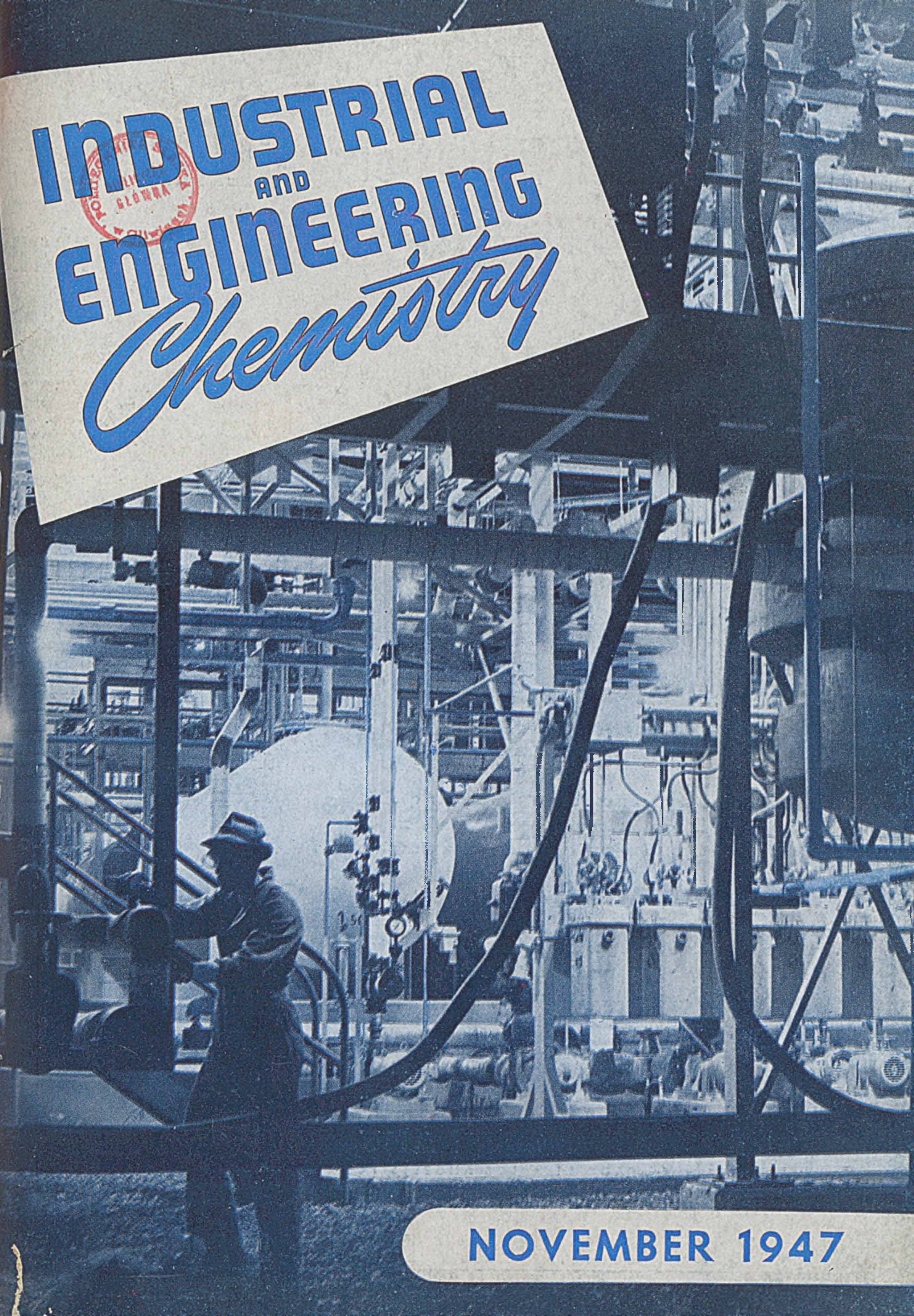
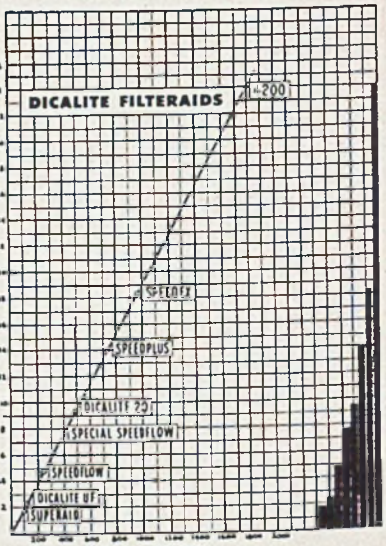
INDUSTRIAL AND ENGINEERING Chemistry



NOVEMBER 1947


but so is Flowrate


DICALITE FILTERAIDS
4200
SPEEDEX
SPEEDPLUS
DICALITE 215
SPECIAL SPEEDFLOW
SPEEDFLOW
DICALITE UF
SUPERAID
RELATIVE FILTRATION RATE - GAL/FT²/HR.
% RELATIVE FLOWRATE

INDUSTRIAL and ENGINEERING Chemistry

NOVEMBER
1947

VOLUME 39 NUMBER 11
ISSUED NOVEMBER 14, 1947
40,600 COPIES OF THIS ISSUE PRINTED

Industrial Edition, I&EC
Consecutive Number 21

Shown on the cover is a section of tank farm for storing silicone raw materials and intermediates at General Electric's new silicone plant at Waterford, N. Y. Photo courtesy General Electric Company

Published by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. Executive Offices and Editorial Headquarters, 1155 Sixteenth St., N. W., Washington 6, D. C. Advertising Office: 332 West 42nd St., New York 18, N. Y. Branch Editorial Offices: Chicago 4, Ill., Room 819, 25 East Jackson Blvd.; Houston 2, Tex., 413 West Bldg.; New York 17, 60 East 42nd St.; San Francisco 2, Calif., Room 454, 760 Market St. Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year: Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of Oct. 3, 1917, authorized July 13, 1918.

Annual subscriptions: Industrial Edition and Analytical Edition sold only as a unit, members $3.00, nonmembers $4.00. Postage to countries not in the Pan-American Union $3.00; Canadian postage $1.00. Single copies: current issues, Industrial Edition $0.75, Analytical Edition $0.50; back numbers, Industrial Edition $0.80, Analytical Edition prices on request; special rates to members. Claims for missing numbers will not be allowed if received more than 60 days from date of issue. No claims allowed from subscribers in central Europe, Asia, or the Pacific Islands other than Hawaii, or because of failure to notify the Circulation Department of a change of address, or because copy is "missing from files."

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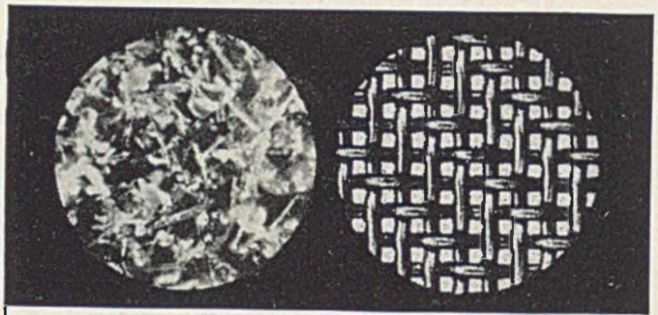
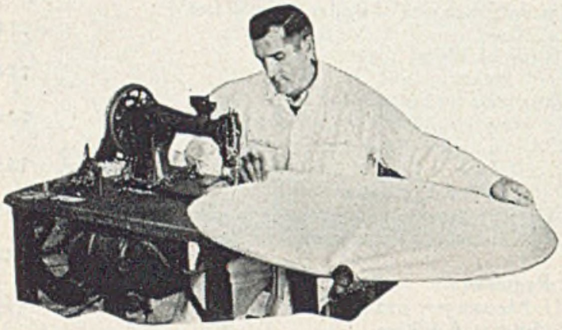
Celite*

means longer life for filter cloths because THE CAKE not the cloth DOES THE WORK



These two photomicrographs show that a Celite filter cake has smaller openings than the finest filter cloth. It's the filter cake—not the cloth—that removes the suspended impurities.



