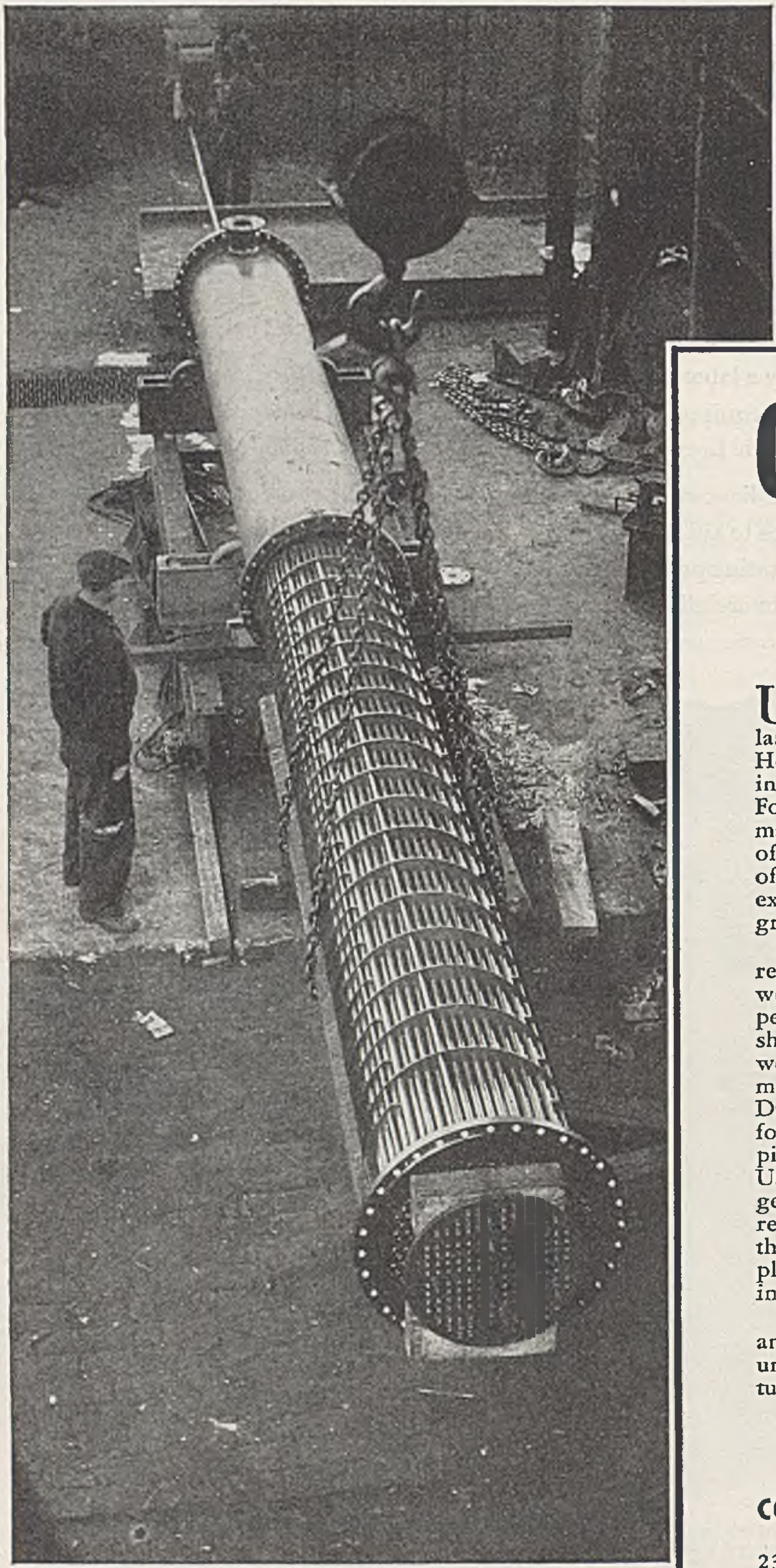
CATALYTIC CRACKING
POLYMERIZATION
REFORMING
THERMAL CRACKING
UNIVERSAL PROCESSES
UOP



BEFORE ordering condenser tubes

CONSULT REVERE

Users of condenser tubes naturally are interested in obtaining tubes that will last long, because that means economy. However, the life of a tube may depend only in part upon the alloy of which it is made. For that reason Revere is always glad to make a thorough study of all the conditions of use when tubes have to be replaced oftener than they reasonably should. This extra service offered by Revere often adds greatly to economy.

For example, there was the case of a refinery where tubes in a heat exchanger were failing within a year. A study of temperatures and other operating conditions showed that changing to Admiralty tubes would result in sufficiently longer life to more than pay for the slightly higher cost. During examination of the exchanger it was found that the tubes showed considerable pitting at the inlet side of the hot vapors. Use of a baffle plate at this point was suggested. The superintendent followed both recommendations, and when last checked, the equipment had given 20 months of completely satisfactory service and was still in operation.

Revere suggests you go over your records, and ask for collaboration on any cases of uneconomical performance of condenser tubes.

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COPPER AND BRASS INCORPORATED
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• • •

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Equipment and Design

Some new types of plant auxiliaries have been developed to decrease expenses and increase production.

by Charles Owen Brown

The progressive and shrewd plant manager regularly devotes a reasonable amount of time in searching for and studying new equipment and new methods for improving plants and products. Frequently, advancing technology develops apparatus or materials which have a remarkably efficient use in fields far removed from the industry. We have recently learned that the chlorinated rubber compound Koroseal is not only suitable for raincoats but can be used in place of felt in the hammers striking the wires of the highest quality pianos. Compared to Koroseal, the felt used for so many years is actually a makeshift now. Moths, moisture, or wear have no effect on the Koroseal hammers. Equally remarkable changes have taken place in plant equipment lines and auxiliaries.

Metal filters

The Micro Metallic Company of Forest Hills, N. Y., offers a new filter medium composed of various stainless steels (Figure 1). These filters are made from powders which are prepared from stainless steels of the desired composition and quality. Bars of 18% chromium–8% nickel with and without molybdenum, 20% chromium–12% nickel, and molybdenum-nickel alloy are first heat-treated and then disintegrated to powders in which each grain has the true alloy composition. These powders are sized carefully into several uniform grain sizes and are then molded into sheets or special shapes for direct mounting into the filter frame. By this method of preparation it is easy to obtain a medium having mean pore openings from 4 to 165 microns. When such filters are subjected to a differential pressure of 10 pounds per square inch, 1 square foot will pass 2 to 750 gallons per minute, respectively. As the all-metal material is strong and rigid, the filter can be cleaned by a relatively fast, high pressure backwash. The pure alloy construction enables this filter to handle hot concentrated nitric and sulfuric acid and sodium hydroxide solutions.

Semisensitive balance

Another useful tool, developed because of the need for peak production during the war, is a semisensitive analytical balance with a pointer and dial reading the correct weight in one swing. The Roller-Smith Division of Realty and Industrial Corporation of Bethlehem, Pa., developed an attractive balance of the beam, pointer, and dial type which has an accuracy of 0.1% (Figure 2). The sample is suspended from the beam, directly if possible, the beam is unlocked, and a pointer reads the weight directly on a graduated dial with the aid of a vernier. The sample is enclosed in a case to avoid drafts, and the operator has nothing to do after the sample has been placed on the hook. Although this balance is not nearly so sensitive as the double-pan and beam analytical balance, it is very fast and convenient to use up to its maximum accuracy. One could probably weigh 50 grams within ±20 mg.

Motors

A great many years ago Edison commercialized the variable-speed direct current motor. By using a controlled secondary circuit to excite the field of the motor, the speed could be varied, with good torque, from 10% up to full speed of the motor. Our entire power transmission technique in those days made speed variation not only convenient but usually necessary. When the constant-speed induction motor and alternating current circuits were offered because of the better over-all efficiency, the greatest

(*Continued on page 72 A*)

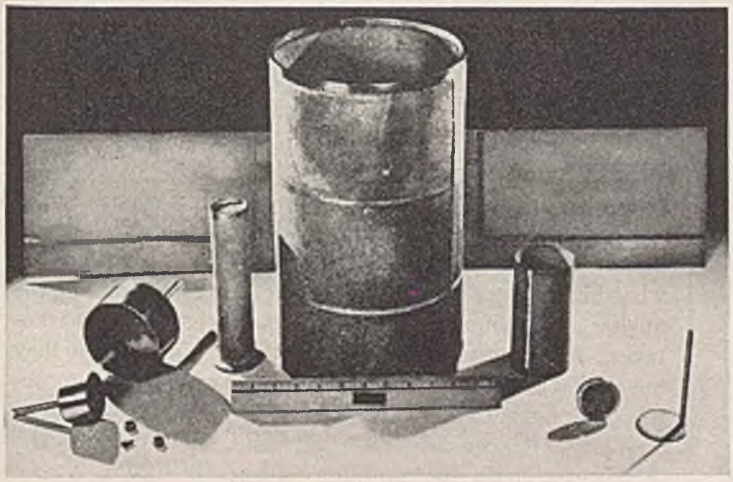


Figure 1. Fabricated Micro Metallic Stainless Steel Filters

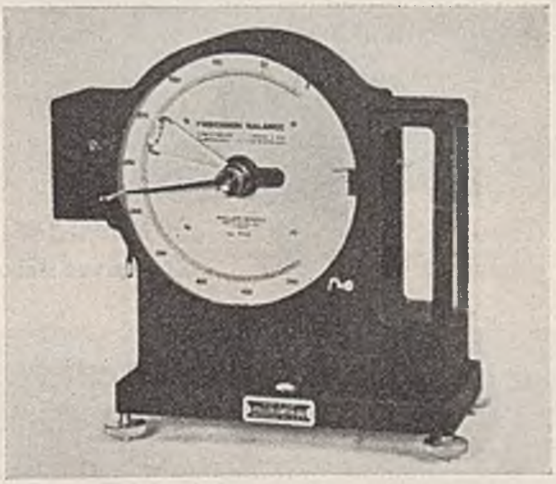


Figure 2. Roller-Smith Balance with Beam, Pointer, and Dial

factors retarding development were the "snap" with which the motor came to full speed and the lack of any speed variation. Belts were used extensively then, and frequent troubles arose from breaks, slippages, and riding off the pulley. These troubles were real enough to force the development of variable speed alternating current motors of the slip-ring type. This motor serves a useful purpose, but even today its initial cost is high and it requires expensive installation and control devices.

During World War I the first synthetic ammonia plant in the United States was erected at Sheffield, Ala. The process was new, and the flow diagram and quantity flows were not definitely known for maximum efficiency or highest production. The research men insisted that great flexibility and variation of the capacity of all pumps and compressors were necessary. The problem was solved by generating alternating current power in a central power station; this was all converted to direct current power and then distributed through the plant in massive copper bars to dozens of direct current motors. Of course the cost and losses were very high.

A recent electronic development to serve those applications where variable speed, fast stopping, and even reversing is required makes use of the older direct current motor but converts the direct current from an alternating current supply by means of electronic three-element vacuum tubes. The tube units are small and light in weight and make a very convenient package which may be placed at or near the motor. In the modern machine shop each power tool is individually driven. Widespread variation with full power at low speeds is essential. In cutting threads, fast revising is required. For all these applications the Varitronic units, of Electron Equipment Corporation, are finding greater applications with favorable results. Direct current motors may be utilized at any point in a factory now equipped only with alternating current power by using one of these rectifying tube units ahead of the motor.

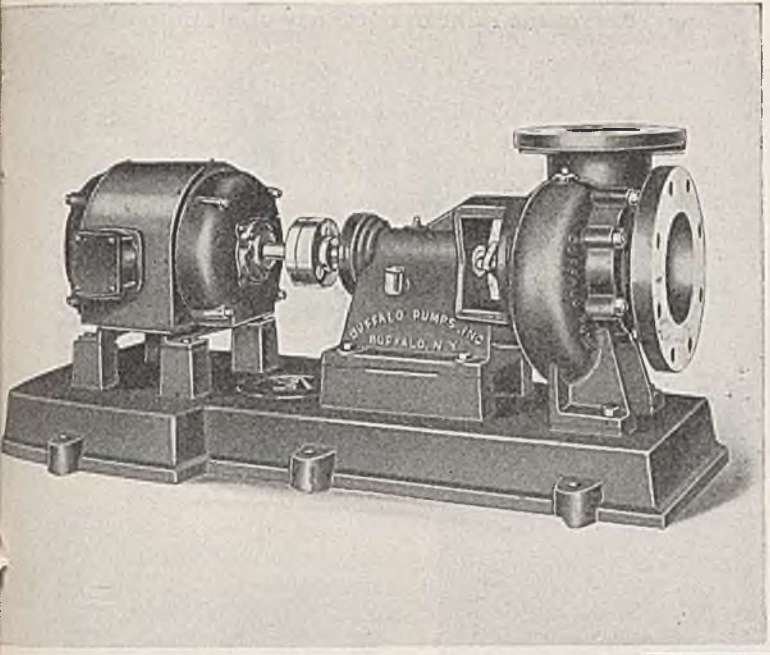
Rectifiers

There is another consideration to the direct current problem. In many electrochemical processes direct current is required because of its unidirectional energy flow. The manufacture of caustic soda and chlorine, the refining or recovery of all metals by deposition, the production of oxygen and hydrogen, and chemical oxidations and reductions require a direct current flow of thousands of amperes. Until recently there was no efficient way of converting alternating current to direct current except by the use of one rotating or two mechanically connected rotating machines. These devices, the rotary converter and the motor-generator set, were both superseded by the mercury-arc rectifier, which has no moving parts and is used today to furnish most of the direct current for electrochemical processes.

The position of the Varitronic rectifiers is to serve those uses between 1 and 300 kilowatts, usually for direct current motor drivers. The cost of the rectifier is approximately 400 to 75 dollars per kilowatt in the larger sizes. These prices are somewhat higher than the cost of mercury-arc rectifiers, but the application is simpler and the performance has special advantages. Many users select these Varitronic tubes because they are available, whereas two to three years are required to obtain motor-generator sets. The mercury-arc rectifier is not used much in sizes below 300 kilowatts, partly because the rectifier requires a vacuum pump to keep the bowl at a very low pressure, and this demands attention and maintenance.

ACETIC ACID TO ZINC SULPHATE

PUMPING EFFICIENCY



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PUMPS

Buffalo Chemical Pumps such as this Class "CS" may be "tailored" to each job by the proper lead or alloy fittings . . . assuring the utmost service life and efficiency for the particular liquid pumped. Write for Bulletin 982.

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Yet operators can avoid premature wear and other pumping "headaches" by ordering the right "Buffalo" Pump. For practically every liquid handled, there is a husky, high-delivery "Buffalo" Pump of the proper alloy, lead or rubber construction to give you *added years* of trouble-free service.

Why not write us about your problem, describing liquids pumped, heads, temperatures, etc? We'll be glad to make cost-cutting recommendations.

BUFFALO PUMPS, INC.
153 Mortimer Street Buffalo, N. Y.
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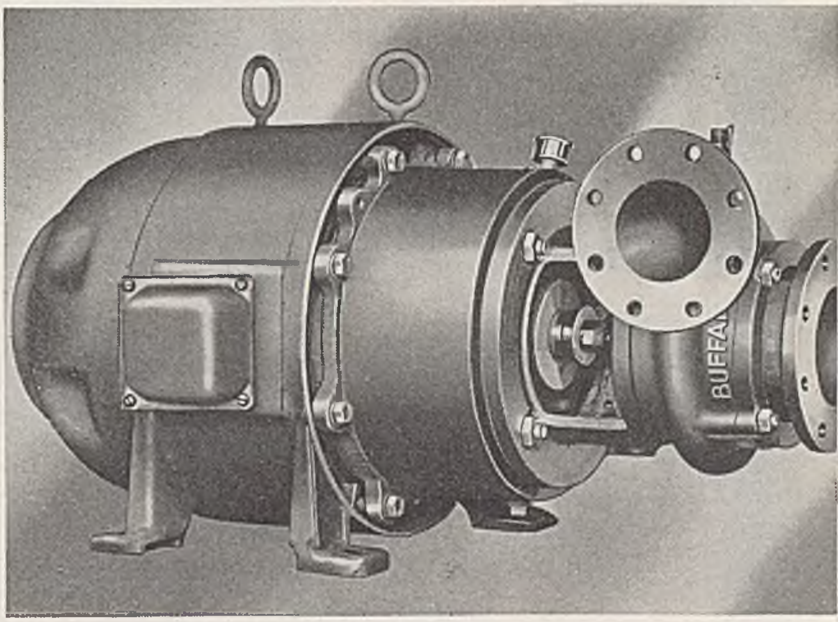
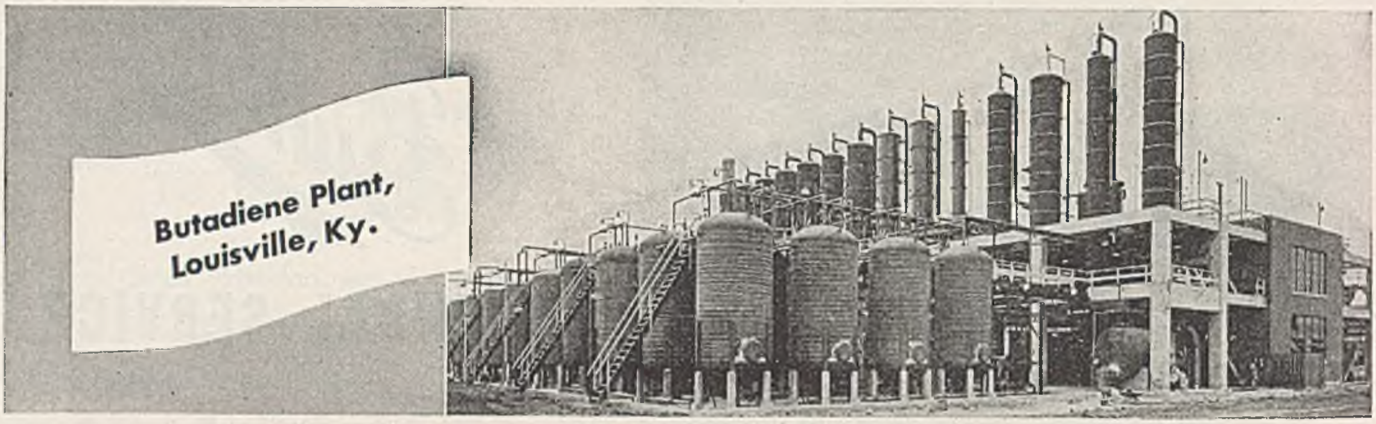
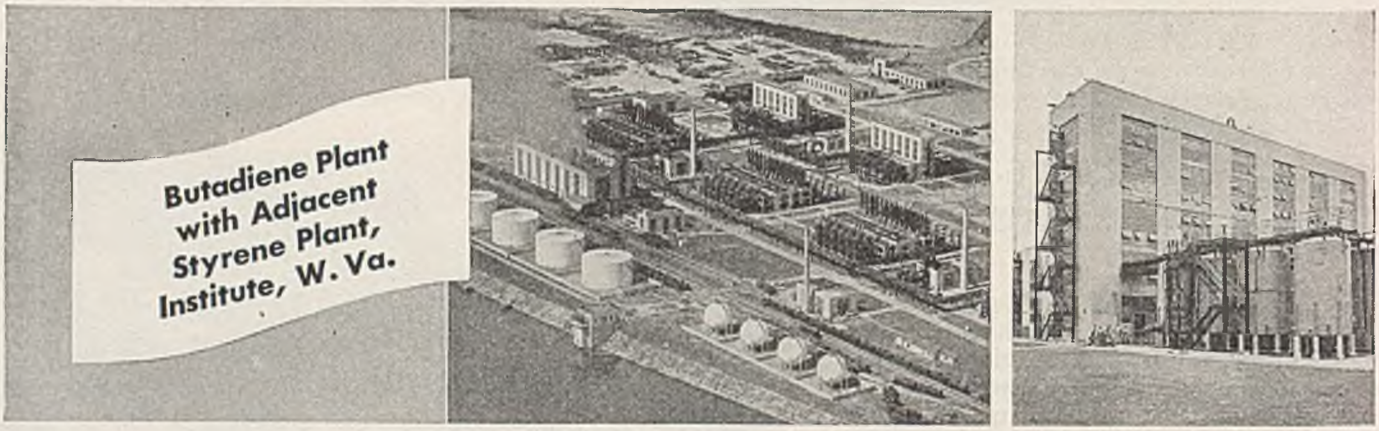
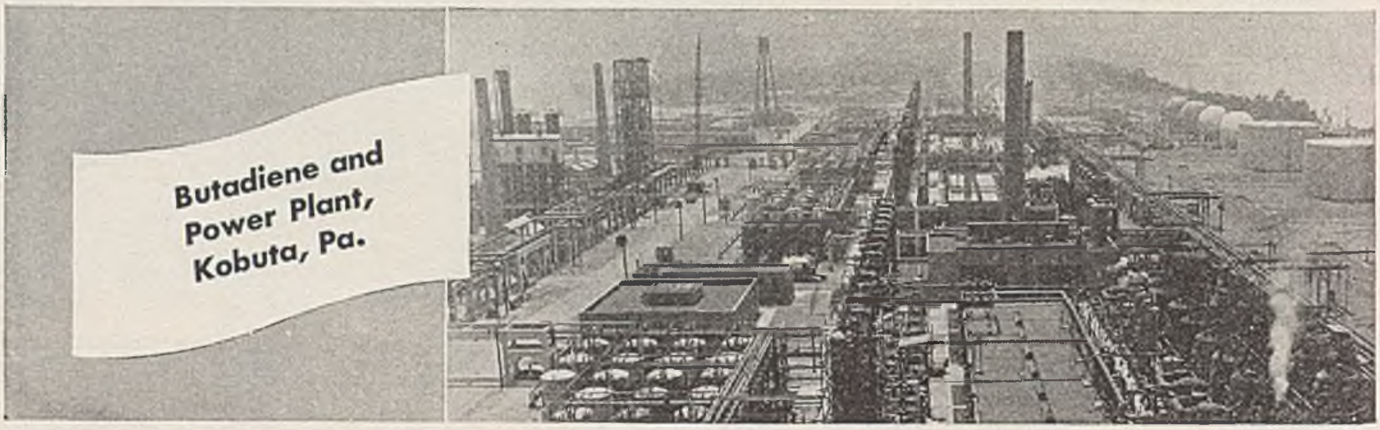