Saves Tailoring

Prevents Ripping

Reduces Washing

FILTER CLOTHS and their care often amount to considerable expense—especially when they must be washed in harsh bactericides and fungicides. The use of Celite* can substantially reduce this expense.

Celite is a chemically inert diatomaceous earth, used both for pre-coating and in the liquid to be filtered. The cake of Celite which builds up on the cloth forms a screen many times finer than the finest filter cloth mesh. This cake becomes a protective coating that traps gummy substances and harsh particles—prevents the impurities from clogging or damaging the cloth.

CELITE PRODUCES THE CLEAREST FILTRATES AT THE FASTEST FLOW RATES

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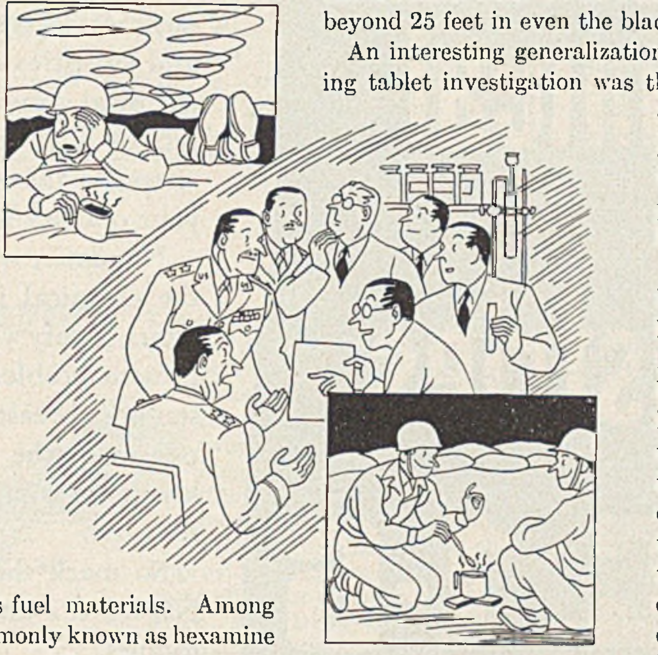
INDUSTRIAL and ENGINEERING CHEMISTRY....
Reports
ON THE CHEMICAL WORLD TODAY

HOT PILLS

During the most severe days of the campaigns of World War II every effort was made, although not always successfully, to give each man at least one hot meal a day, even if only of C and K combat rations. The latter, not renowned for their gustatory allure, were at least more tolerable with the addition of a few B.t.u.'s. For this reason the United States Army Quartermaster Corps enlisted the cooperation of Mellon Institute and various industrial laboratories to find a solid fuel suitable for the individual soldier to use in heating combat rations in the field.

Specifications were many and limiting. The fuel had to be usable for direct heating of the food receptacle without the use of a stove and had to burn with a flame of low luminosity. Lightness in weight, high heat content per unit weight, nontoxic combustion products, and low sooting rates were other desirable characteristics. It was also necessary that the fuel be easy to tablet and that it contain no habit-forming ingredients.



This latter qualification ruled out the familiar solid alcohols long used by peacetime campers, and for a while the Army adopted for field use a pellet of wax with a 15–20% wood flour content. The soot coats that burning wax imparted to utensils, however, made it objectionable, and the search was extended to less obvious fuel materials. Among these hexamethylenetetramine, commonly known as hexamine or Urotropin, seemed promising for a while. It was easy to tablet and ignite, and burned with a blue flame of low luminosity. Unfortunately, the incomplete combustion that resulted when its flames were in contact with a cold vessel yielded hydrogen cyanide, carbon monoxide, and various oxides of nitrogen, all decidedly unhealthful companions in a small closed space, such as a small tent or a covered foxhole.

Metaldehyde also came up for consideration. It burned with a comparatively nonluminous flame that gave off nontoxic fumes, possessed a high heat content per unit weight, and was unaffected by moisture. It was prevented from filling the bill, however, by the limited supply, its own toxicity, difficulties in tableting, and instability of some batches that were supplied.

Polyethylene glycol and paraformaldehyde were two other organics studied that failed the tests. Both burned with a hot blue flame that was highly wind resistant but gave off a choking odor and disagreeable fumes, which for the latter product were formaldehyde.

The most of the best qualities, as far as these organic heating tablets were concerned, was found in trioxane, a cyclic polymer of formaldehyde. Its chief immediate drawback is its relatively high cost. When briquetted with a few per cent of magnesium stearate and carbon black, it forms hard, light fuel cakes that possess a reasonably good heat content per unit weight, approximately 7000 B.t.u. per pound. In tablet form it burned with a flame of low luminosity invisible beyond 25 feet in even the blackest night.

An interesting generalization that resulted from the heating tablet investigation was that, whenever more than two carbon atoms occurred adjacently in the molecular structure of a given fuel, the latter probably would burn with a luminous flame.

Research in combat ration heating devices has not been limited to the fuel tablet. Many ingenious devices have been investigated, and some have been developed to potentially usable states. Among these are double-walled food cans which carry the food in the central chamber, water in the side chamber, and anhydrous lime in the bottom chamber. When the barrier between the latter two is pierced with a sharp instrument, the lime becomes slaked and the heat of hydration does the job. Unfortunately, such a container must, of necessity, be large and heavy. In another variation water could be added from an external source.

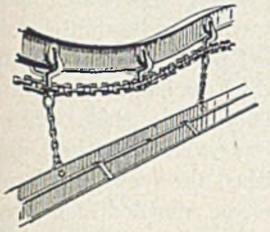
Another type of self-heating food container is that in which a central chamber is loaded with a modified thermit mixture at the time the food is canned. When this heating charge is set off by an igniter composition, the food is warmed radially with a large amount of heat

(Continued on page 8 A)

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

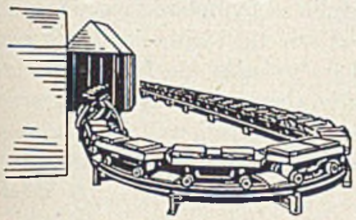
Reduce Costs in Handling Parts and Packaged Goods the Modern LINK-BELT Way

. . by overhead conveyor



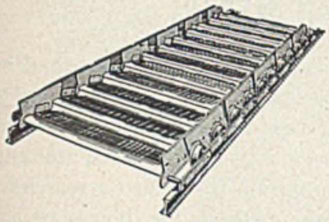
Link-Belt overhead conveyors put ceilings to work, save valuable floor space, prevent congestion, interference and damage to materials in transit. Can be installed in existing plants without costly remodeling. Link-Belt Overhead Trolley Conveyors can be supplied for mono- or multi-plane service; with short or long turns; for light, medium or heavy loads; for low, medium, high, or variable speeds.

. . by car type conveyor



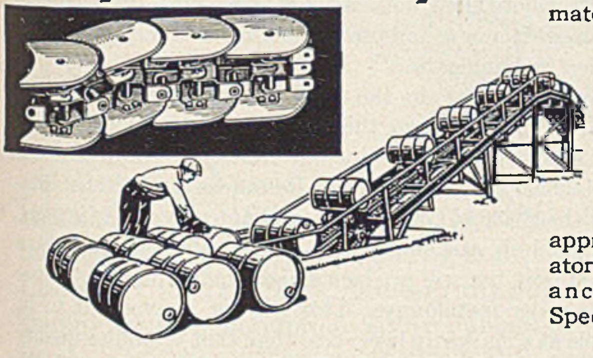
The Link-Belt Tru-Trac car type mold conveyor is designed for handling both large and small snap flask molds and to operate in irregular paths—up and down inclines. It has heavy cast-iron car tops, is fully equipped with anti-friction bearings and is low in both maintenance and H.P. requirements. The unit illustrated, automatically discharges the molds.