CRAMPED FOR SPACE? A rugged, compact Buffalo Close-Coupled Pump may be just your answer. For the many types of liquids it handles, all performance and construction details, simply write for Bulletin 975-B.

"Buffalo" "CS" AND "CC" PUMPS







UNITS YOU NEED

Functional Units Comprising Distillation, Fractionation and Catalytic Process Equipment, Easily Convertible to Manufacture of Various Chemical Products

1

PLANT: Plancor 1207 consists of land, buildings, machinery, and equipment for the manufacture of Butadiene from industrial alcohol. The following buildings, of permanent type construction and with a total floor area of approximately 156,000 sq. ft., house the functional units which comprise the three 20,000-ton units: Two Dowtherm furnace buildings, 3 distillation conversion buildings, 2 catalyst manufacturing buildings, together with other smaller service buildings.

UTILITIES: Process water is obtained from the Ohio River. Five centrifugal, motor-driven pumps, located in a pumping station, are capable of delivering a total of 78,000 g.p.m. at approximately 50 lbs.

Domestic water is obtained from 2 driven wells, each equipped with electric-driven pumps.

Process steam is furnished by a high and low-pressure plant with a combined total rated capacity of 700,000 lbs. steam per hour.

Electricity and gas supplied by the Louisville Gas and Electric Company.

TRANSPORTATION: Rail, water and highway transportation available.

★ ★ ★ ★ ★

2

PLANT: Plancor 229 consists of land, buildings, machinery, and equipment for the manufacture of Butadiene from ethyl alcohol. The production area comprises 4 units for conversion, each unit having rated capacity of 20,000 short tons per annum; 2 Dowtherm furnace buildings; a catalyst building; a water treating building; 2 water pump houses; 5 foam houses; a switch room; a machine shop; a stores building; totaling 270,000 sq. ft. floor area. All structures of permanent type.

UTILITIES: Water-cooling and fire protection water is pumped from the Kanawha River from two identical pump houses, each containing 6 electric-driven centrifugal pumps with total capacity of 66,000 g.p.m. and one steam turbine-driven, centrifugal pump with capacity of 11,000 g.p.m. A 2,000 g.p.m. treating plant provides treatment for boiler water.

Steam boiler plant comprises rated capacity of 750,000 lbs. of steam per hour at 415 p.s.i. Complete with pulverized coal, oil and/or gas firing.

Electricity and natural gas supplied by public utilities.

TRANSPORTATION: Rail, water and highway transportation available.

PLANT: Plancor 1055 consists of land, buildings, machinery, and equipment for the manufacture of Styrene from ethylene secured from others by pipe line. The rated capacity is 25,000 short tons of Styrene per annum. The production area comprises 2 Styrene distillation units; Tetralin furnace building; one catalyst building; totaling approximately 40,000 sq. ft. floor area.

UTILITIES: Available from the adjacent Butadiene plant.

★ ★ ★ ★ ★

3

PLANT: Plancor 483 consists of land, buildings, machinery, and equipment for the production of 80,000 short tons of Butadiene from alcohol feed stock annually. Production area includes 4 identical Butadiene productive units, each rated at 20,000 tons annual capacity; 2 Dowtherm units. Each Dowtherm building contains two Dowtherm Vaporizers (gas or oil-fired) rated at 24,000,000 b.t.u. per hour, surge tanks and two Methane gas compressors with auxiliary pumps.

The power plant building contains boiler bay, turbine bay, powerhouse annex, and there are 11 substations. The boiler bay contains 4 boilers, 350,000 lbs. steam per hour continuous rating each, at 800 lbs. per sq. in. Steam passes either through a 35,000 kw Westinghouse "Topping" turbogenerator unit, or through a battery of reducing stations which reduce the pressure from 750 p.s.i. to 165 p.s.i. Designed capacity of turbogenerator is 43,750 kw at 80% power factor, ½ lb. hydrogen cooling pressure. Powerhouse annex receives coal by conveyer or chute from main boilerhouse and contains one Combustion Engineering, four drum, natural circulation boiler, 200,000 lbs. steam per hr. total capacity at 450 p.s.i. saturated temperature, with tubular air heater, combination forced and induced draft fan, Raymond fuel pulverizing equipment and 2 Allis-Chalmers boiler feed pumps.

UTILITIES: Water for industrial and fire protection purposes is pumped from the Ohio River. Drinking water is obtained from 2 deep wells.

Electric power and light is obtained from the generating station adjacent to the boilerhouse.

TRANSPORTATION: Rail, water and highway transportation available.

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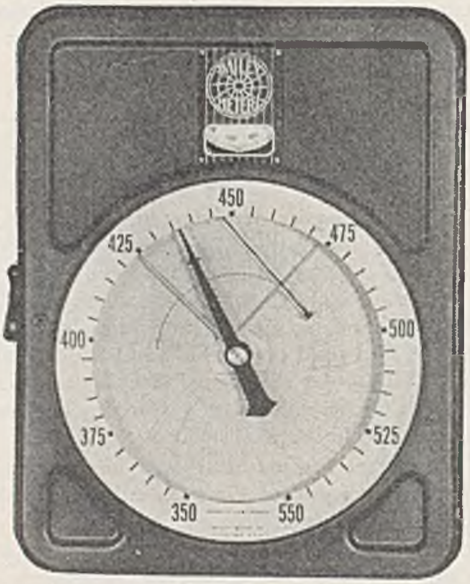
BAILEY METER
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Instrumentation

A low-cost resistance-thermometer temperature controller is discussed this month.

by Ralph H. Munch

THE economics of instrumentation is a subject which has received much less attention than its importance would justify. This is not because the importance of the subject is not realized, but because facts and figures on which to base a discussion of the subject are not readily available. In a paper presented at the Texas Agricultural and Mechanical College's Instrument Course last September, C. S. Comstock of Monsanto Chemical Company discussed this subject. He based his discussion on experience and data available from the operation of the Monsanto Texas City styrene monomer plant, where nearly a thousand major instruments are employed. His paper contains food for thought for those interested in instrumentation. In addition to an excellent general discussion of the subject, Comstock presents interesting data on the average installed cost and the average yearly cost of operation for an instrument. He indicates that the average installed cost of an instrument in this plant was about $750 and that the operating cost amounts to about $56 per year. Taking a 10% yearly depreciation and assuming a 20% return on the gross investment, he arrives at a total yearly cost of $281 for his typical control instrument. The instruments considered were recorder controllers.

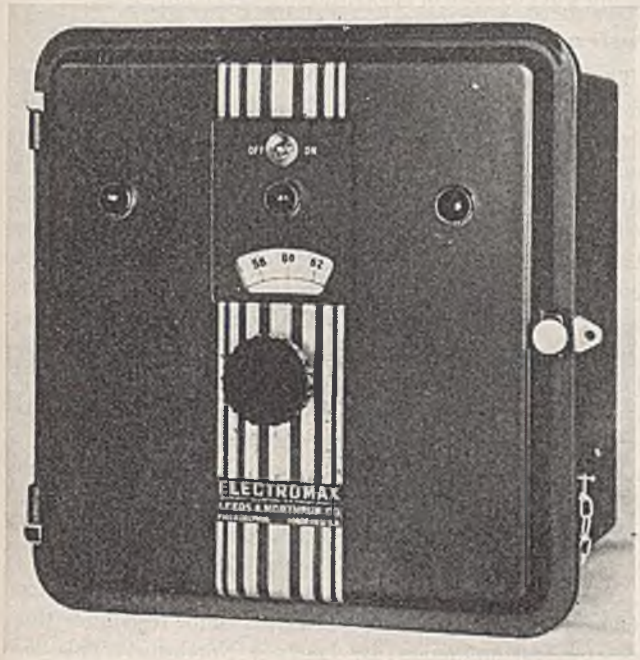


Figure 1. Electromax Temperature Controller

Low cost controller

In many applications a record is not required. Nonrecording controllers are, in general, much less expensive than recorder controllers. Their use makes possible a substantial saving in instrument costs wherever records are not essential. The lower cost is due partly to lower initial cost and partly to lower maintenance cost of the simpler instruments. Even where a record of the variable being controlled is required, using a number of simple controllers in conjunction with a multipoint recorder may turn out to be considerably less expensive than using recorder controllers.

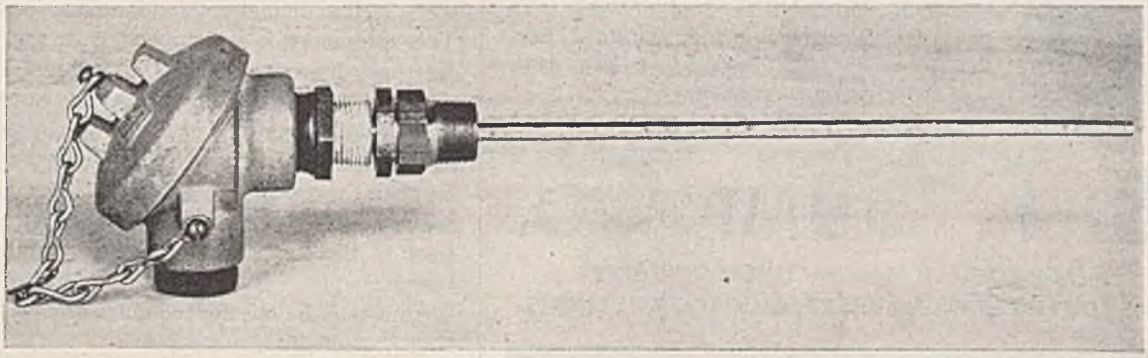
The use of several simple controllers in conjunction with a multipoint recorder works out well where temperature is the variable being controlled. Leeds & Northrup Company, Philadelphia 44, recently announced a new line of inexpensive temperature controllers designated by the trade name Electromax. These instruments, specially designed for applications of the type discussed above, are illustrated in Figure 1. The Electromax controllers are designed for use with resistance thermometers as the sensitive elements. Fundamentally, the instrument is a Wheatstone bridge. Three arms of the bridge are within the instrument case; the fourth is the resistance thermometer which must, of course, be located where the temperature is to be controlled. The power supply for the bridge, and therefore its output, is alternating current.

Control mechanism

To detect bridge unbalance, a vacuum tube amplifier is used to operate a single-pole double-throw relay. As long as the process is at the control

(*Continued on page 78 A*)

Figure 2. Industrial Platinum Resistance Thermometer



temperature, the thermometer resistance is at the value that balances the Wheatstone bridge, so that no signal is fed to the amplifier. The relay is then in neutral position. When the temperature rises above the control point, the thermometer resistance increases and unbalances the bridge. The unbalance voltage acting through the amplifier closes the high relay contact and lights a red pilot lamp. In like manner, when the temperature drops below the control point, the thermometer resistance decreases. The unbalance voltage, now opposite in phase to that produced by a temperature rise, acts through the amplifier to close the low relay contacts and light a green pilot lamp. Small solenoid valves, motor-operated valves, and alarms can be operated directly from the Electromax relay, which is rated to make or break 0.75 ampere at 115 volts, 60 cycles. To control heavy electrical loads, such as electric furnaces, an auxiliary power relay must be used.

For many applications a simple on-off controller such as that described above cannot give adequate control. For these applications the Electromax is available as a position-adjusting type of proportional controller with manual reset, or as a duration-adjusting type of proportional controller with automatic reset. The first type is more readily used to control processes heated by gas, oil, or steam; the second is more readily used to control electrically heated equipment.

Desirable characteristics

The Electromax has many valuable features. Because there are no moving parts other than the relay contacts, maintenance is low. Accuracy is $^1/_2$% of the range. Standard ranges are 0° to 1000° F. and 0° to 250° F. Sensitivity is ±0.5° F. The unit operates entirely from the 115-volt 60-cycle line; no dry cells or standard cell are required. Fluctuations of ±10% in line voltage do not effect performance. Temperature readings may be obtained at any time by turning the control point-setting knob until both red and green pilot lamps are out. The instrument has been carefully designed to "fail safe". Practically all possible failures—such as an open circuit in the resistance thermometer, slidewire contacts, input transformer, power transformer, or relay, or a short circuit in the input transformer, power transformer, or relay, or vacuum tube failures caused by age or opens—would cause the relay to drop to the de-energized position and make the red pilot lamp glow continuously.

An ideal primary element to use with the Electromax controller is a new type of industrial platinum resistance thermometer just announced by Leeds & Northrup. This 25.5 ohm resistance bulb, which is suitable for use up to 1000° F., is pictured in Figure 2. The stainless steel outer sheath is $^5/_{16}$ inch in diameter; standard lengths are 6 and 12 inches. This thermometer is equipped with the standard Leeds & Northrup head to protect the terminal block and facilitate mounting. In speed of response this resistance thermometer is said to be essentially as fast as a miniature pipe-type thermocouple. Its accuracy and stability are substantially better than thermocouples provide. Three No. 14 copper wires are required to connect the bulb to the Electromax in contrast to the compensating lead wires required for use with thermocouples. In addition, the price of the resistance thermometer bulb is not too much greater than that of a similarly protected thermocouple.

FILTERS DESIGNED TO SOLVE SPECIFIC FILTRATION PROBLEMS

GENERAL AMERICAN Conkey and Peterson filters comprise both vacuum and pressure filters in a wide range of sizes for continuous or batch filtration cycles.

Special features of design and construction are incorporated in the different filters which contribute to the end result of efficient, dependable performance.

A General American engineer, experienced in the design and operation of filtration equipment of all types will be glad to work with you toward modernizing your existing equipment or installing new units.

CONKEY ROTARY DRUM VACUUM FILTERS

PETERSON SYNCRO-DRUM RESERVOIR TYPE FILTERS

CONKEY ROTARY DISC VACUUM FILTERS

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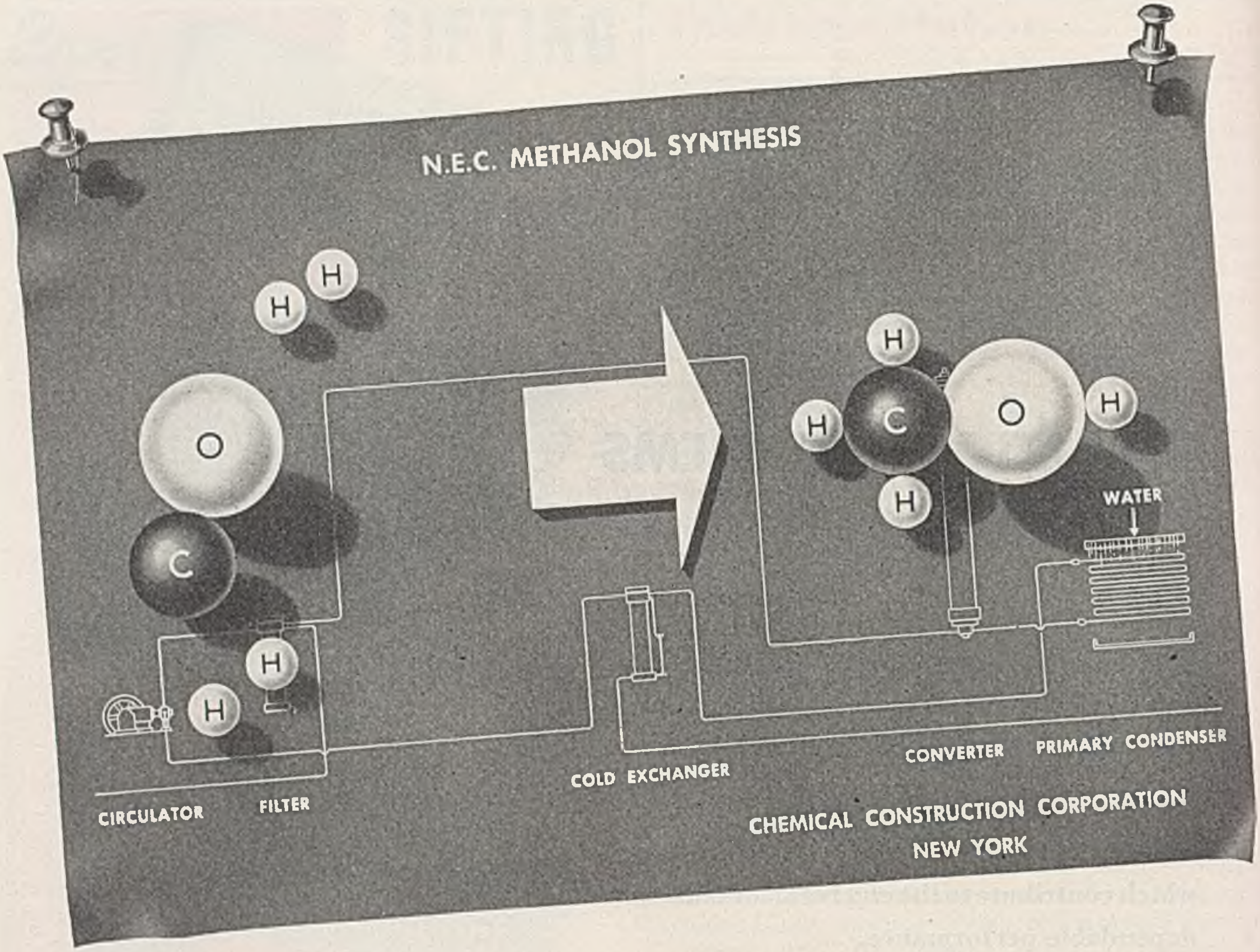
N.E.C. METHANOL SYNTHESIS
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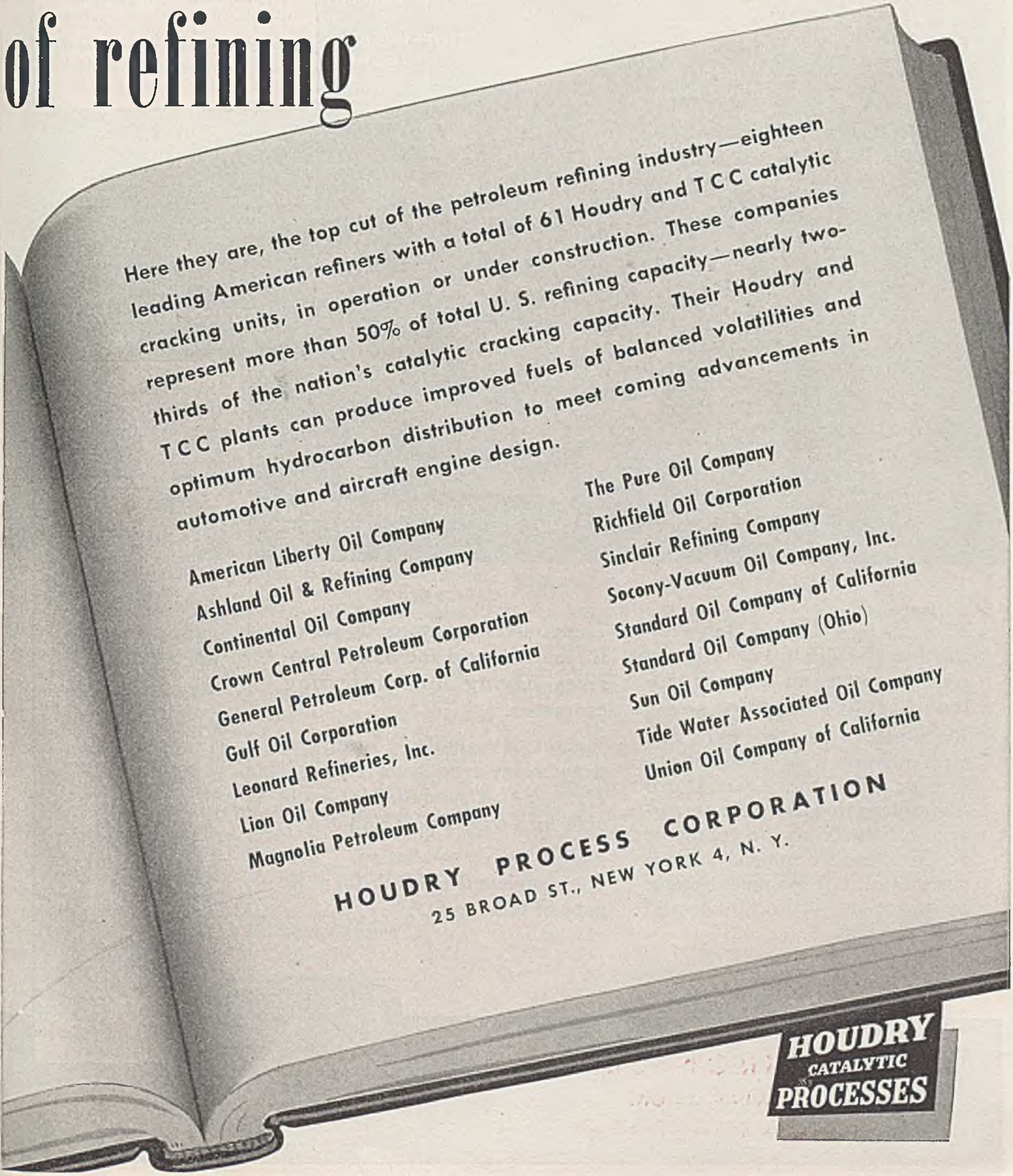
FILTER
COLD EXCHANGER
CONVERTER
PRIMARY CONDENSER
CHEMICAL CONSTRUCTION CORPORATION
NEW YORK

The list of Houdry licensees is the Blue Book of refining



Here they are, the top cut of the petroleum refining industry—eighteen leading American refiners with a total of 61 Houdry and T C C catalytic cracking units, in operation or under construction. These companies represent more than 50% of total U. S. refining capacity—nearly two-thirds of the nation's catalytic cracking capacity. Their Houdry and T C C plants can produce improved fuels of balanced volatilities and optimum hydrocarbon distribution to meet coming advancements in automotive and aircraft engine design.

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Ashland Oil & Refining Company
Continental Oil Company
Crown Central Petroleum Corporation
General Petroleum Corp. of California
Gulf Oil Corporation
Leonard Refineries, Inc.
Lion Oil Company
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The Pure Oil Company
Richfield Oil Corporation
Sinclair Refining Company
Socony-Vacuum Oil Company, Inc.
Standard Oil Company of California
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Sun Oil Company
Tide Water Associated Oil Company
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HOUDRY PROCESS CORPORATION
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HOUDRY
CATALYTIC
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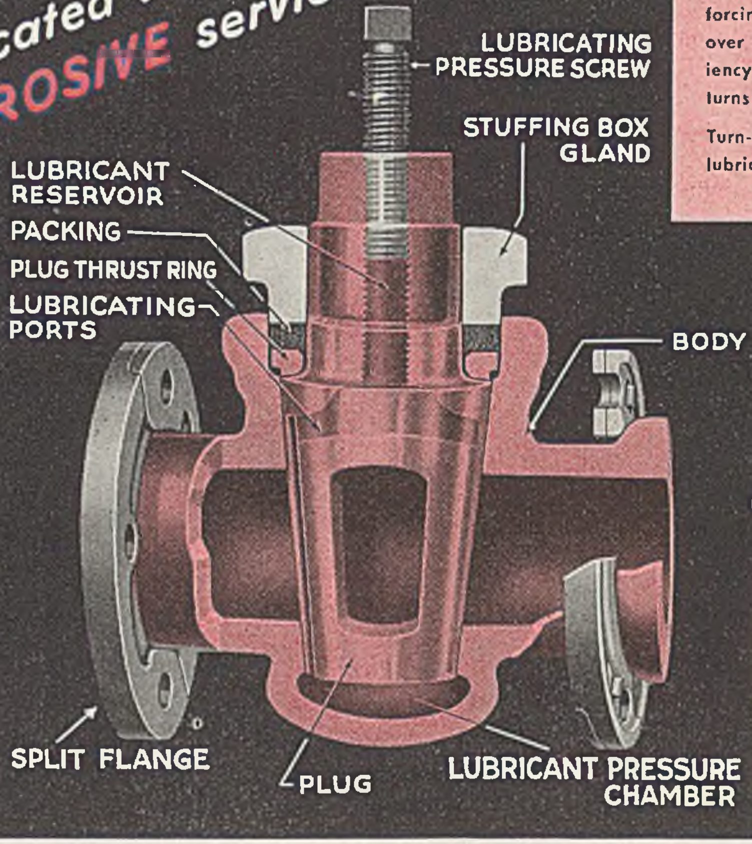
INSIDE STORY

of a lubricated valve for CORROSIVE service



HOW THE VALVE OPERATES

The screw in the stem forces lubricant through the channels of the plug into the reservoir and pressure chamber at the bottom of the body. A turn of the pressure screw lifts the plug hydraulically from the seat for easy turning, at the same time forcing lubricant from the grooves over the seating surface. The resiliency of the acid-resisting packing returns the plug to its normal position.

Turn-stops prevent exposure of the lubricant channels to the liquid.

This look inside a Durco top lubricated plug valve tells the story of permanent, through-and-through corrosion-resistance.

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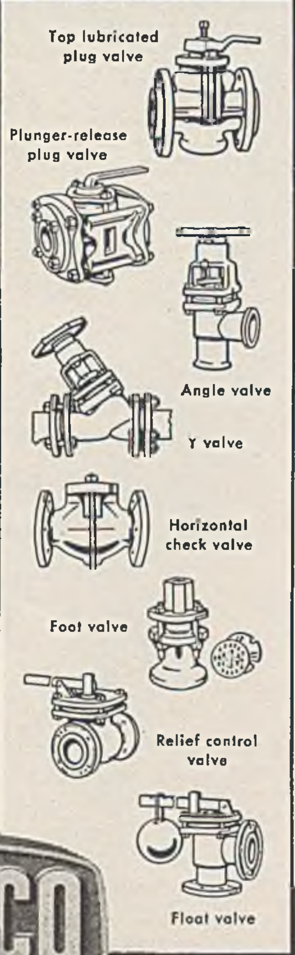

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Corrosion

Economics of materials demands consideration in chemical plant construction.

by Mars G. Fontana

The present tax and labor situation accentuates the need for low cost operation in the chemical industry and in other fields. A substantial portion of the operating cost is due to maintenance. This, in turn, depends largely on the materials used for the construction of the plant. In general, the chemical industry is more concerned with shorter life of equipment than are most other industries, because of comparatively rapid obsolescence and relatively severe corrosion conditions. The selection and specification of suitable and economical materials are important functions in connection with new construction and replacement of equipment.

Several factors to be considered from the materials standpoint are investment, expected life, cost of replacement or repair (including labor), loss of production because of failure, contamination, and safety. Many expensive materials would be satisfactory for a given service, but in most cases cheaper materials are used because of the better balance between investment cost and service life. Cheaper process equipment is often preferred even though costlier equipment presents a more favorable return, particularly if the life required to justify the costlier equipment is over five years, or the advantage is not great. In some cases this tendency is due to the desire of maintenance personnel to keep cost figures low on a monthly basis.

A student's answer to an examination in a course on corrosion serves to illustrate a point in economics. The problem called for selection of materials for a variety of equipment handling nitric acid and sodium hydroxide. The student knew that tantalum was a very corrosion-resistant material, so he specified tantalum for all of the process valves. His plant might operate satisfactorily, but the stockholders would probably be quite unhappy. Materials of about 1% the cost of tantalum would have been suitable for the chemicals involved. This does not mean that tantalum is not used in the chemical industry. In fact there are many applications where tantalum is an economical material—for example, the heating of c.p. hydrochloric acid.

If valuable chemicals, loss of production, high repair costs, contamination, and/or dangerous compounds are involved, it is desirable to lean in the other direction as far as materials of construction are concerned. This same tendency is often followed in the construction of plants for new processes where numerous uncertainties or "bugs" are anticipated, aside from corrosion difficulties. Economical changes can be made later. For example, the original nylon plant contained several items made of stainless steel, but they have been replaced by ordinary carbon steel during expansion and construction of new plants. The new plastic Teflon now costs about 10 dollars per pound, and it is expensive compared to older conventional materials. This material, however, found many uses as a gasket material even when it cost 25 dollars per pound. One example concerns a high pressure high-temperature system handling acetic acid. The Teflon paid its way, not only on a life basis but also on the basis of less hazard to safety and decreased "down" time.

The numerous recent developments in materials of construction indicate that there will be sharp competition between widely different materials for many applications. These materials will replace many older and so-called standard materials. Personnel selecting materials of construction should be thoroughly familiar with these developments to ensure the choice of the most economical materials. In addition, designers and others may be required to ignore traditions in specifying materials in order to obtain more serviceable and economical plant equipment.

Cooperation

Cooperation between the chemist, chemical engineer, and the personnel doing the corrosion work is highly desirable. Cooperation in the early stages of the developmental work may minimize the need for elaborate and expensive corrosion tests, and, more important, quite reliable information may be obtained. This is particularly true during the semiworks or pilot plant stages. Costly mistakes and difficulties during actual plant operation could be avoided in many cases.

An example may serve to illustrate this point. Several research chemists and chemical engineers worked out a process for attacking an ore with strong sulfuric acid and thus obtained a rapid and complete reaction with good yields. The operation was carried out successfully in a pilot plant. The corrosion engineer was then consulted with regard to recommendations for actual plant equipment. The first questions raised concerned the material used in the pilot plant and the corrosion indications obtained. Only cast iron and steel were used in the pilot plant, and the equipment was almost completely destroyed during the few runs made. The only interest at the time was to determine with least cost, whether or not the process would work. It would have required little effort and expense to expose various materials in the pilot plant to obtain corrosion data under actual operating conditions instead of depending on later laboratory tests which did not simulate actual conditions.

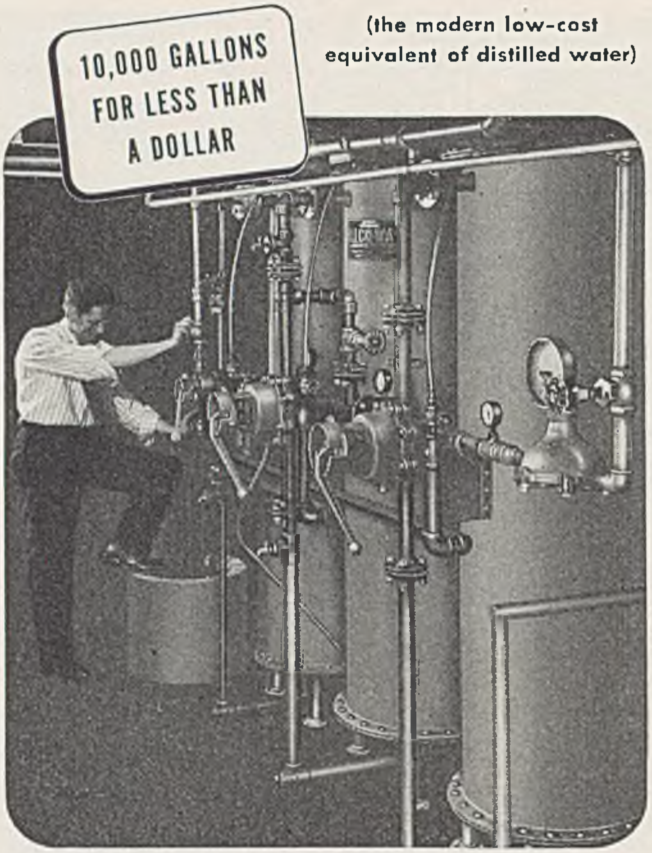
Standard expression for corrosion rate

A large number of expressions or units are used in the literature to express the corrosion resistance of materials. Most of these units indicate penetration per unit of time or weight loss for a given area per unit of time. Some of the more commonly used expressions are: inches per year, milligrams per square decimeter per day, inches per month, grams per hour, grams per square foot, ounces per square foot per year, grams per 100 hours, and per cent weight loss. In fact, many combinations of units for time, fractions, depth, and weight in both the metric and English systems are in use. This situation causes confusion and difficulty in interpreting and comparing results reported in the literature. In some cases the units are practically meaningless—for example, percentage loss in weight. This is a deplorable situation indeed, since standardization could be readily accomplished.

The primary purpose of a corrosion rate is to provide the basis for an estimation of the life of a given metal under conditions of the test. For cases where contamination of the product by the metal is involved, the corrosion rate provides an indication of the amount of metal dissolved.

Some of the requirements for a suitable expression for corrosion resistance or corrosion rate are as follows: (*a*) The units must be familiar to all technical personnel. (*b*) Calculation of the corrosion rate, on the basis of laboratory or service measurements, should be such that chances of error are at a minimum. (*c*) The units must be readily convertible to life of equipment, preferably in years. The units should express the rate of penetration of the metal. (*d*) Decimals are undesirable,

(Continued on page 84 A)



Corrosion

particularly carried to several places after the decimal point. Tabulation of results should be as simple as possible. (*c*) The specific gravity and area of the test specimen should be included in the calculation of the corrosion rate.

Let us consider how some of the corrosion rates in fairly common use at present fulfill these requirements. (*a*) Milligrams per square decimeter per day (m.d.d.) has the advantage of eliminating decimals, since very low rates of attack can be expressed as whole numbers. However, the specific gravity or density of the material is not included. To illustrate this point, let us assume the same corrosion rate in m.d.d. for aluminum and 18–8 stainless steel. Although the corrosion rates are the same, the amount of aluminum corroded or dissolved is approximately three times the amount of corroded 18–8 because of the threefold difference in the densities of these materials. In other words, the m.d.d. must be converted to a penetration factor before life can be estimated. (*b*) Inches per year meets the requirements quite well; it is one of the better methods now in fairly common use but has the definite objection of too many places to the right of the decimal point. Corrosion rates that apply to usable materials for a given set of conditions involve a zero to the left and often as many as three places to the right of the decimal point. This situation involves difficulties in tabulation (pity the typist) and provides cumbersome figures in plotting data. Furthermore, errors in calculation are readily made because of the decimals, particularly where the slide rule is used, as is often the case. These same remarks also apply generally to inches per month. Inches per month has the added disadvantage of requiring a conversion to inches per year before estimation of life can be made. (*c*) Per cent weight loss is obviously of little practical value because the size and shape of the specimen would be a controlling factor. To take an extreme case as an example, it would take considerably longer to dissolve a sphere than a thin sheet of the same weight. Also, the time factor is not included in the expression. (*d*) Most of the other expressions do not include either penetration, specific gravity, area, and/or time.