. . by apron conveyor



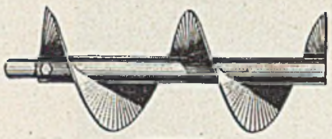
The steel-pan type, consisting of pans mounted on multiple strands of chain, is ideal for conveying fine or lumpy materials, light or heavy-duty service. The wood-slat type is recommended for handling packaged goods, parts, crates, barrels, boxes, etc.

. . by chain conveyors

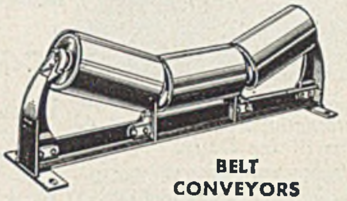


Link-Belt Chains and their team mates, Link-Belt Sprockets have aided expanding industry since 1875—pacing progress through the years for ever-better operation, ever-longer service life. In handling materials and transmitting power this winning combination has earned the approval of engineers and operators alike for efficient performance. Let Link-Belt Chain Specialists supply your needs.

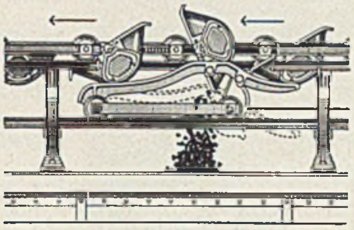
The money wasted in materials handling is a cost that does not add to product quality. Save in handling your materials and products. Consult Link-Belt Conveyor and Power Transmission Specialists.



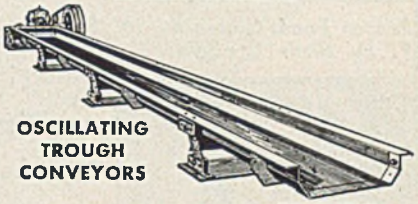
SCREW CONVEYOR



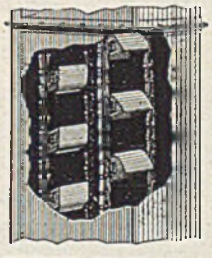
BELT CONVEYORS



BUCKET CARRIERS



OSCILLATING TROUGH CONVEYORS



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

LINK-BELT

Conveyors

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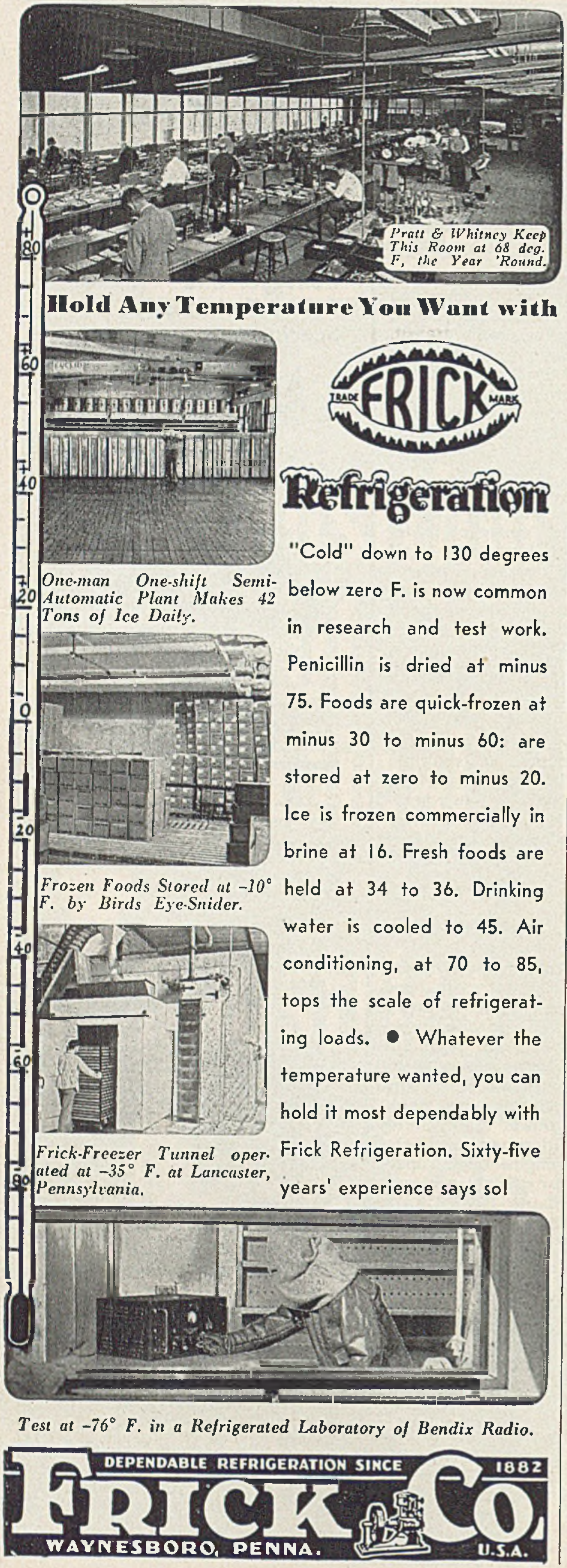


I&EC reports

generated at a high temperature. The method is excellent for heating fluid foods, such as soups, which by convection currents carry the heat away from the center core. It is not well suited, however, for the thicker foods which char at the surface of the heater from local superheating.

An attempt is made to avoid this difficulty in the design of a new immersion-type thermit heater. The unit consists of a metal holder into which an expendable, thermit-containing metal cartridge can be inserted. A spring-activated plunger in the holder is tripped when the charge is to be set off. The entire unit, holder and cartridge, is then immersed in the food and used as a stirrer to permit good heat dissipation. When the heating is finished the spent cartridge is ejected from the holder, which can be reloaded at the next meal time.

The Quartermaster-sponsored studies are continuing, with the emphasis on basic research in pyrophoric reactions suitable for the heating of food and the synthesis of new compounds with desirable characteristics for fuel tablet use. Actual laboratory research on these problems will be carried out in the colleges and research institutions. One such contract is already in effect, and others are under consideration.

R.L.D.

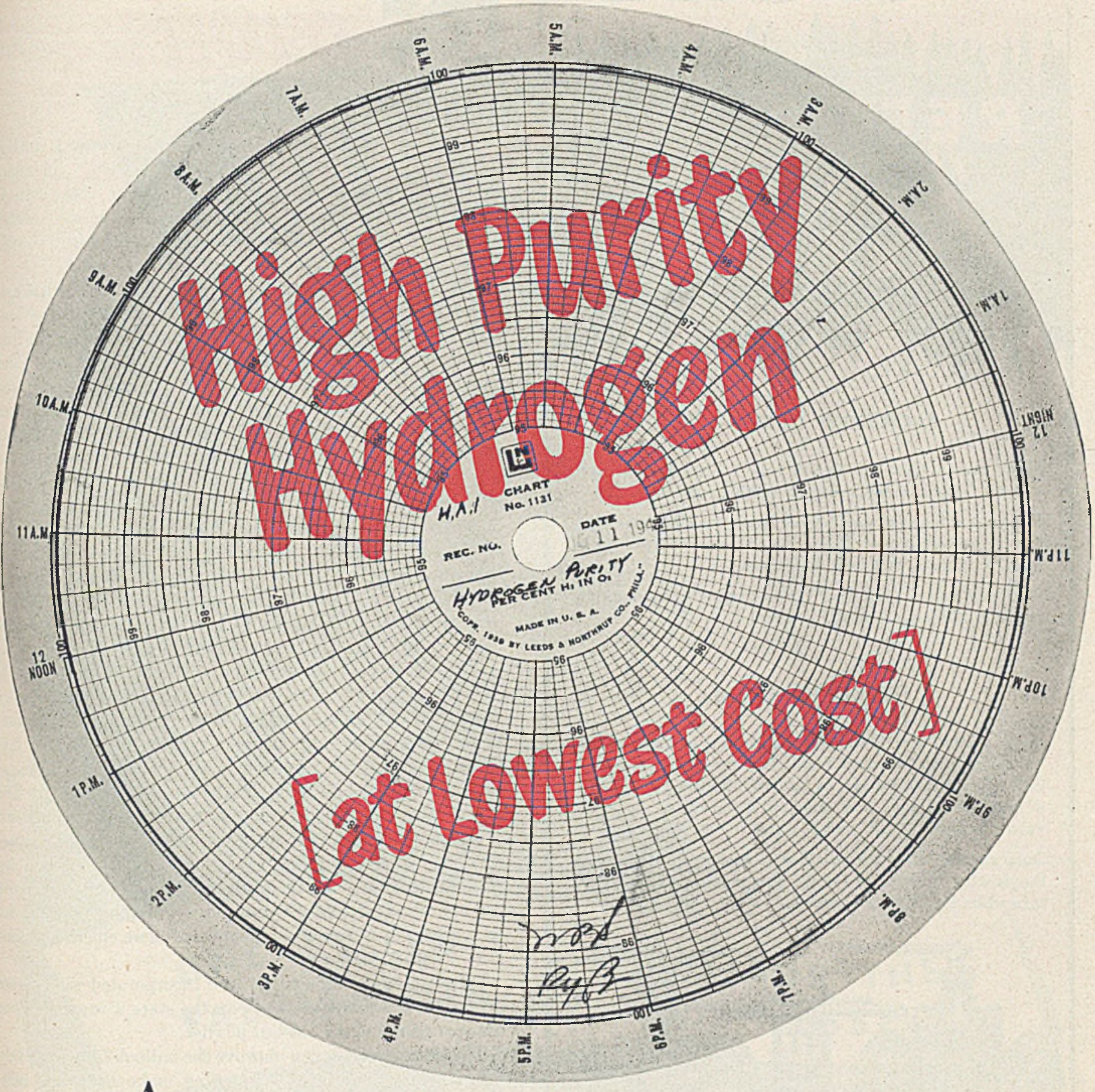
IRON POWDER FROM THE MESABI

In the technical development of natural resources, emphasis and research are directed to the finding of new or improved, and consequently increased, uses of the refined products. The resulting increased consumption leads into a search for new sources of raw materials or methods for their more efficient processing. Not often does one technological achievement contribute along both of these lines, but it does happen. An example is a new iron ore refining method now going into operation in Minnesota.

A new plant now in the final stages of construction at Aurora, Minn.—through the cooperation of Iron Incorporated, a division of Continental Machines, Inc., and the Commissioner of Iron Range Resources and Rehabilitation of the State of Minnesota—will not only bring into use low grade iron carbonate slate, previously neglected as a source of iron, but will produce a high grade iron powder useful in powder metallurgy. This powder is expected to be available at a markedly lower cost than that of similar quality now on the market, according to John R. Daesen, president of Iron Incorporated.

Iron powder metallurgy, although receiving considerable attention, has not been extensively developed. Metal powders have had wide acceptance in bearings, in friction materials, and in special shapes difficult to form by machining operations; but these fields, in which the powders have had comparatively little competition, have yielded a relatively limited tonnage of consumption. The backers of this new project expect their product to cause a wider acceptance of metal powders in fields more competitive and greater in tonnage, by avoiding the wear on dies which results with impure powders and by developing

(Continued on page 10 A)


High Purity
Hydrogen
[at Lowest Cost]
H.A.1
CHART No. 1131
DATE
11 1946
REC. NO.
HYDROGEN PURITY
PER CENT H2 IN O2
MADE IN U. S. A.
COPR. 1939 BY LEEDS & NORTHRUP CO. PHILA.
12 NIGHT
1 A.M.
2 A.M.
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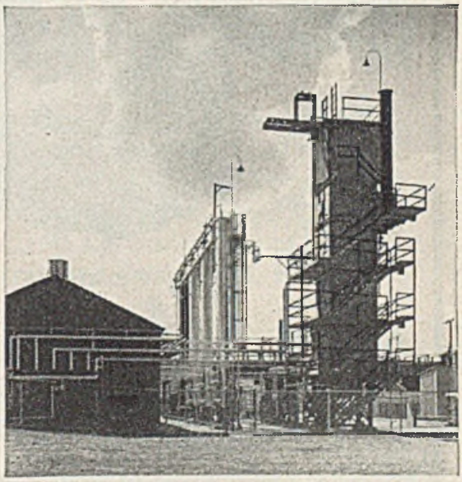
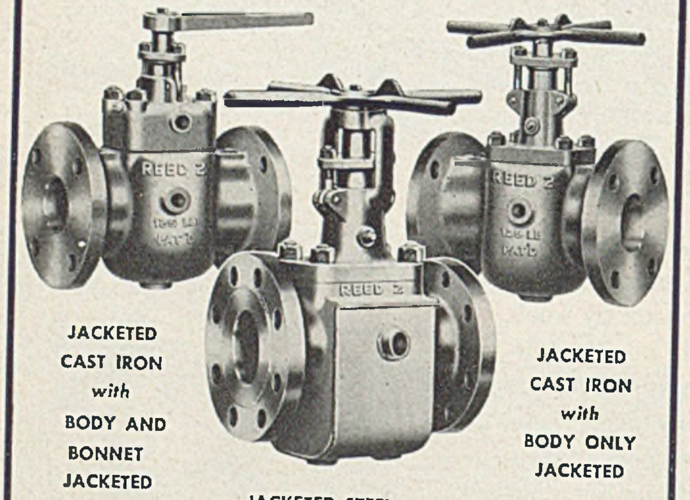




improved methods of use. One of the important factors is the cost of iron powder of the quality needed. In many units made as foundry castings the major cost item is machining, which would not be necessary in the powder metallurgy process. These are potential users of iron powder once the powder cost *vs.* quality problem is solved.

The process was developed by the late Charles V. Firth and his co-workers of the Mines Experiment Station of the University of Minnesota. It is continuous, starting with iron carbonate slate which is crushed, ground to −48 mesh, and digested with sulfuric acid to dissolve a major portion of the iron as ferrous sulfate. The undigested residue is discarded. Copperas ($FeSO_4.7H_2O$) is crystallized from the digester effluent after evaporation. This salt, which is contaminated with sulfates of aluminum, calcium, magnesium, and manganese, is passed through a rotary dryer to remove water of crystallization and thence to a calcining furnace, where, under carefully controlled conditions, the iron sulfate is oxidized to hematite (Fe_2O_3). The contaminated sulfates are unaltered and, being soluble, are leached out with water in the next step. The iron oxide, in the form of briquets, is heated in a reducing furnace using blue water gas (hydrogen plus carbon monoxide) at a temperature above 1700° F.; this converts it to a spongy form of iron in which the fine particles cluster together in grapelike bunches. After cooling in an oxygen-free atmosphere it is ground in a pulverizer, separated into various particle sizes by means of air separators and screens, and is ready for use as a powder of 99+% purity. The particle sizes range from about 100 mesh to about 20 microns.

The present plant is of demonstration scale. It has a capacity of 5 tons per day of finished powder and is being built by Iron Incorporated for the State of Minnesota. Minnesota has appropriated $650,000 from its ore mining tax fund for the venture as a part of its program of more efficient utilization of natural resources.

On completion of the plant, Iron Incorporated will operate it under a ten-year lease and pay the state a royalty of one cent per pound on all finished powder.