Mils penetration per year, or simply mils per year (mils/yr.) is proposed as a standard for expressing corrosion rates or the corrosion resistance of metals and alloys. Mils/yr. appears to fulfill all of the requirements for a suitable expression. A mil is a thousandth of an inch, and this unit should be familiar to all persons interested in corrosion. It can be readily interpreted into an answer to the usually all-important question, How long will the equipment last? Only whole numbers would normally be involved, because a corrosion rate of less than one mil/yr. has little practical significance.

The formula for calculating this corrosion rate is as follows:

$$\text{mils/yr.} = \frac{527{,}000\,W}{DAT}$$

where W = weight loss in grams
D = specific gravity of test specimen
A = area of specimen, square inches
T = the time or duration of test, hours

The specific gravities of metals and alloys are readily available from manufacturers' literature, handbooks, textbooks, and other sources. The other values in the formula are directly obtained during the corrosion test.

Mils/yr. has been advocated at every opportunity. Favorable comments were made on this expression by corrosion investigators during a discussion at the annual meeting of the National Association of Corrosion Engineers last May. Mils/yr. has been used exclusively at The Ohio State University in the course on corrosion, with favorable results. Mils/yr. has begun to appear in the corrosion literature. It is hoped that this trend will continue, if for no other reason than to facilitate comparison of corrosion data in the literature and other sources.

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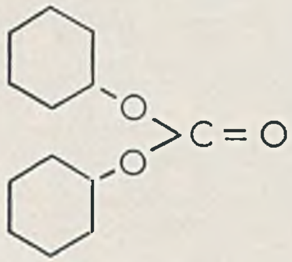
Structural Formula:



Physical Properties:

Appearance: white crystalline solid, white needles from alcohol.

Molecular Weight: 214.
Melting Point: 78° C.
Boiling Point: 302° C.
Specific Gravity:
Liquid 1.122 at 87° C.
Solid 1.272 at 14° C.

Chemical Properties:

1. Can be halogenated and nitrated in characteristic manner.

2. Readily undergoes hydrolysis and ammonolysis when treated respectively with inorganic bases, ammonia and amines.

Solubilities:

Insoluble in water.

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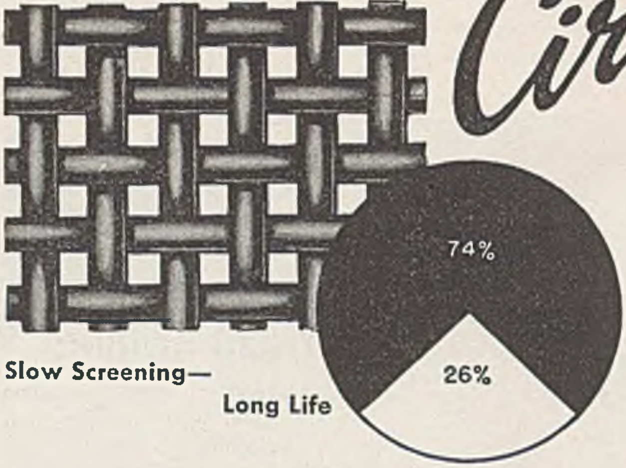
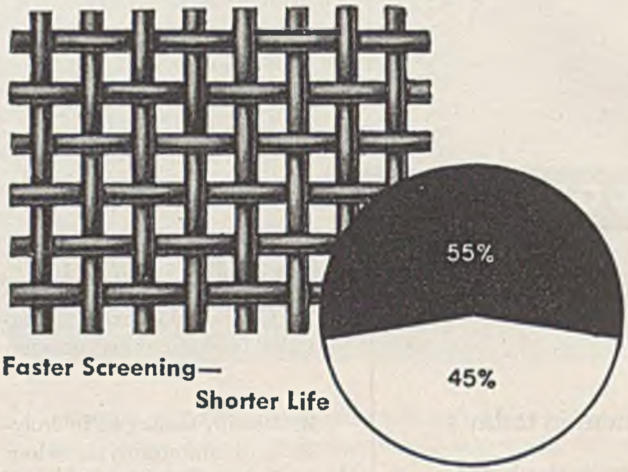
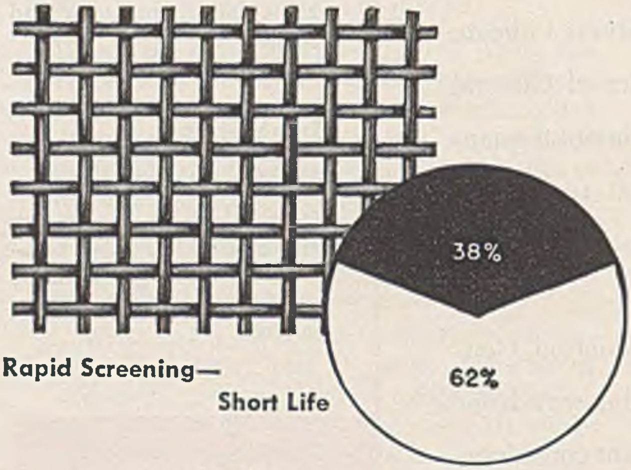


Slow Screening—
Long Life



Faster Screening—
Shorter Life



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If you have a problem involving wire cloth we can probably answer it, for during the past 87 years Wissco and Calwico Wire Cloth have been meeting the needs of over 100 industries.

Our service covers the precision fabrication of wire cloth in a dozen different weaves. And whether you use wire cloth for screening, filtering, grading, cleaning or processing, you'll find Wissco and Calwico Wire Cloth will give long, dependable service. Made in all commonly used metals, these famous brands are designed to withstand chemical action, corrosion, abrasion, moisture or high temperature.

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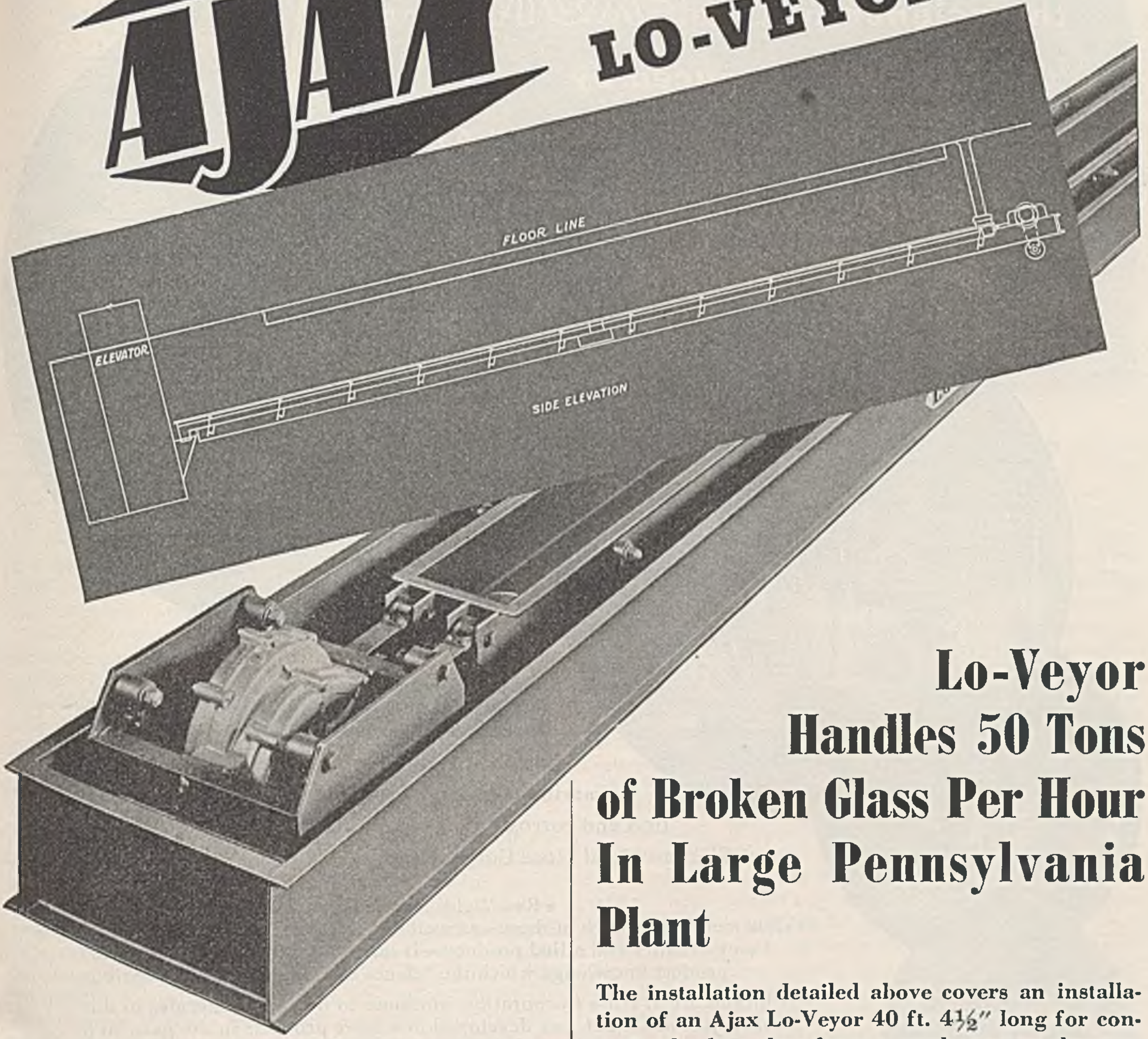
AJAX LO-VEYORS



Lo-Veyor Handles 50 Tons of Broken Glass Per Hour In Large Pennsylvania Plant

The Ajax Lo-Veyor is a vibrating type of conveyor consisting of an open or enclosed pan or tube, a V-shaped trough, a screen or other type carrier driven by a reciprocating drive. Pan or tube can be made airtight to prevent contamination or explosion in process operations.

Drive mechanism is the Ajax-Shaler Shaker, a self-contained, enclosed motor driven drive unit consisting of 2 revolving weights in automatic balance.

Conveyor pan and drive float on rubber mounted springs. Conveyor is simple to install . . . requires little head room (averaging less than 18″) . . . can be set on floor, in a pit, on wall brackets or suspended from ceiling.

10 years engineering and field experience in a wide range of industries will aid you in reducing material handling costs.

The installation detailed above covers an installation of an Ajax Lo-Veyor 40 ft. 4½″ long for conveying broken glass from a crusher to an elevator. Capacity of the Lo-Veyor is 50 tons per hour, and it operates under difficult abrasive conditions encountered in handling cullet.

This installation is an integrated part of processing operations and is saving space, operating and maintenance costs for one of America's foremost glass manufacturers.

It is typical of how Ajax Lo-Veyors are being used with outstanding success by many of America's leading manufacturers.

Write giving an outline of your specific requirements.

Ajax Flexible Coupling Co. Inc.
Conveyor and Screen Division
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as advanced by

CHICAGO METAL HOSE CORPORATION

Photograph by courtesy of Standard Oil Company of California.

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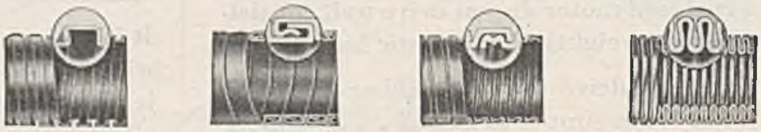
"FLEXON" *identifies C. M. H. products, which have served industry for more than 44 years.*



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Reasons for successes and failures of suggestion systems in chemical plants

by Walter von Pechmann

OPINIONS vary considerably among production executives in the chemical industry in regard to the advantages and disadvantages of suggestion systems. Many believe that suggestion systems stimulate constructive thinking, bring about plant-wide improvements, and foster good employer-employee relations because workers receive official recognition for ideas submitted and, in addition, a cash award. Many chemical plants point proudly to a record of accomplishment in which expenditures for suggestion awards represent only a small percentage of the money saved by accepting those suggestions. The fact that employees submit their ideas to an impartial body of experts is said to eliminate the possibility that some executive might present a suggestion received as his own. Some production executives claim that the suggestion system allows better selection of supervisory personnel, since the suggestions turned in by workers are indicative of mentality, initiative, and ingenuity.

On the other hand, one often hears that a suggestion system has killed initiative and constructive thinking because employees expect a cash payment for suggestions which management thinks should be submitted in the line of duty. It is claimed that suggestions are expected from workers anyway; frequently production executives are not notified of conditions urgently in need of improvement because workers and supervisors prefer to turn in a formal suggestion in order to get a cash award.

Other bad features of a suggestion system are the tendency of employees to air departmental grievances on a plant-wide scale and to put executives "on the spot" by calling plant-wide attention to minor irregularities which occur in production departments. Where a suggestion system is in operation, supervisory personnel often claim that it is extremely difficult to discuss production problems with workers; in discussing future improvements, for example, an employee might submit his foreman's thoughts as his own suggestion, and thereby picture the foreman as an incompetent man who has to be told what to do.

Some chemical plants have found it difficult to define the circumstances under which an employee becomes unqualified to submit a suggestion and to determine what constitutes a suggestion. The casual observer may think that these problems can be solved easily, but the writer, who has served on suggestion committees, often found these decisions difficult. An employee whose suggestion is accepted without award is naturally inclined to believe that management is taking advantage of his idea; on the other hand, a company should not be required to pay for a suggestion which should have been made in the line of duty, nor should it grant awards for "why don't you" complaints which do not contain sufficient practical suggestions for effecting the recommended change. Management must always explain why a suggestion is not accepted, and often it is necessary to furnish proof—a time-absorbing, uncreative, and sometimes costly task. Occasionally management has good reason for rejecting a worthwhile suggestion but cannot publicize it. Then it becomes necessary either to turn down the suggestion without comment or to find a good excuse for not accepting it. One can easily see how a system designed to help employees and to improve morale may accomplish the opposite result at times.

Inquiries

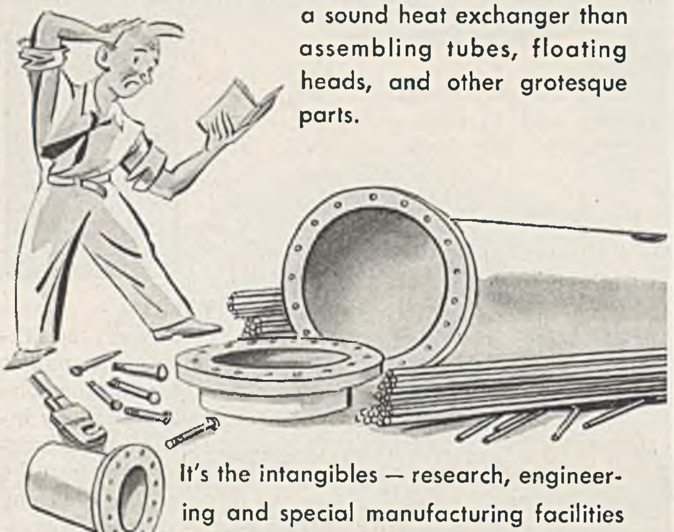
A chemical plant that sends inquiries to other concerns to benefit from their experience before installing a suggestion system is likely to receive apparently contradictory answers. One company may claim success, another failure. In order to untangle this apparent confusion, one should look at the inquiries which were made. In many instances the questions asked are too general. The term "suggestion system", for example, may be interpreted to mean the active participation of all employees in suggesting anything which may be of benefit to management and/or to employees; it may, however, mean management's willingness to compensate workers only for outstanding suggestions leading to technical improvements. The word "successful" may be taken to mean a considerable financial return on the money invested in setting up a system, or it may indicate merely that the interest of employees in their work was stimulated. A company which intends to install a suggestion system must therefore decide what the system is supposed to accomplish. The company should also establish a broad outline of how the system is to be operated. If questions on these points are contained in inquiries, answers received are likely to make more sense. However, the possibility still exists that two companies operating similar systems may claim different degrees of success or failure. This is due to the fact that a system must be executed properly in order to be successful. Depending upon the degree of thoroughness with which a system has been installed, the interest displayed by management in making it a success, and the proper selection of a board making the awards, suggestion systems either work or fail.

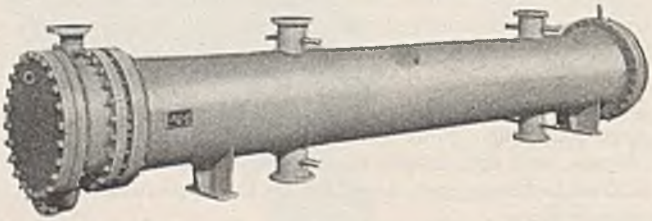
Suggestions eligible for consideration must be recorded, preferably acknowledged, investigated, judged, and answered. These steps require quite an organizatorial setup, the magnitude of which is sometimes underestimated. Some companies have tried to cut red tape by eliminating one or more of the steps mentioned; but confusion, dissatisfaction among employees, and accusations that management has little or no interest in the suggestion system are the usual results of oversimplification.

Requirements

The announcement of a suggestion system should clearly state to employees the type of suggestion management intends to receive. General statements such as, "Any suggestion which will be of benefit to the company or the employee is eligible for consideration", are without value and are likely to cause outright criticism, as well as interference by employees in managerial problems. An announcement should include a classifying list of the type of suggestions desired, and the suggestions received should fall within these classifications in order to be considered.