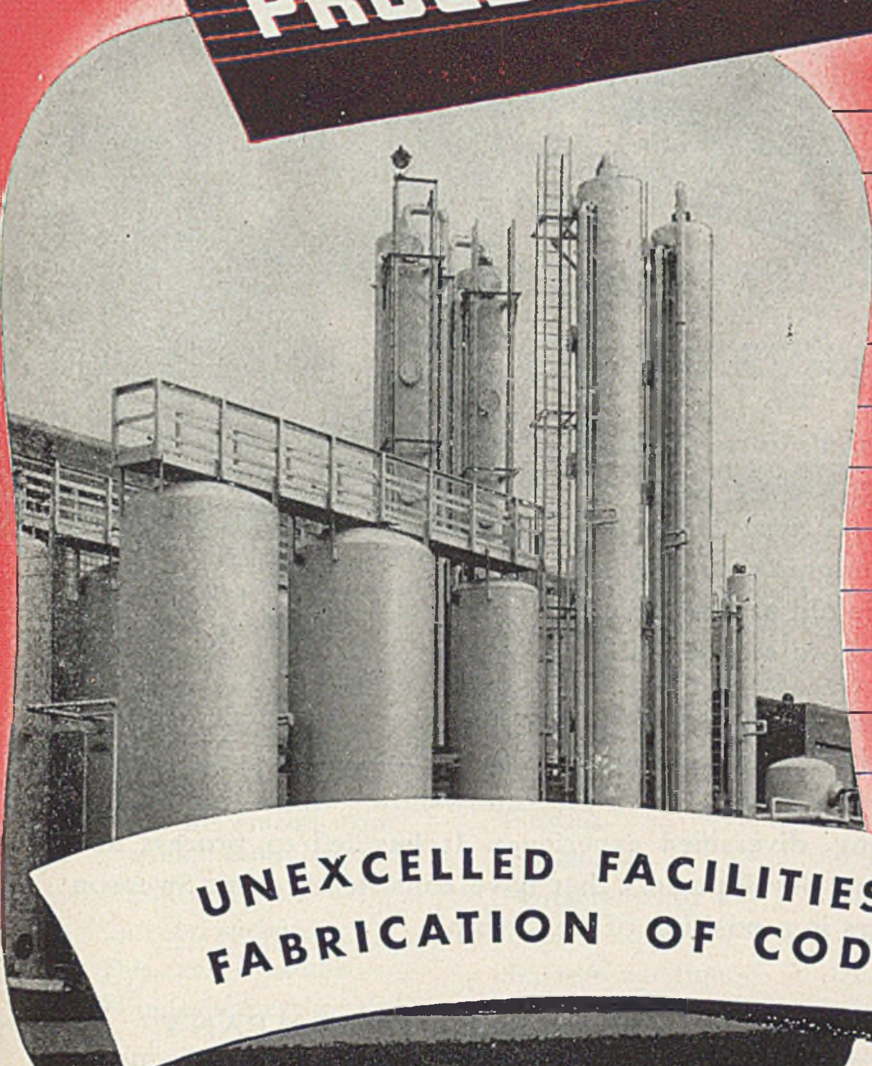
Thus a new process can improve the outlook for a relatively young industry and, at the same time, make useful and valuable previously submarginal mineral resources. R.L.K.

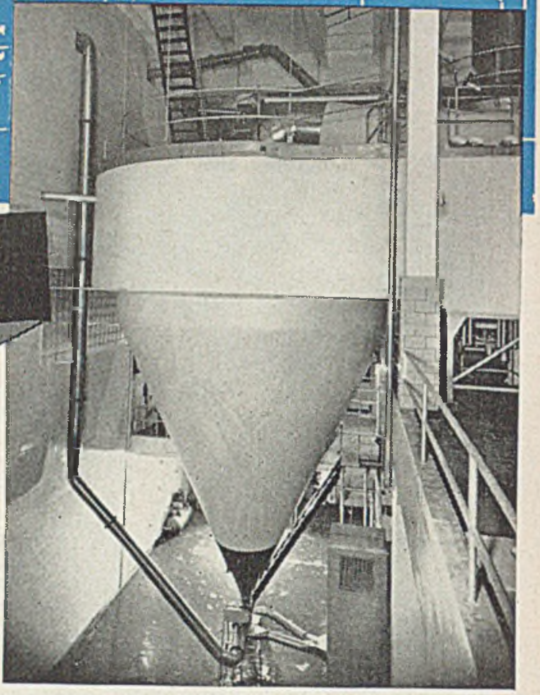
NEW JOBS FOR THE X-RAY

As a technique for the determination of crystalline structures, x-ray diffraction is not exactly a newcomer to the research worker. The crystallogram resulting from the passage of these rays through a crystal onto a photographic film has cleared up many mysteries for the chemist and physicist.

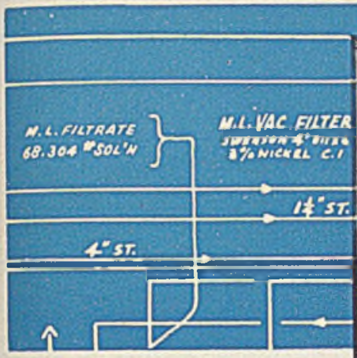
More recently the x-ray has been given bigger and more important tasks to perform in chemical research and manufacturing. It is supplementing or replacing ordinary chemical analyses in various phases of fine chemical and pharmaceutical plant control. A newer instrument known as the Geiger counter x-ray spectrometer even obviates photographic exposure and development.

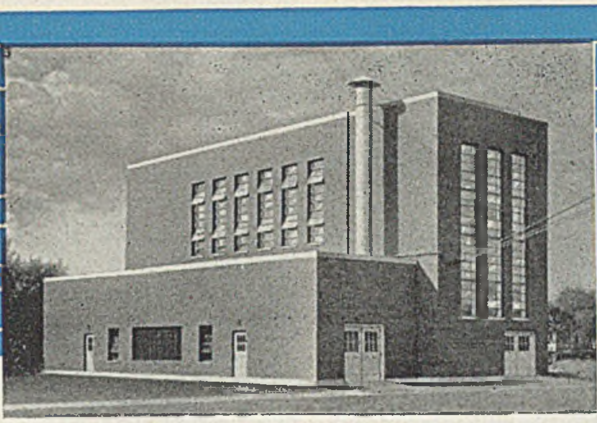
(*Continued on page 14 A*)

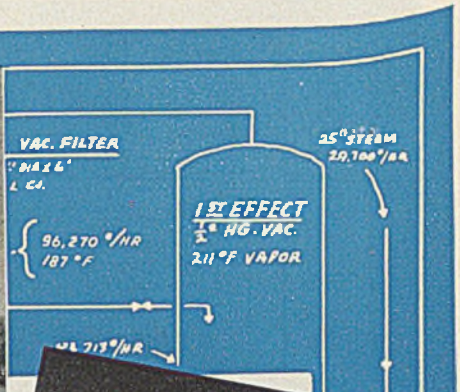




Main drying chamber of a plant in operation.

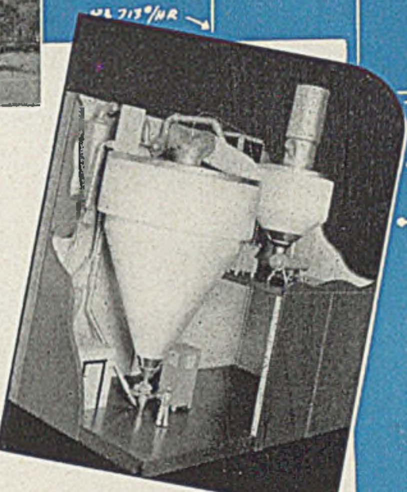



Swenson's new spray dryer research facilities at Harvey, Illinois.



Now...

SPRAY DRYING is being adapted to numerous chemical processes

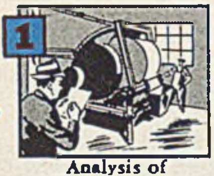

Model showing principal elements of a chemical spray-drying installation.

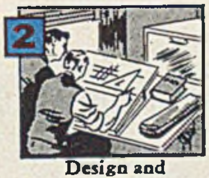
For more than 60 years Swenson has been concerned with concentration and recovery processes, involving evaporation, crystallization, filtration. Now Swenson has added Spray Drying . . . by the most successful of all methods, the Gray-Jensen process.

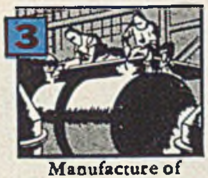
In our full-scale Research Plant (recently completed) test runs are made almost daily. Following are a few representative chemical products of the many which have been successfully spray dried. (Food and dairy products are omitted from this list.)

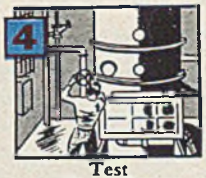
- Pigments (such as zinc sulfate monohydrate)
- Manganese sulfate
- Calcium carbonate
- Dyes and dyestuffs
- Magnesium carbonate
- Plastics
- Insecticides
- Pentaerythritol
- Tannin liquors
- Sulfite waste liquor and lignins
- Distillery slop
- Detergents
- Starch (textile)
- Animal blood
- Alfalfa extract

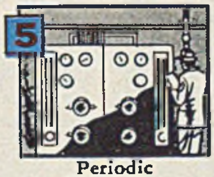
If you have a product or process which spray drying may logically benefit, we will gladly schedule a test run on a prearranged cost basis.


Analysis of Requirements

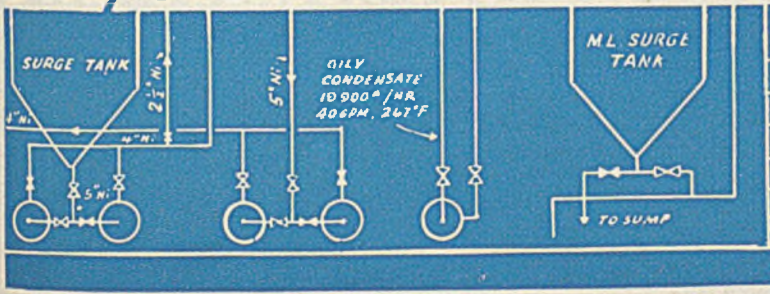

Design and Layout


Manufacture of Equipment


Test Operation

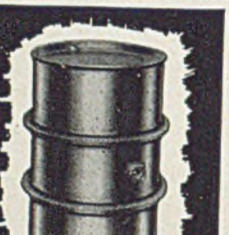

Periodic Check-Ups

Only SWENSON PROVIDES THIS FIVE-WAY SERVICE



SWENSON EVAPORATOR CO
HARVEY, ILL., U.S.A.

Req	Title - FLOW SHEET & MATERIAL BALANCE
Ch'd FM	Capacity
Scale ½" = ONE FT.	For
Appr.	D-8265
Appr	



It supplies rapid analyses through the use of a scanning device wherein a Geiger counter tube traverses a graduated quadrant of the diffraction image.

In the laboratory of a large chemical manufacturer such as Merck & Co. at Rahway, N. J., the x-ray performs almost daily tasks of analysis and identification. It readily identifies various types of closely related penicillin substances, and records for future reference the crystal structure patterns of the amino acids, those protein substances which are essential to life and which the chemist is striving to synthesize.

In the searching gaze of the x-ray the organic chemist is able to identify even a relatively crude reaction product with a compound of known structure confirming the utility of a more simple and practical synthesis. This happened only a short time ago in connection with *p*-aminosalicylic acid (4-amino-2-hydroxybenzoic acid), a compound which was originally developed in Sweden and which is being investigated, as are many other compounds, as a possibility in the treatment of tuberculosis.

In establishing production of streptomycin, our No. 2 antibiotic, on a commercial plant basis, x-ray diffraction was one of the control means which kept a constant check on the product. It permitted technicians to measure variations that were taking place in the manufacture of streptomycin. With its aid they were able to maintain a high degree of purity.

The efficiency of cathode ray tubes employed in television and oscilloscopes depends in a great measure upon the uniform crystallinity of coprecipitated calcium, strontium, and barium carbonates from which the cathode emission coatings are prepared. Barium carbonate is the lattice into which the two carbonates must fit, and the x-ray permits precise study of the physical nature of the coprecipitate, even though the particles are less than 0.5 micron in size.

The x-ray is a daring subterranean explorer in that it often brings to light strange, unfamiliar structures in the world of physical chemistry. It reveals arcing deposits on an electrical switch to be silver oxide, where a casual visual inspection might indicate carbon. It shows the physical results of stresses in metals and uncovers weak spots. Synthetic fibers yield the mysteries of their atomic formations. As an instrument of research the x-ray is old, and yet at the same time it is one of our most advanced tools of science. H.S.

PAINLESS FINISH FOR STAINLESS

Mechanical finishing of metals is far from obsolete, but a new and economical tool for the metal finisher that is not to be taken lightly is available in Du Pont's electropolishing solution for stainless steel. Developed jointly by Armco and Du Pont, this method is the subject of a newly issued operating manual entitled "Du Pont Electropolishing Solution for Stainless Steel." Specified in the original patent as a mixture of citric acid, sulfuric acid, and water, the composition of the new electrolyte is 55% glycolic acid, 30% sulfuric acid, and 15% water, with a considerable variation from these percentages being permitted as operating limits.

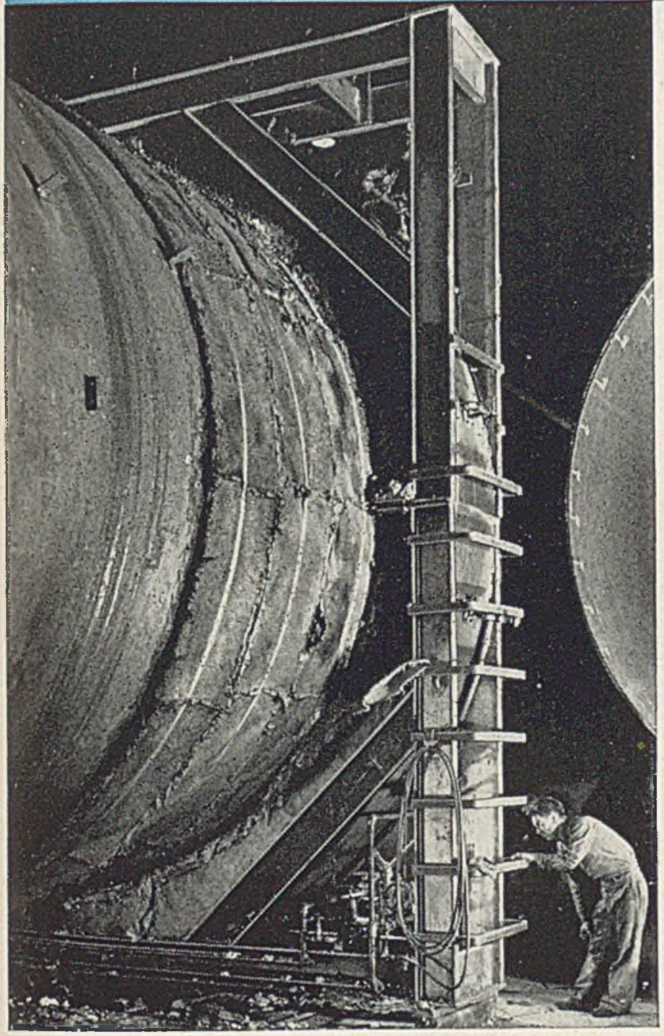
(*Continued on page 16 A*)