(Continued on page 90 A)





A list which might be used follows:

1. How to save what is now lost or wasted
2. How to economize on time, machinery, materials, etc.
3. How to make a better product
4. How to improve a tool, jig, or fixture
5. How to eliminate hand or machine operations by changes in tools or patterns
6. How to handle the work better or more quickly
7. Where machinery can be used instead of handwork
8. How arrangement of machinery, tools, or supplies can be improved
9. How to use material now being scrapped
10. How to improve the appearance of products and packages
11. How to introduce new features for increasing the usefulness of products
12. New trade names and slogans
13. How to improve handling of materials or finished products to eliminate unnecessary transportation
14. How to improve ventilation, sanitation, and other matters which will promote health, safety, and comfort of employees
15. How to improve methods of filing and handling information and reports

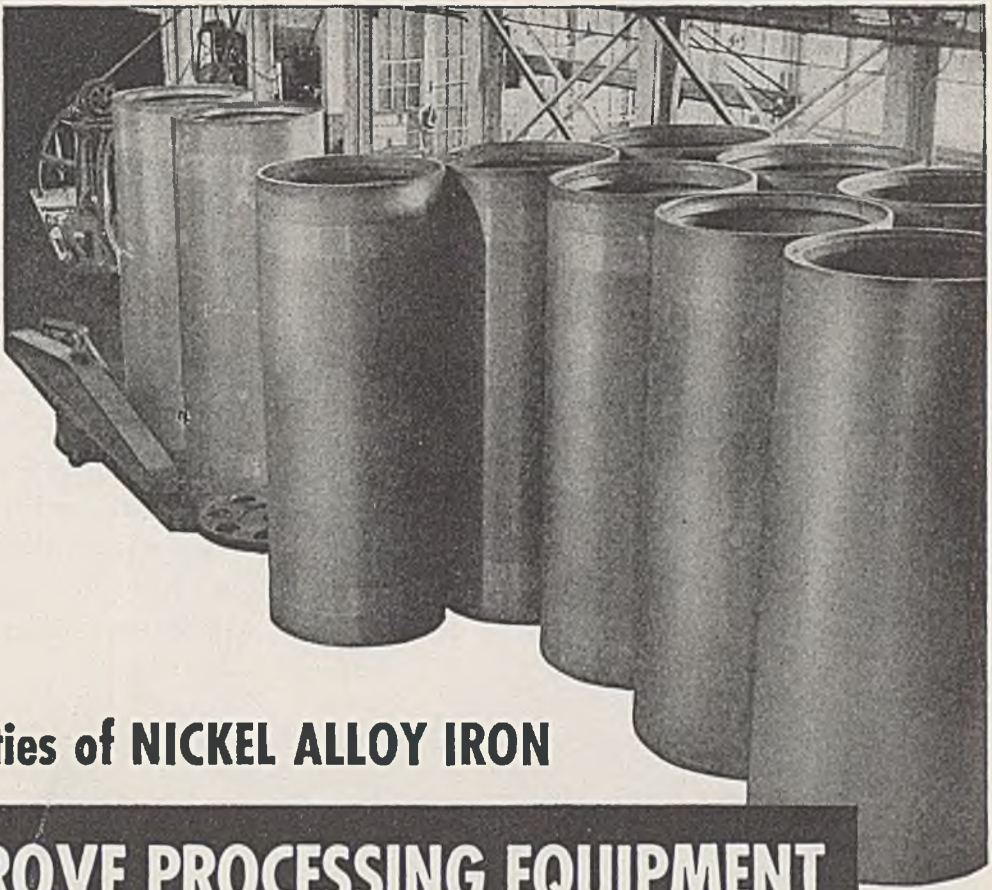
Suggestions received should be investigated promptly and impartially. It is not practical to refer suggestions back to the department in which they originated, since this defeats the purpose—namely, to give employees the opportunity of airing ideas which, in their opinion, are not given sufficient consideration. A committee consisting of representatives of management, workers, and technically trained personnel should pass impartial judgment on new ideas. This committee should be under the jurisdiction of top management and should be provided with facilities for investigating worth-while suggestions without having to depend on the judgment of one department head. A definite limit should be established for time a member of the suggestion committee can serve.

Sometimes one of the most difficult tasks of a suggestion committee is to pass judgment on the originality of an idea. This applies especially if a suggestion is received which contains a unique thought. In this instance not only will claims be received to the effect that the idea was stolen, but the suggestion committee will be swamped with suggestions of a similar nature which consist of nothing but minor variations on the original idea. A suggestion system should be set up so that individual employees and even production executives can be interviewed and awards granted or refused without necessitating detailed explanations of why the action was taken.

Awards

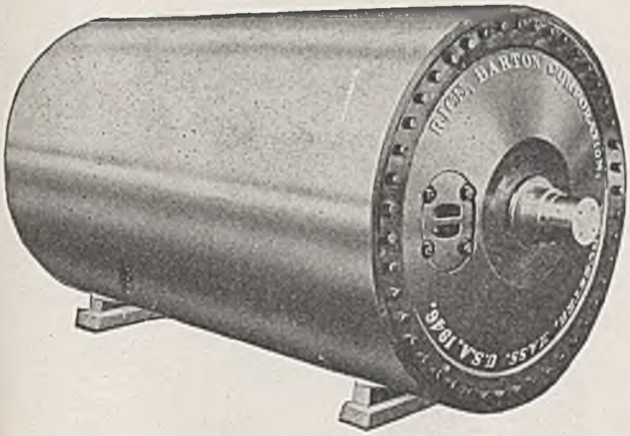
A caution against excessive generosity in granting awards: A suggestion should be original and helpful and should include a practical method for effecting the proposed plan. In order to restrict the number of suggestions to those that will prove worth while, some companies define an amount of money which the suggestion must allow the company to save before an award can be granted. Admittedly, the value of a suggestion cannot always be determined accurately by the amount of money it saves. Occasionally suggestion systems are introduced with the announcement by management that it will pay a certain percentage of the money which will be saved after an accepted suggestion has been put into operation. This procedure is not recommended, although it does seem fair. In many instances it is difficult to determine exactly how much is saved. Even in the event this can be done, suggestors frequently question figures and demand the right to audit production records and even accounting records. There is no reason why management should have to tie itself down to paying a certain percentage of savings. Management would do better to hand out money according to its own judgment and financial ability and to consider a suggestion award an extra bonus given to the employee instead of a fixed payment for services rendered.

These Nickel alloyed iron roll shells produced by Rice Barton Corp., for use in high finish dryers, contain approximately 3.00 percent total carbon, 1.40 percent silicon, 1.50 percent Nickel and .40 percent chromium.



How Special Properties of NICKEL ALLOY IRON

HELP TO IMPROVE PROCESSING EQUIPMENT



Paper mill dryer rolls are one of countless applications that show the advantages derived from using Nickel alloy iron in process equipment.

Dryers of the type shown above, made by Rice Barton Corporation, must hold steam pressures up to 60 pounds. And, since they vary from 24″ to 84″ in diameter, with faces any length from 60″ to well over 200″, these shells require cast iron that assures pressure tightness and strength throughout.

In addition, the iron must be readily machinable, since each roll is machined inside and out for uniform heat transfer and balance. Moreover, in rolls for producing special fine papers, the metal must be finished to mirror-smoothness on the face.

Nickel alloyed iron meets these exacting requirements. Nickel additions give the iron a dense grained, homogeneous structure . . . easy to control in the foundry, easy to machine, and adaptable to countless applications demanding properties superior to those of unalloyed iron.

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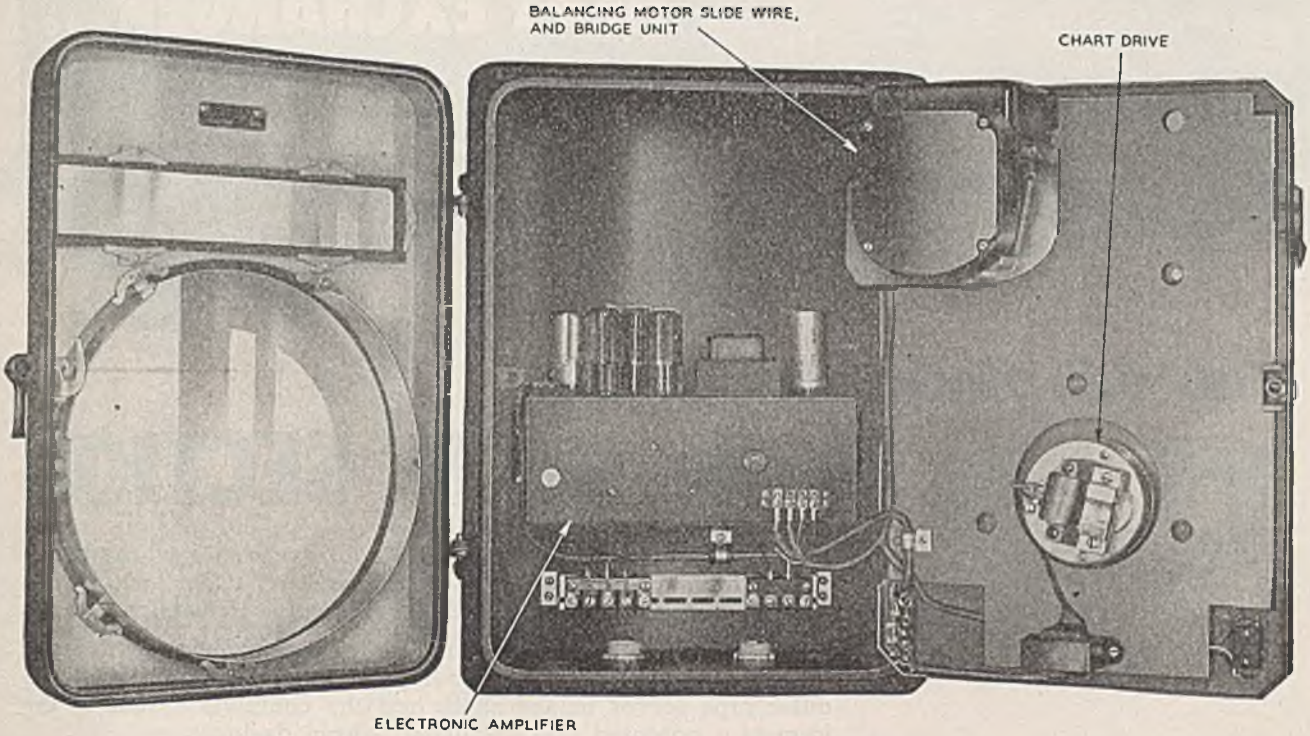

Indicating-Recording Dynamaster, Model Q1531 — Door Open and Panel Swung Out. Note Simplicity of Design and Accessibility.

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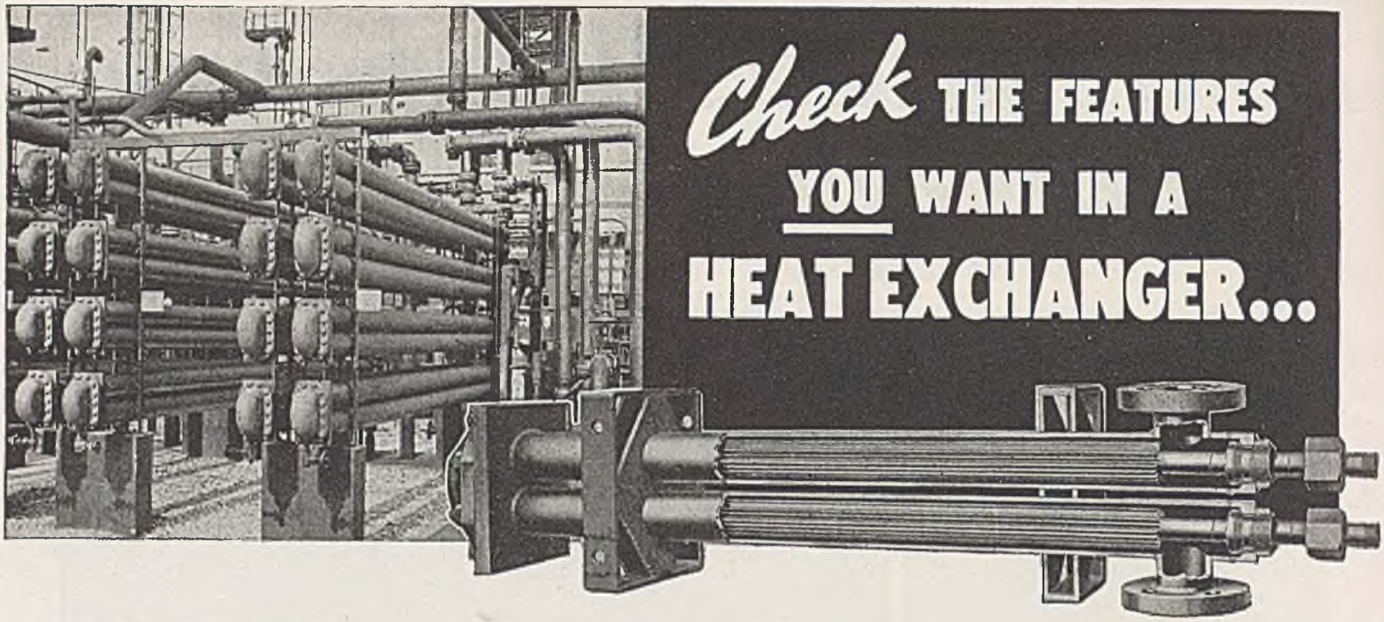
AND RECORDING INSTRUMENTS



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G-R TWIN G-FIN SECTION

Here is a cooler, heater, condenser and heat exchanger whose many advantages have been tested . . . and *proven* . . . in installations totaling more than 40,000 units and by 14 years of performance records.

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- ✓ **STURDINESS** . . . units may be furnished for pressures up to 5000 psi. in the elements and up to 2000 psi. in the shells.
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- ✓ **SERVICE ADAPTABILITY** . . . may be used for a wider variety of services than any other type of heat transfer apparatus . . . and may be readily converted from one service to another.
- ✓ **INTERCHANGEABILITY** . . . units are standard and interchangeable, permitting easy changes in installations to meet changes in capacity, temperature range, or other service conditions.
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- ✓ **LOW MAINTENANCE EXPENSE** . . . assured by rugged construction, absence of stuffing boxes and rolled tube joints, free expansion and contraction, ready accessibility of all parts, and ease of inspection and cleaning.

Write for Bulletin 1614 describing the G-R Twin G-Fin Section in detail.

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GR-129

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AMERICAN production of tartaric acid goes all the way back to Civil War days. Then Chas. Pfizer & Co., Inc., already well established as manufacturing chemists, imported as raw material crude "argols" which are by-products of European wine-making countries. Today Pfizer utilizes domestic argols to supplement requirements.

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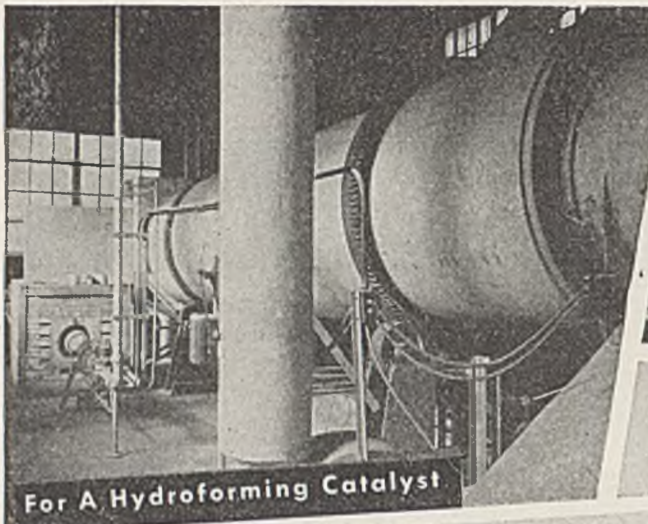
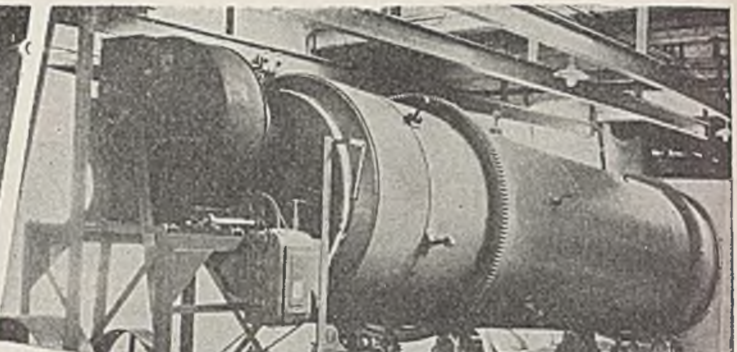
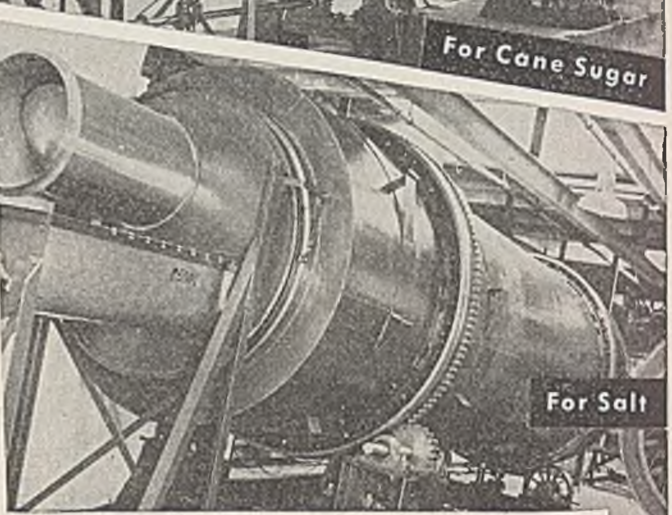


For A Hydroforming Catalyst

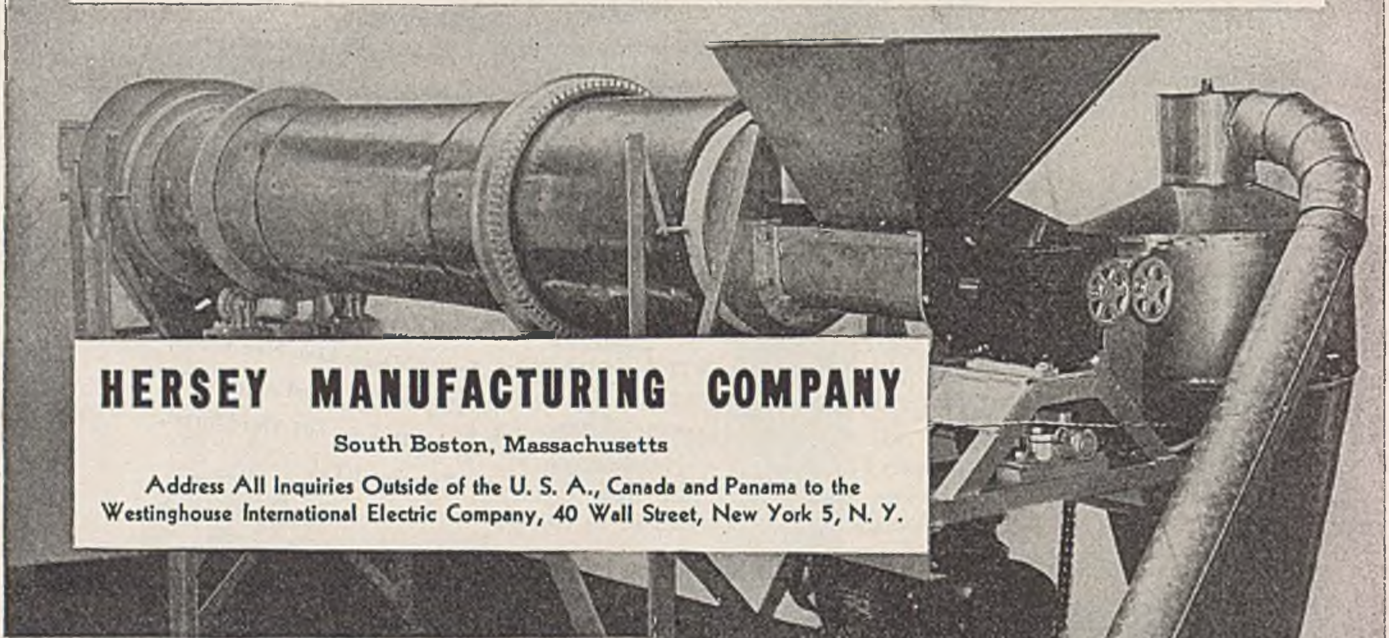


For Cane Sugar

For Citrus Pulp



For Salt



For Citric Acid

For Sodium Bromide

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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.

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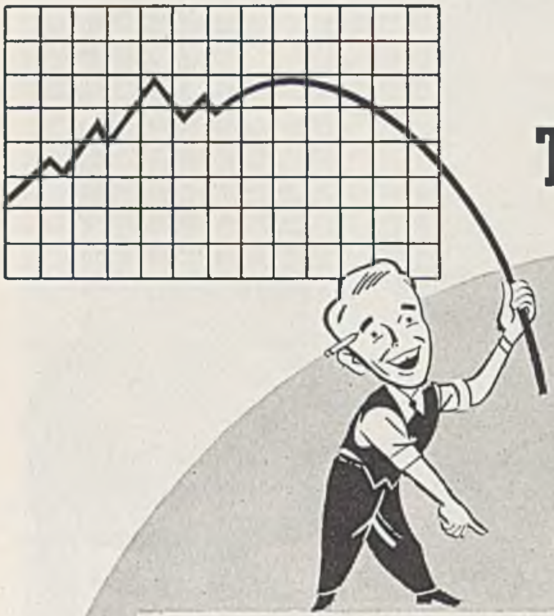

TO TURN A COST CURVE

DOWN

Lower cost per gallon of liquid handled is shown in one case history after another on the LaBour Type Q centrifugal pump. The reason is twofold.

Because the Type Q has an open impeller operating with generous clearances, this pump is slow to wear, and its high initial efficiency is hardly impaired at all over long periods of severe use.

Because of the famed simplicity of LaBour construction, mechanical difficulties are almost completely eliminated—"down time" and maintenance costs are at a minimum with the LaBour Type Q.

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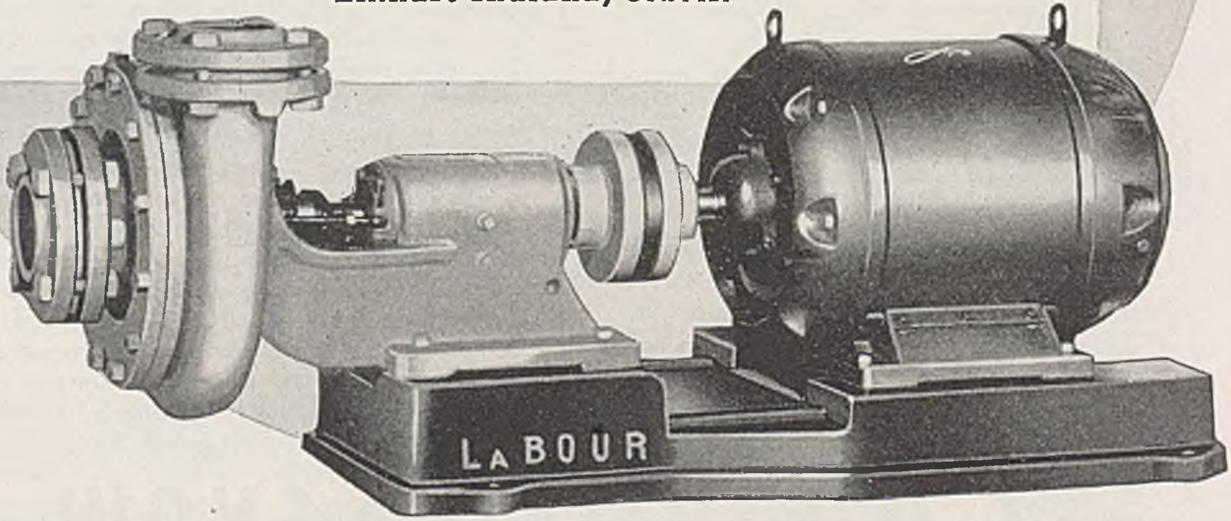
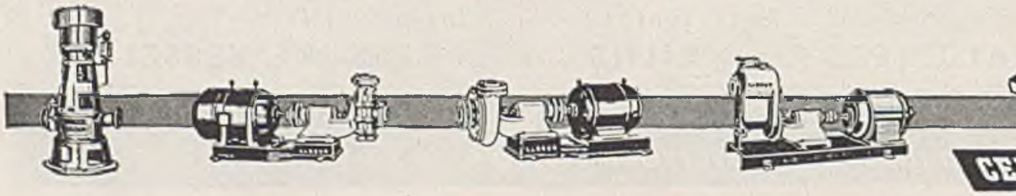
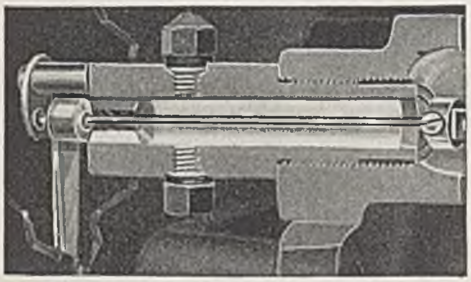
THE LaBOUR COMPANY, Inc.
Elkhart Indiana, U.S.A.



IF YOU NEED A **LaBOUR** NOTHING ELSE WILL DO



LaBour
CENTRIFUGAL PUMPS



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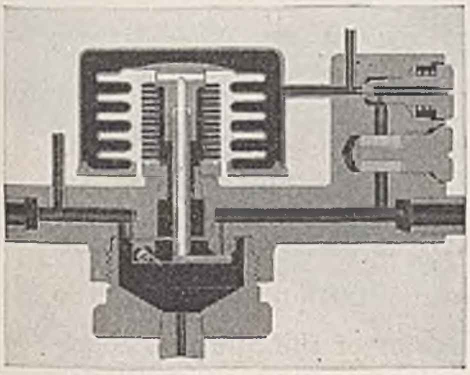
The connection between float and lever assembly. Chrome-Vanadium steel shaft is lapped to clearance of .00005" at bearing surfaces. No stuffing box or packing required. Bearing is filled with suitable grease for the particular service and pressure.



CONTRIBUTING TO POSITIVE CONTROL

NON-BLEED BOOSTER PILOT

Precision manufactured to minimum tolerances throughout. Non-bleed construction permits use of large intake and exhaust ports for rapid control valve operation. Uses air only when increasing valve pressure, thus reducing air consumption to a minimum.

LOOK first at the meter body—the measuring element—of a flow controller. Does it have simplicity of design, rugged construction and permanence of calibration? Does the pen respond instantly to the slightest change in differential? In short, will it give continuous precision measurement of flow?

Look next at the control unit. Has it been designed and constructed so that it can easily be "tuned-in" to specific requirements, without guesswork, and will then "line out" control exactly at the set point without cycling, drifting or shifting?

No controller can be better than its measuring system. That is why years of research and engineering have been devoted to the development of an instrument that delivers precision measurement of flow—at all times. This continuous accuracy of flow measurement in combination with the automatic control afforded by the *Air-o-Line* unit makes the Brown Flow Controller outstanding for any process requiring continuous, positive flow control.

Look twice . . . for the features of Brown Flow Controllers contributing to precision measurement and control . . . and remember . . . you can't have positive control without precision measurement. Write for the Brown Flow Control Catalog 2221.

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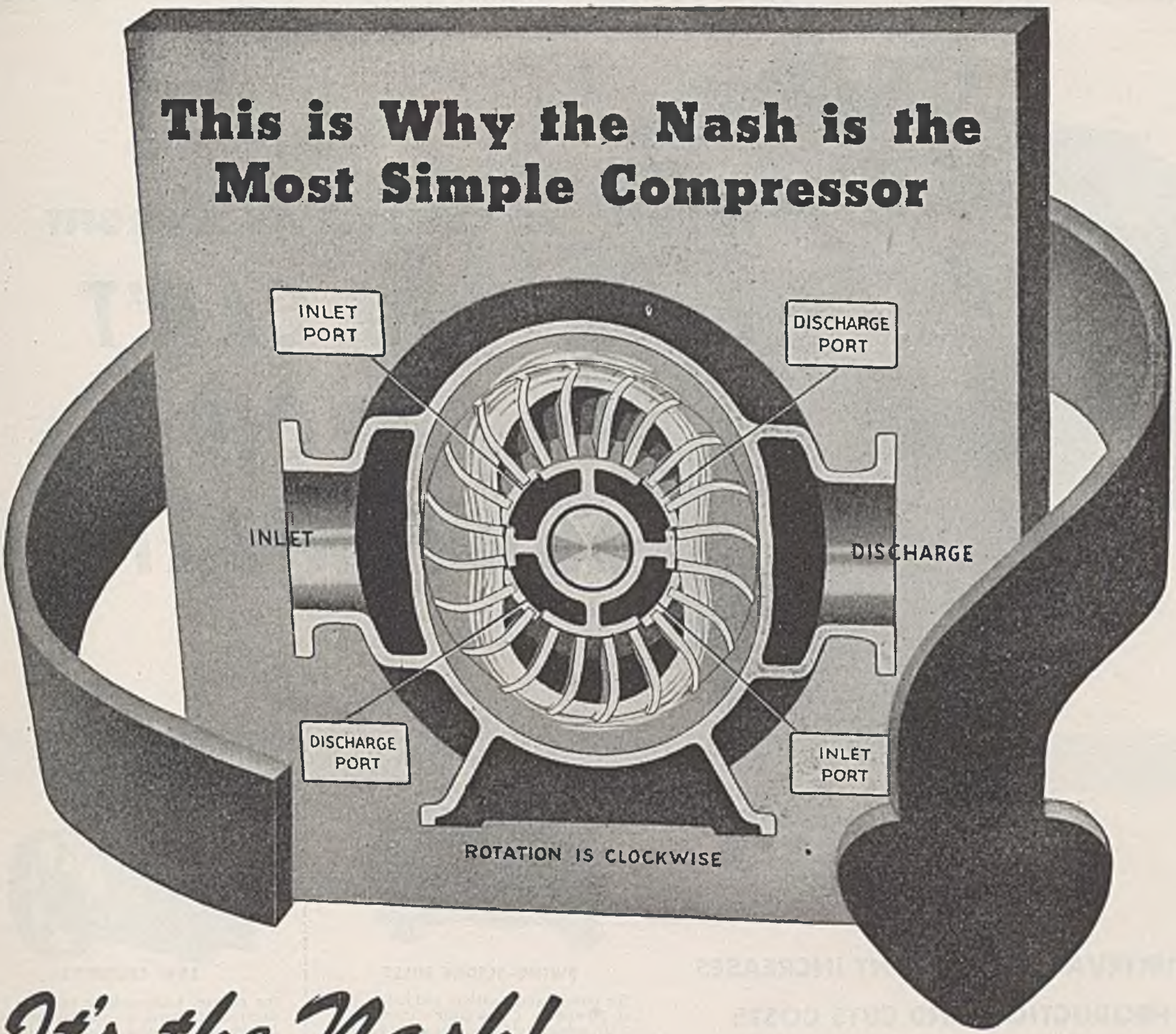
Volume V — Systematizes and correlates the physical properties with the structures of the Hydrocarbons of Homologous series, thus disclosing possible errors in experimental values. Interrelationships between other properties of Hydrocarbons yet unknown.

This is Why the Nash is the Most Simple Compressor



It's the Nash!

There are no mechanical complications in a Nash Compressor. A single moving element, a round rotor, with shrouded blades, forming a series of buckets, revolves freely in an elliptical casing containing any low viscosity liquid. This liquid, carried with the rotor, follows the elliptical contour of the casing.

The moving liquid therefore recedes from the rotor buckets at the wide part of the ellipse, permitting the buckets to fill with gas from the stationary Inlet Ports. As the casing narrows, the liquid is forced back into the rotor buckets, compressing the gas, and delivering it through the fixed Outlet Ports.

Nash Compressors produce 75 lbs. pressure in a single stage, with capacities to 6 million cu. ft. per day in a single structure. Since compression is secured by an entirely different principle, gas pumping problems difficult with ordinary pumps are often handled easily in a Nash.

Nash simplicity means low maintenance cost, with original pump performance constant over long periods. Data on these pumps sent immediately on request.

No internal wearing parts.

No valves, pistons, or vanes.

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Low maintenance cost.

Saves floor space.

Desired delivery temperature automatically maintained.

Slugs of liquid entering pump will do no harm.

75 pounds in a single stage.

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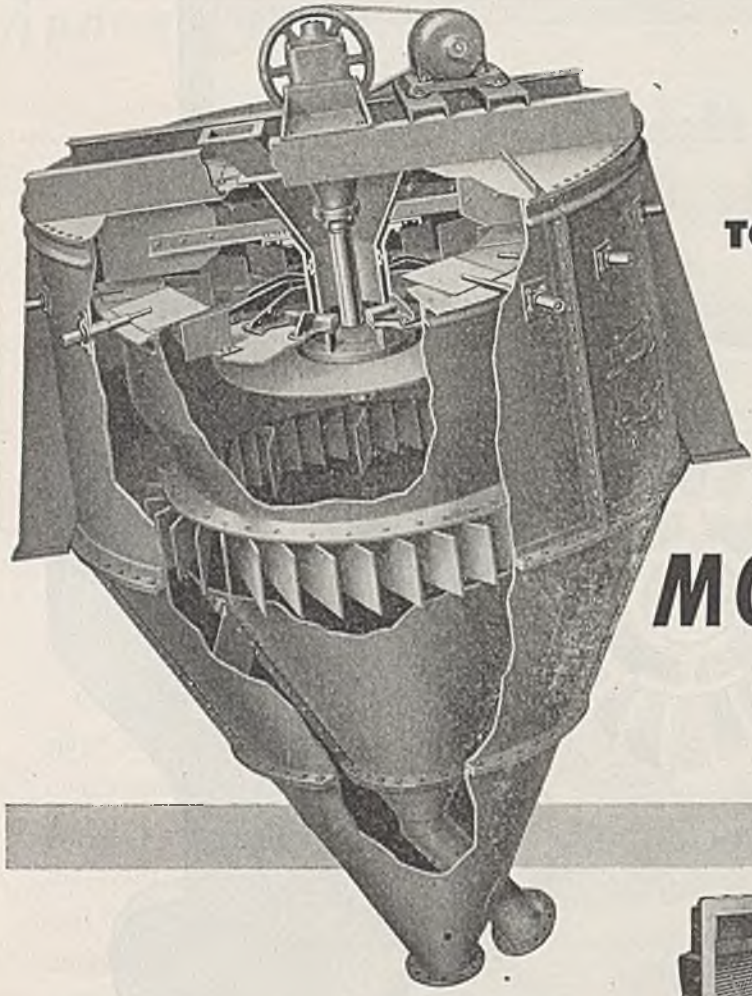

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for coarse and medium reduction (1" to 20 mesh). Open door accessibility. Soft, moderately hard, tough or fibrous substances. Built in several types and many sizes.

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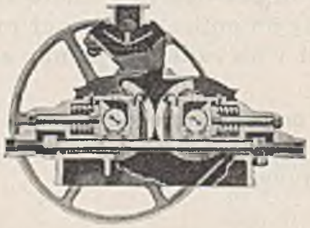

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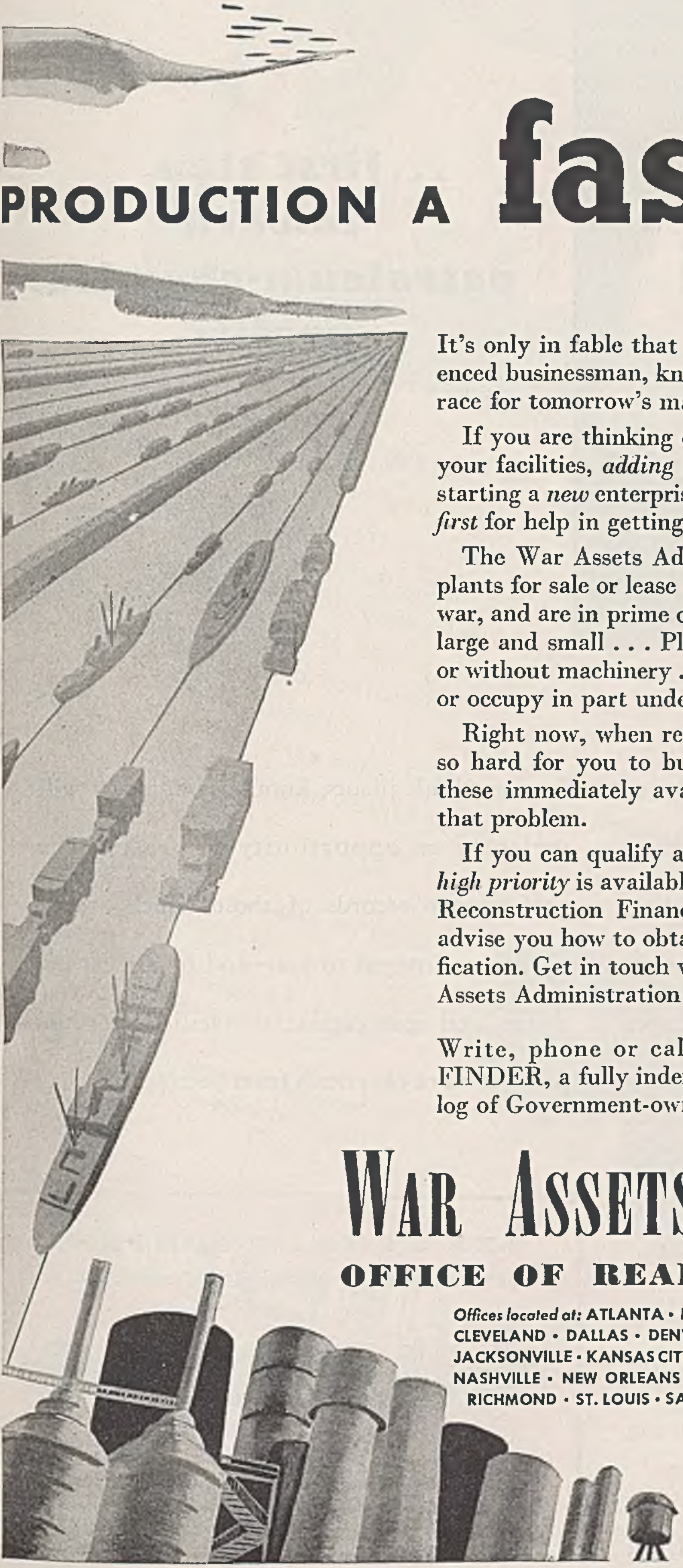

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If you are thinking of *expanding* your production, *modernizing* your facilities, *adding* a new process, *relocating* your business or starting a *new* enterprise—look to the War Assets Administration *first* for help in getting that vital headstart.