VESSEL DIVISION

NEWS

A. O. SMITH Corporation

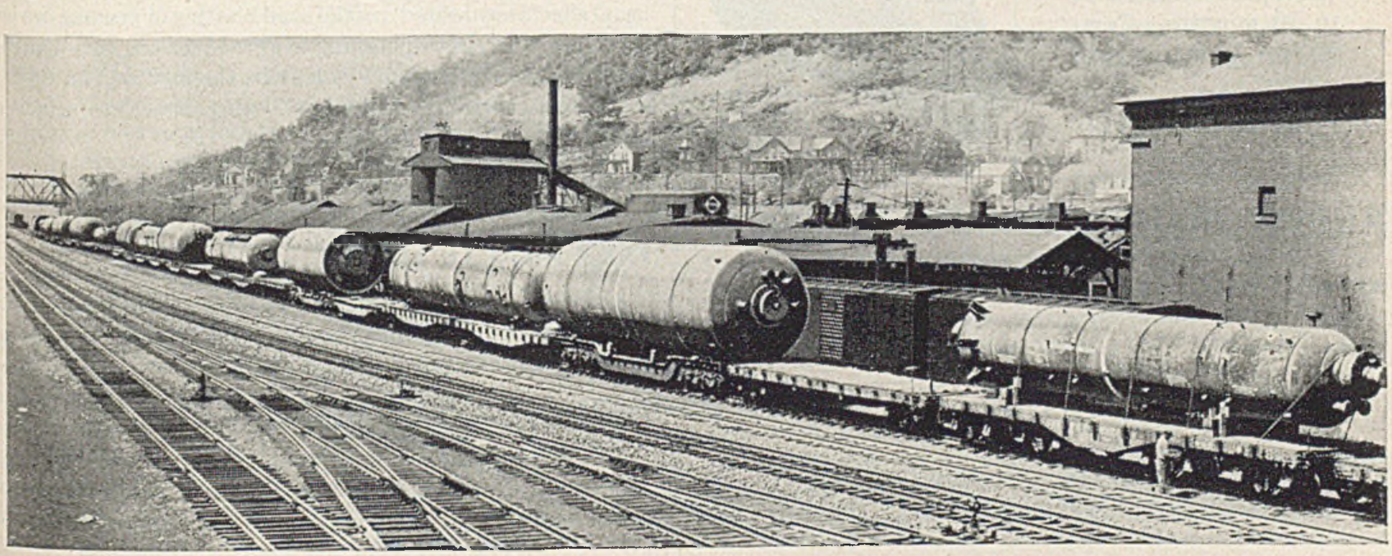
New York 17 • Philadelphia 5 • Pittsburgh 19 • Atlanta 3 • Chicago 4
Tulsa 3 • Houston 2 • Seattle 1 • Los Angeles 14
International Division: Milwaukee 1

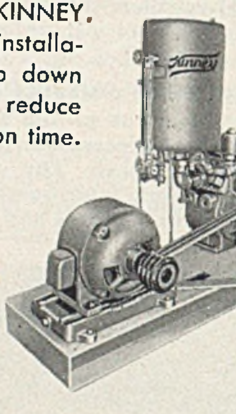


STRESS-ANNEALING BY THE INCH! (*above*) When a vessel is too long, or its diameter too great, to fit into one of the monster A.O. Smith furnaces, the engineers devise a portable furnace and stress-anneal section by section and the final closing seam.

MILLION ELECTRODE MAN. (*above*) In his twenty-one years of painstaking welding on SMITHway pressure vessels, John Binder has used up 975,744 SMITHway electrodes—at last count!

REFINERY ON WHEELS! (*below*) Not long ago this train pulled out of the A. O. Smith yards bearing almost the entire vessel equipment for a completely new refinery unit. The single shipment included coking drums, fractionating towers, stripping columns, flash chambers and coke chambers.





Kinney Single Stage Pump

i&ec *reports*

Electropolishing equipment is similar to that used in electroplating, and particularly advantageous qualities of the solution are its nonfreezing characteristic at room temperature, satisfactory operation over a wide range of current densities, and ease of handling by nontechnical personnel. Equipment may be either manual or automatic, lead-lined batch units being used up to 500 gallons, and automatic units with lead lining but glass or ceramic bottoms for greater capacities. To avoid breakdown of the solution, internal heating of the electrolyte must be employed, by the use of either steam coils or immersion heaters.

Either copper or lead may serve as cathode material, although copper is preferred. Cathodes are usually spaced about a foot apart, and the material to be polished, serving as the anode, is placed between. Copper anode contacts, consisting of pinch V-type hooks for wire or bar work and flat notched strips for sheets, are employed.

With a low voltage rectifier or a motor generator set of sufficient capacity, 6 volts is usually the maximum found necessary. A further recommendation is a current capacity of about 1 ampere per square inch of surface to be polished. There is a definite relation between the power and the size and shape of the unit. The amount of work that can be put into the tank is limited by the resistance of the solution, about 400 amperes for a 100-gallon tank being considered the maximum current which can be used without causing an undesirable rise in temperature.

Under these conditions, the time required for satisfactory treatment and the smoothness of the final surface depend primarily on the condition of the original surface. Normally, metal is removed at the rate of 0.001 inch per 10-minute period, and 2 to 10 minutes of treatment are sufficient. A bright surface will be produced by the electroplating even on rough material, but if deep marks or scratches are present and are not desired some mechanical work may be necessary. Dirt, oil, and similar impurities will cause foaming but will not affect solution performance, and light scale can be effectively removed. Removal of hard scale is, however, not satisfactory.

Color of the finished work is found to vary with the grade of steel used. Chrome-nickel steels polish best; high carbon grades polish better if prehardened. Nitrided or carburized stainless steel cannot be electropolished satisfactorily. If unusual effects are desired, partial sand blasting or peening can be combined with electropolishing to give a pleasing two-tone effect. No matter how you look at it, the method is a bright solution to what has heretofore been a thankless grinding task.

W.H.S.

FROM NUTS TO SOAP

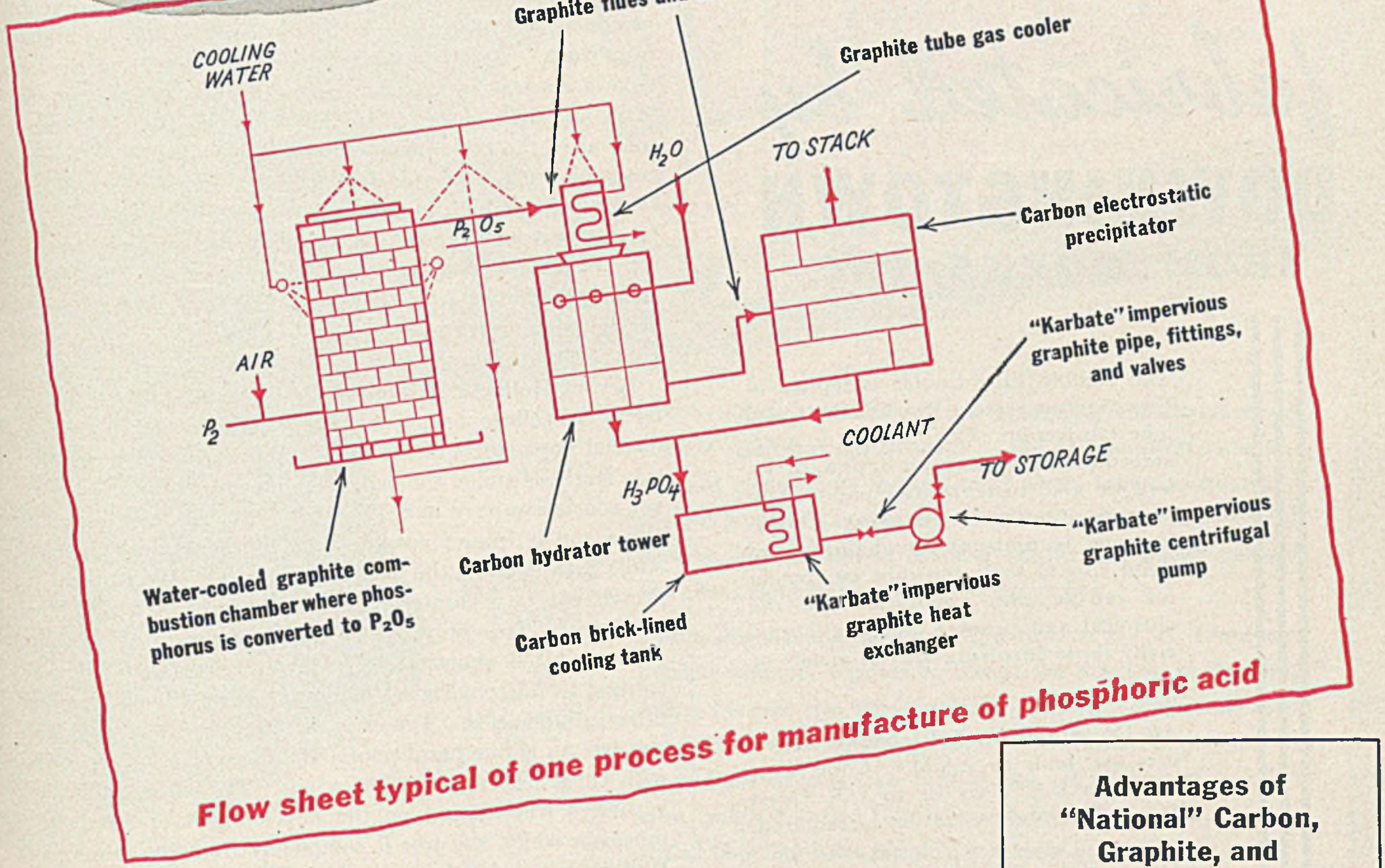
Sapium sebiferum is one of the most ornamental trees in Texas and certainly one of the fastest growing. It was commonly called the Chinese tallow tree, and the Chinese long ago used the fruit to make candles and soap.