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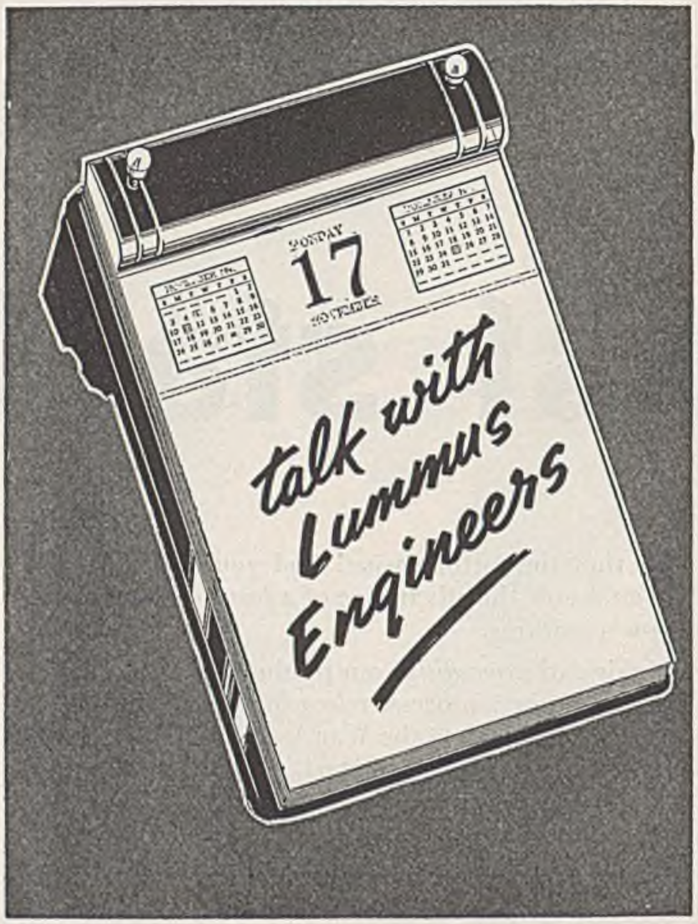

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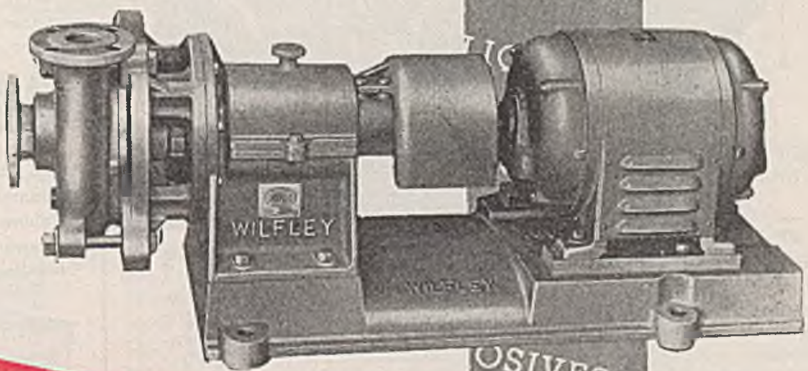
- *Uninterrupted 24-hour-a-day production.*
- *Individual engineering on every application.*



WILFLEY
centrifugal **PUMPS**

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PEERLESS
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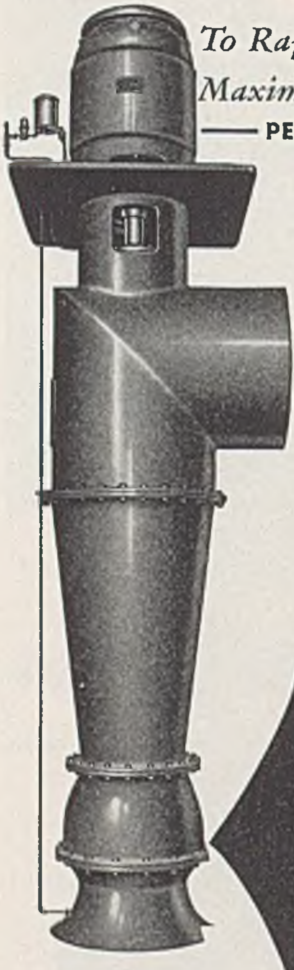
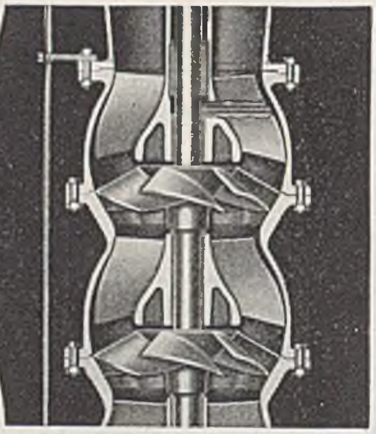


To Rapidly Move and Re-move Maximum Amounts of Water.

— **PEERLESS MIXED-FLOW PUMPS**

Most modern principles of aero and hydro-dynamic design are embodied in Peerless Mixed-Flow pump design and construction, attaining new high efficiencies in large volume water lift and lowering overall maintenance and pumping costs.

Numerous successful applications of Peerless Mixed-Flow Pumps include: drainage; sewer and flood control service; de-watering; irrigation water diversion; flooding of agricultural lands; industrial and process work including condensers, circulation of liquors, etc.



PEERLESS
MIXED-FLOW PUMPS
CAPACITIES:
UP TO 220,000 G.P.M.

Cutaway view of Mixed-Flow multi-stage pump impeller and bowl construction revealing high efficiency impellers utilized for more economical water lift.

PROPELLER TYPE PUMPS

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PEERLESS PUMPS

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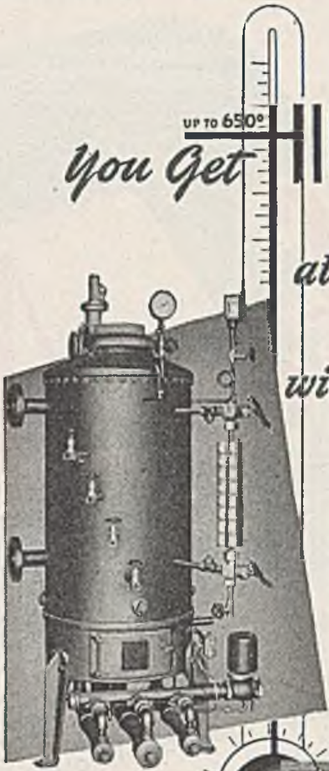

You Get HIGH *temperatures* *at* LOW *pressures*

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with DOWTHERM VAPORIZERS

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In the McKee-Eclipse Dowtherm Vaporizer, you get a *complete package*, consisting of boiler with combustion chamber, burner, combustion safety equipment, electric-pressure controller, low-level fuel cut-off, etc. Write for bulletin giving full details. ECLIPSE FUEL ENGINEERING CO. 779 South Main, Rockford, Ill.

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McKee Eclipse

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McKee Gas Burners for high-pressure steam boilers—gas or oil

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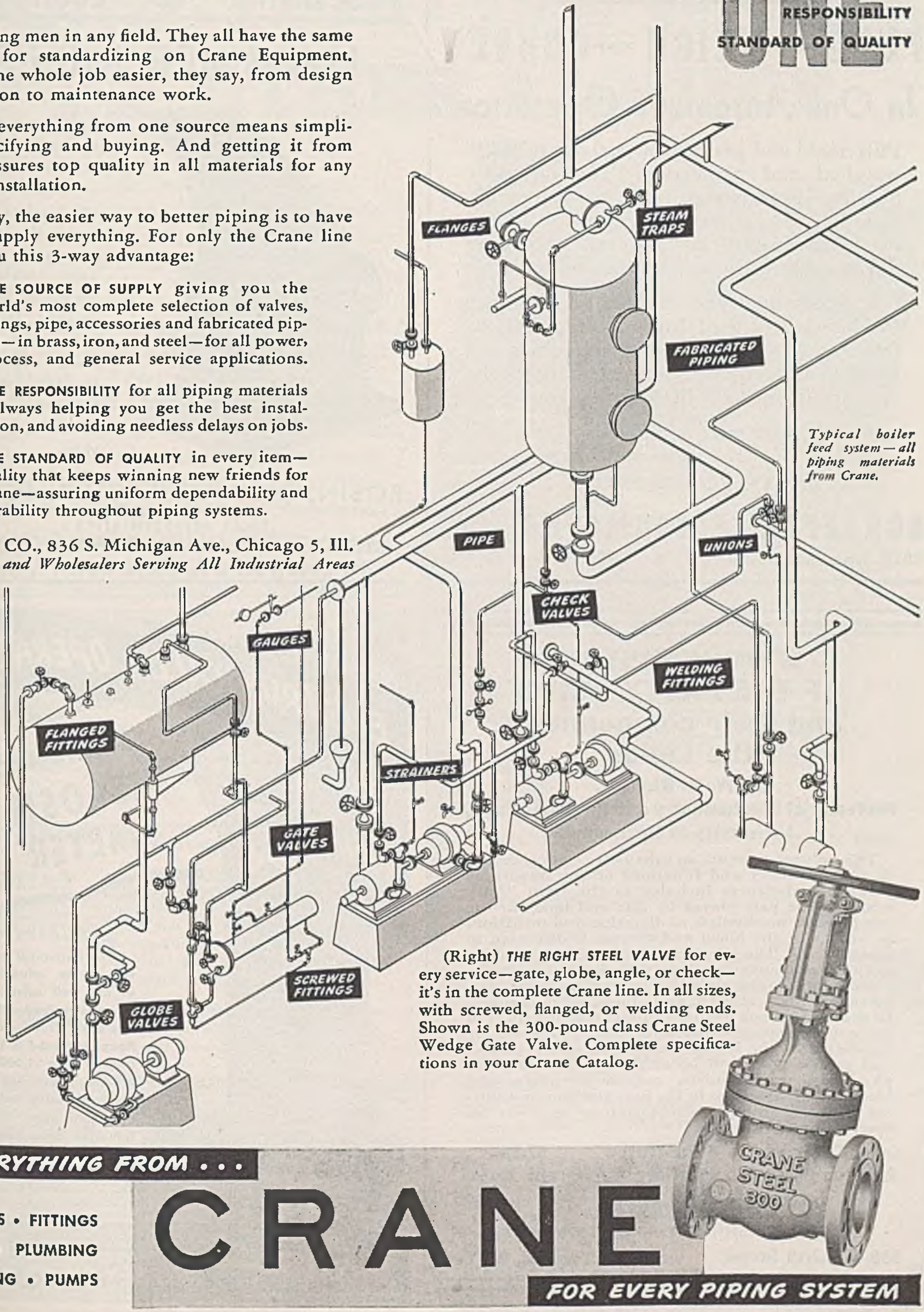

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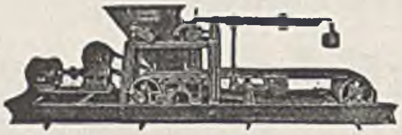

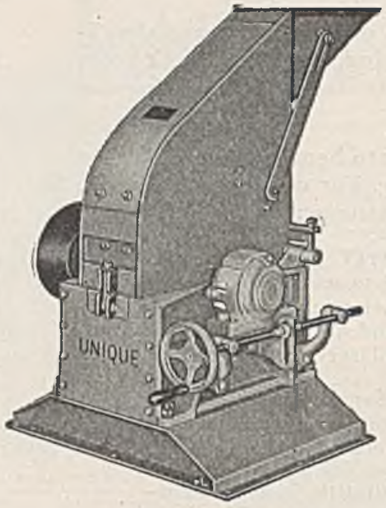
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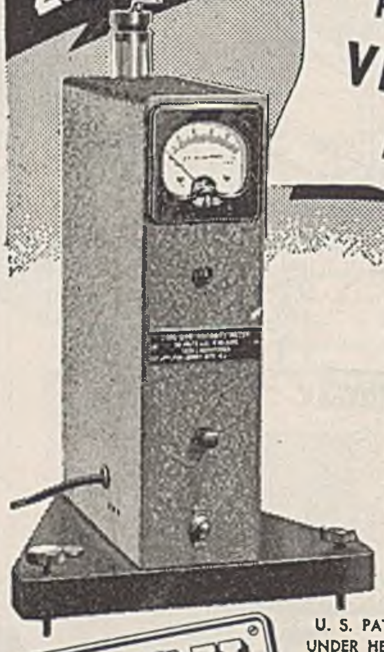

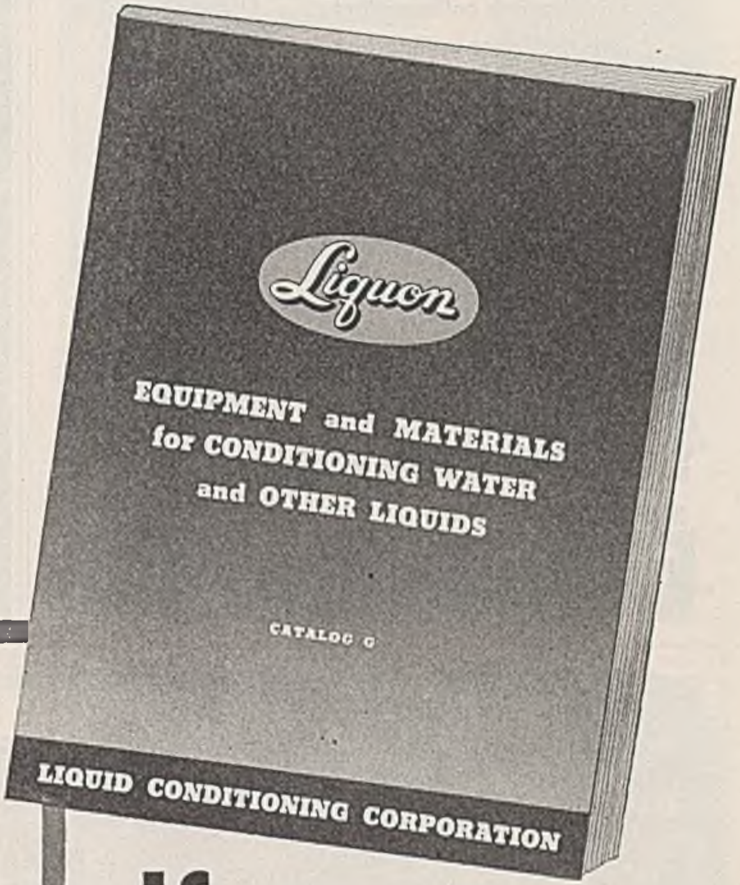
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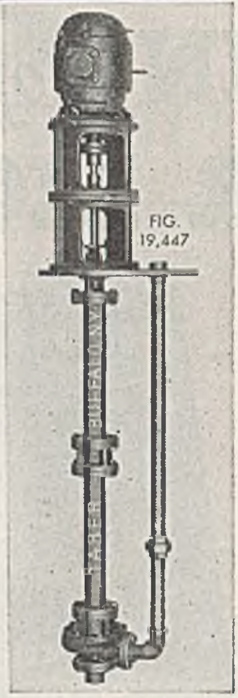

FIG. 19,447

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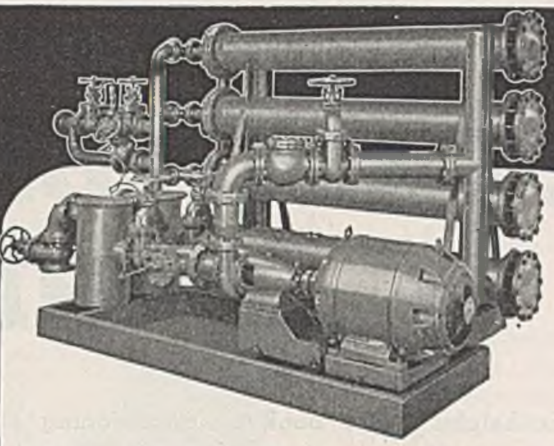

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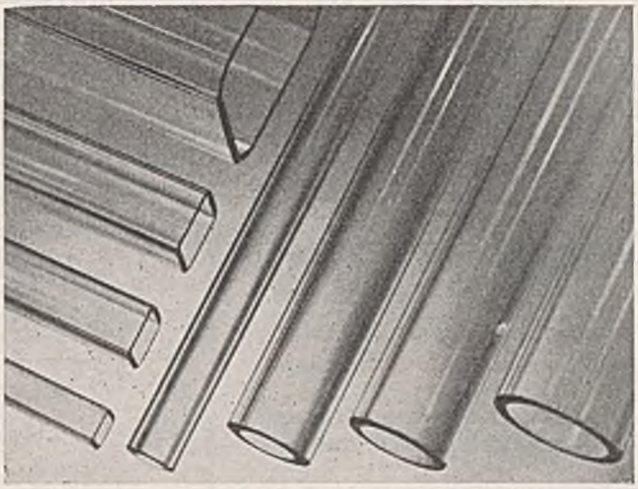

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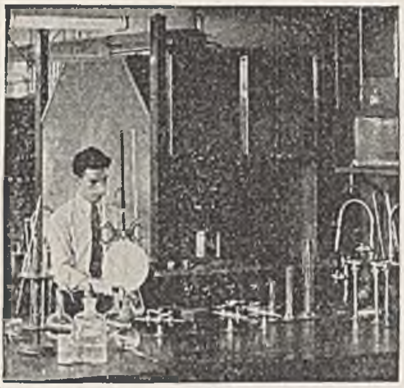

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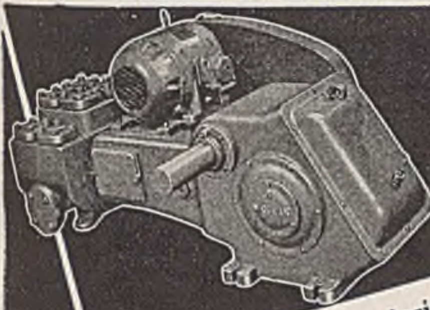

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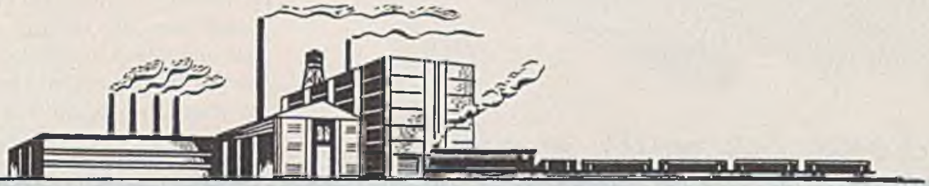



RESEARCH
FABRICATION
OPERATION

Sidelights and TRENDS

■ The British Cast Iron Research Association has announced a new kind of cast iron of great corrosion resistance with twice the tensile strength and three times the shock resistance of ordinary cast iron. (*Chemical Trade Journal and Chemical Engineer*, p. 728, Dec. 20, 1946)

■ A type of resin made from petroleum and natural gas can be formed into thin sheets and wrapped around highly perishable food products to prevent spoilage during prolonged storage. (News release, Standard Oil Co. of N. J., Jan. 1947)

■ The value of Canada's imports of chemicals and allied products during the first 8 months of 1946 increased 18% over the same period in 1945. The imports are valued at 61.5 and 52 million dollars for the two years, respectively. (*Chemical Age*, p. 784, Dec. 21, 1946)

■ Electronic stop watches used during the war for measuring projectile velocities are now being produced in quantity for civilian use. The counter accurately clocks one millionth of a second and allows direct reading of results by small neon-light figures on the front panel of the instrument. (*Review of Scientific Instruments*, p. 518, Nov. 1946)

■ A hydraulic pump of the positive displacement type, 6 inches in diameter, 11 inches long, and weighing only 35 pounds, develops 5000 pounds per square inch pressure in continuous duty service. A single bank of plungers delivers 3 gallons per minute at 1800 r.p.m. and 2 gallons per minute at 1200 r.p.m. (News release, Superhydraulic Corp., Jan. 1947)

■ The tristate district of Oklahoma, Missouri, and Kansas produced nearly 25 million tons of lead and zinc concentrates worth more than 1000 million dollars during the past century. The largest annual output of these two metals, mined in 1926, accounted for 54.7 and 14.9% of the national total, respectively. (U. S. Bureau of Mines *Information Circular* 7383, Jan. 1947)

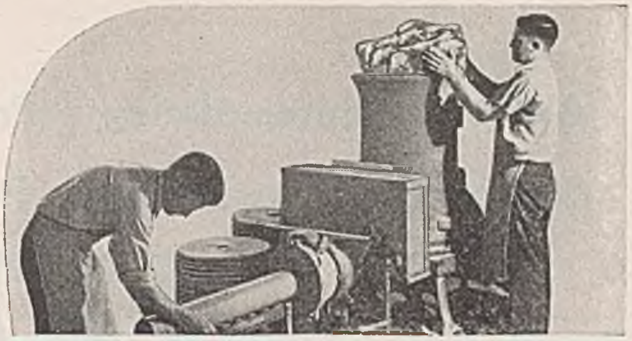
■ The 4.75 million barrels of crude oil produced daily in this country travel through 125,000 miles of petroleum pipe lines to refineries and marketing areas. The lines are operated as common carriers irrespective of ownership or destination of the crude. (*The Lamp*, Jan. 1947)

■ The world's tin production, expected to reach 200,000 tons in 1949, should meet requirements by that year. The 1947 production schedule aims at 140,000 tons, about 20% below the estimated demand. (*Chemical Age*, p. 3, Jan. 4, 1947)

■ A flame hardener with six radially placed jets has been developed for hardening the surface of gears, wheels, and other metal shapes without hardening the interior. Vertical travel of the flame, directed on work which can be spun or held stationary, is hydraulically controlled and adjustable up to speeds of 20 inches per minute, and hardening is controllable to a depth of 0.5 inch. (*Business Week*, p. 52, Jan. 18, 1947)

■ A giant mechanical brain for solving complex mathematical problems is being built in England as an improvement over similar machines at Harvard and the University of Pennsylvania. The advantageous features include a greater "memory" capacity, ability to receive more complex instructions, and higher speed of achieving solutions. (*N. Y. Herald Tribune*, Jan. 2, 1947)

New Catalog



CHEMICAL AND MECHANICAL CHARACTERISTICS

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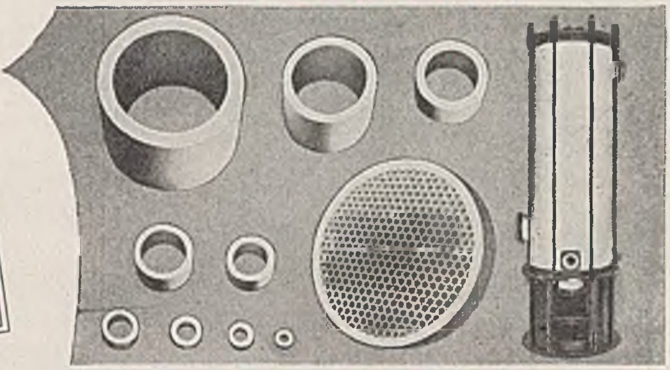
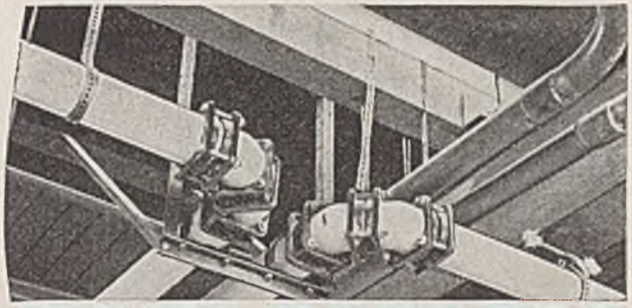


PORCELAIN TOWERS AND TOWER PACKING



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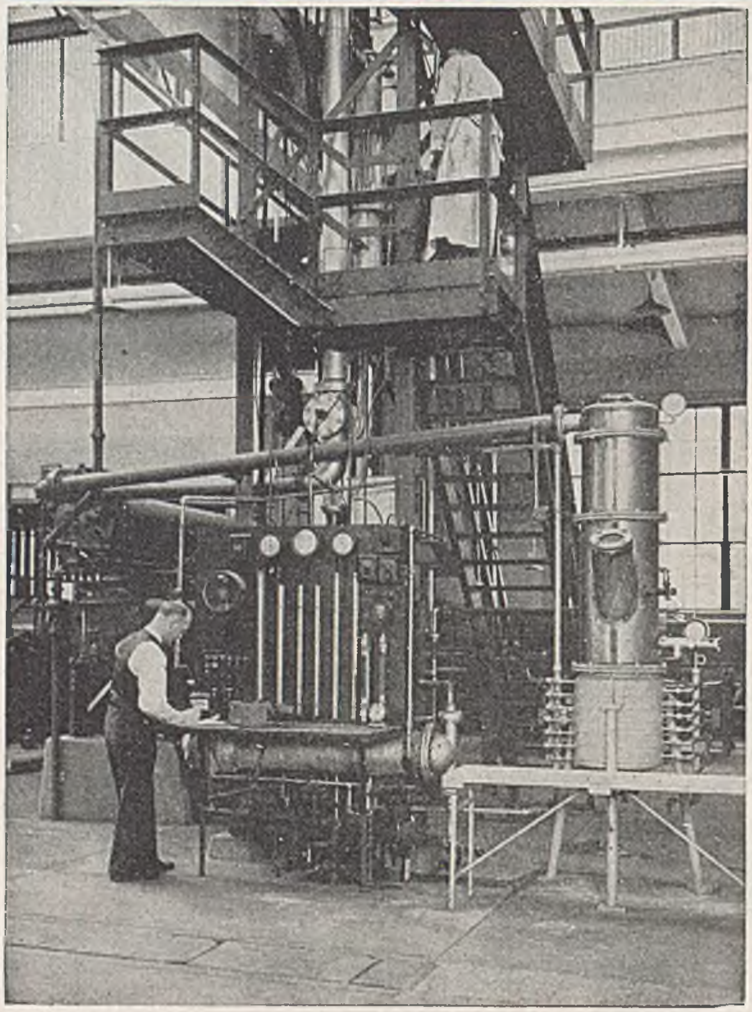

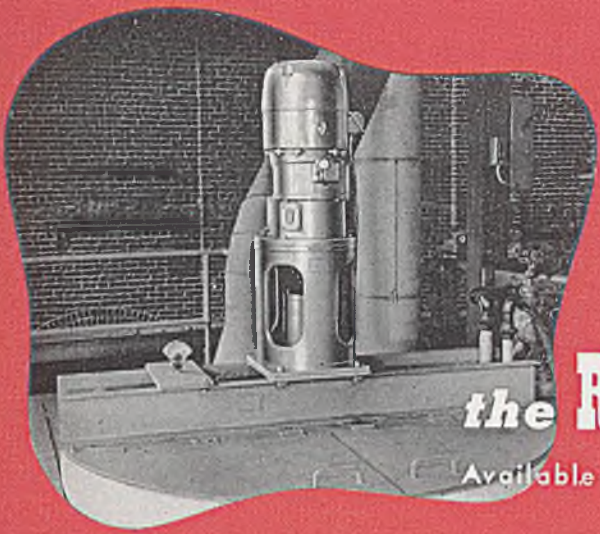

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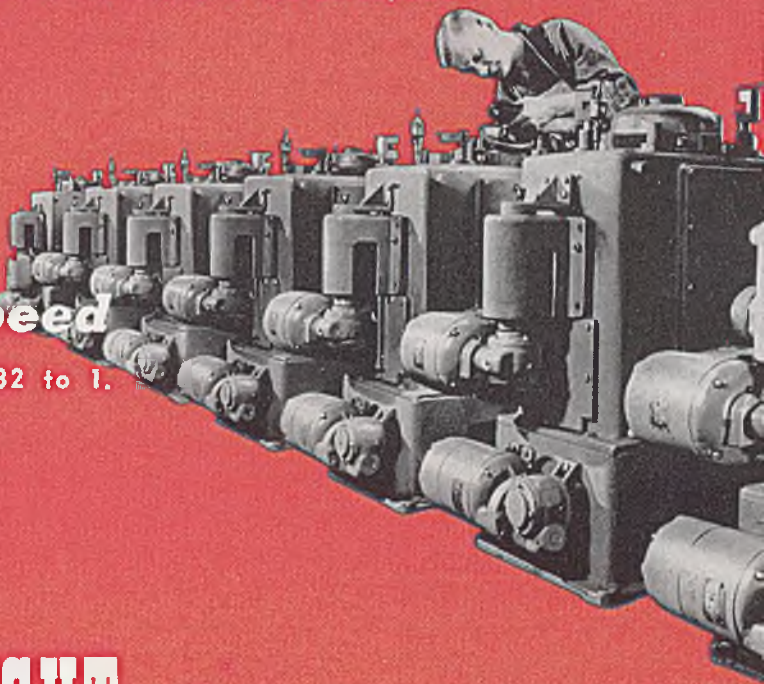

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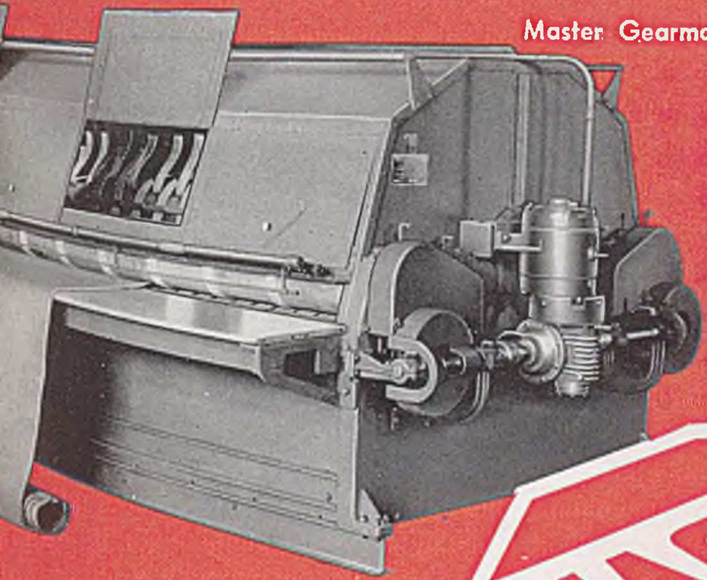

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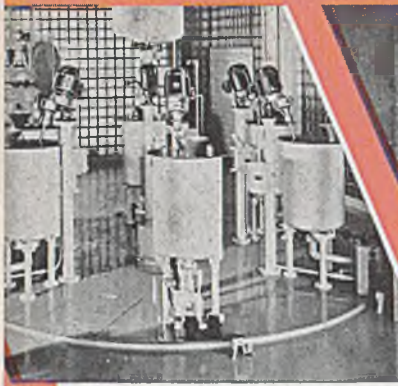
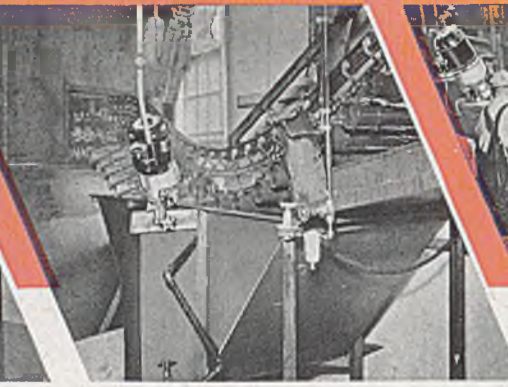
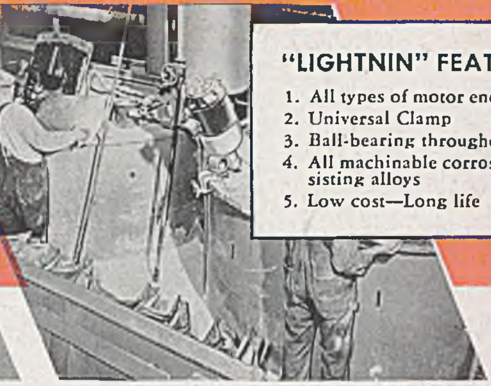


1. Unusual application of Lightnin Mixers to cyclic, automatic batch operation.



2. Paint dip tank irregular shapes easily handled by Lightnin Mixers.



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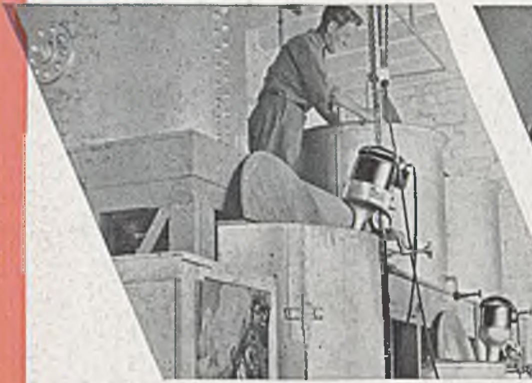
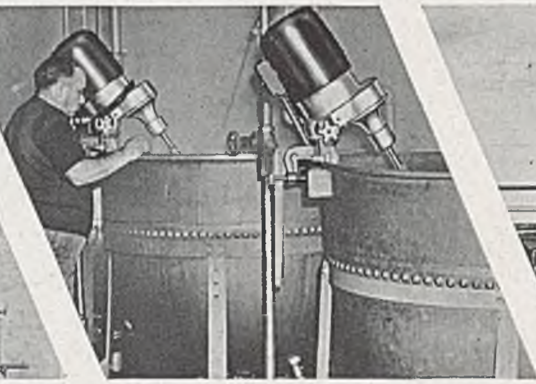
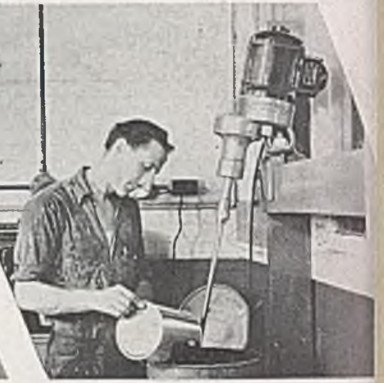


4. Note Lightnin Mixers ability to fit into odd corners and different shaped tanks.



5. For food processing Lightnin Mixers improve heat transfer and uniformity.



6. Lightnin Mixer supported separately for small containers.

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Where to use Portable Mixers

Whether your requirements call for mixers to operate on a wide range of tank capacities and liquid viscosities or for permanent mounting on single tanks, you can adapt "Lightnin" Portable Mixers to solve your problem efficienctly.

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1. The size of the batch does *not* affect the load. You can use a small mixer on a 50 gal. or a 5,000 gal. batch without danger to the motor but mixing action will be reduced to an unusable degree.

2. Watch the effect of viscosity. A mixer specified for water-like material probably operates at 80% full load. Use this on a material like molasses, and you overload and burn out your motor. Specific gravity also affects load on propellers.

3. Don't increase the propeller size. Propeller sizes are selected for specific viscosities. Increasing the propeller size can also overload and burn out motors.

4. Ask Mixing Equipment Co., whether your present mixer is adaptable to a new use or whether a different size mixer will save time and trouble.

The Basis of Our Recommendations

Twenty-five years of experience have resulted in an organization, research facilities and skill which qualify Mixing Equipment Company as a leading authority in the whole broad field of agitation. Mixing Equipment Company offers its services in the solution of any problem involving controlled recirculation of liquids to produce physical and chemical changes. See table.

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

LAB MIXERS — Little brothers to "Lightnin" Portables. 4 models — Electric and Air Driven. Described in Bulletin B77.

TOP ENTERING MIXERS: —A wide range of sizes for large or small tanks —¼ to 50 H.P. for vertical use on pressure or vacuum vessels. Integral mounting, all Impeller types, Radial Turbines and propellers. Illustration above—for open tanks.

SIDE ENTERING MIXERS—1 to
H.P. for horizontal use. Any
tank. Propeller type only. Ma
models and drives. In use on ta
up to 5,000,000 gallons capa

Mixing Equipment Company Offers

Complete coverage of industrial areas with service for individual user and engineers or equipment manufacturer.

Assumption of responsibility for selection of mixer size, types, performance, characteristics within limits of existing technology.

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

MIXING EQUIPMENT CO., INC.
106? Garson Avenue
ROCHESTER 9, NEW YORK

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 fo
Pressure Vessels and Open Tanks
☐ B-75—Portable Mixers (Electric and Air Driven
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet

Name............
Title............
Company............