From an original planting by Edward Teas of Houston about 1910, the number of trees in the city has grown to about a quarter of a million, as

(Continued on page 18 A)

LOCK OUT CORROSION!

. . . in manufacturing phosphoric acid . . . with Carbon, Graphite, and "Karbate" Impervious Graphite



Flow sheet typical of one process for manufacture of phosphoric acid

CARBON, Graphite, and "Karbate" materials are ideal for the construction of complete systems for the manufacture of phosphoric acid and related compounds. They are unattacked by phosphorus, its oxides and acids, or by those contaminants normally encountered in the manufacture of these products.

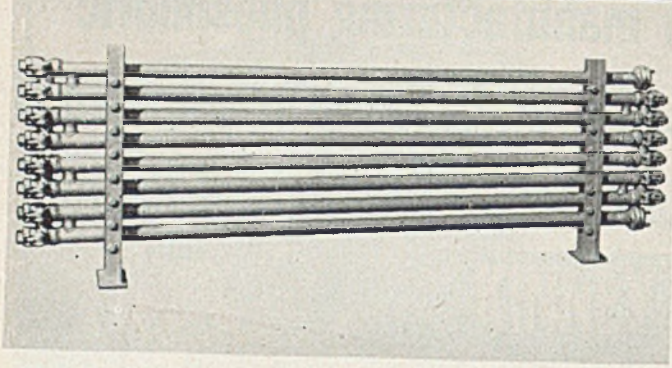
Graphite material, because of its high thermal conductivity, is required for combustion chambers and gas coolers; but either carbon or graphite is suitable for hydrators and precipitators. Chamber and hydrator construction may be either vertical or horizontal, completely of graphite and carbon, or graphite and carbon-lined steel, depending upon individual design considerations.

Advantages of "National" Carbon, Graphite, and "Karbate" materials

- No melting point
- Immune to thermal shock
- No metallic contamination of product
- Light weight with adequate strength
- Easy to machine and install

NATIONAL CARBON COMPANY, INC.
Unit of Union Carbide and Carbon Corporation
UCC
30 East 42nd Street, New York 17, N. Y.
Division Sales Offices: Atlanta, Chicago, Dallas, Kansas City, New York, Pittsburgh, San Francisco

The terms "Karbate" and "National" are registered trade-marks of National Carbon Company, Inc.



estimated by those who have watched developments; it is believed that there may be a million trees in the Gulf Coast area. From blossoms appearing in the spring, pods grow on a 3-inch stem; when the pods open in the fall, inside each one is a cluster of three white nuts about 15 mm. in diameter. A coating of tallow on each nut is the source of the white color, and, according to reported tests, this analyzes about 20% palmitin, 70% stearin, and the remainder vegetable fiber. A mature tree may yield 50 or more pounds per year.

A number of people have become interested in this nut, but perhaps no one has done more enthusiastic research than W. M. Potts of College Station, chairman of the Texas A.&M. Section of the American Chemical Society. Potts has a tree growing in his yard, and his laboratory in the department of chemistry at the Texas Agricultural and Mechanical College is full of the nuts in various stages of experimental processing and samples of the pure white tallow obtained from them. Results of his tests have indicated that the nuts have a content of approximately 20% oil, 24% tallow, 8% fiber, and 36% shell. A mildew forms on the seed coating soon after the pod opens and splits the tallow, producing a large percentage of free fatty acids. The acid number is then much too high to allow use of the tallow as a vegetable fat, but it would be good for soap stock and might be successfully blended with hydrogenated cottonseed oil. The tallow coating is removed from the seed by means of organic solvents or by putting the seeds in hot water and stirring them vigorously.

Bryant Holland, director of the Chemurgic Research Center at the college, has recently become interested in the commercial possibilities of the oil as obtained by solvent extraction methods and of the high protein meal residue. Tests not yet conclusive have indicated that the meal has a high food value and is free of gossypol and other harmful pigments. After extraction of the oil and screening of the residue, the protein can be separated from the fine meal by a mild alkali treatment. It is very soluble slightly above a pH of 7 and is precipitated quantitatively slightly below that pH. According to microbiological determinations, it contains about fifteen amino acids. The oil is classified as a rapid-drying oil and has an iodine number of 180, which places it in a class with tung, perilla, and oiticica oils. Its use in paints and varnishes will depend on the development of satisfactory processes which will free it completely from the tallow, and Holland is hopeful that something like the Solexol process of The M. W. Kellogg Company will provide the answer. A nationally known paint company is considering the erection of a plant in the Gulf Coast area for solvent extraction of the oil.

Principal difficulties in the way of this work lie in the problems involved in harvesting. If the seeds are harvested when tallow content is maximum, difficulties of removing them from the trees are almost insurmountable; by the time the nuts are ready to drop easily, the mildew on the tallow has taken a firm hold. Potts thinks that the trees should be grown where the roots can reach right down into the water table and suggests that the region around Port Arthur is the best on the Gulf Coast. Holland recommends agronomic breeding studies to control dropping qualities of the nuts and tree size, and hopes that a pecan-picking machine may be then adapted to harvesting the nuts.

W.H.S.

LADISH ANNOUNCES AN MPORTANT NEW DEVELOPMENT

A SEAMLESS REDUCING ELBOW

SAVES SPACE

SAVES WELDING COST

SAVES AN EXTRA FITTING

(L) TO MARK PROGRESS

Now from Ladish metallurgical and engineering laboratories comes another significant advancement . . . *the first practical seamless reducing elbow to be forged in one piece.* Featuring maximum physical properties and geometric accuracy, this new development provides improvement in the flow efficiency of piping systems and offers material savings in erection costs.

Now a single Ladish Reducing Elbow replaces the 90° Elbow and Reducer formerly required to change the direction of flow and reduce the pipe size simultaneously . . . AND . . . it eliminates one weld and a reducing fitting. Since the reduction in diameter is gradual and uniform from face to face, piping systems installed with Ladish Reducing Elbows benefit from the smooth, uninterrupted flow that helps maintain maximum pressure.

In addition to the flow advantages of seamless design, Ladish Reducing Elbows provide a fine, compact metal structure of high dynamic strength and toughness. For full information regarding range of sizes, prices and delivery, contact your nearby Ladish Distributor, District Office or write direct.

EAMLESS DESIGN

adish Seamless Reduc- g Elbows are formed om highest quality amless tubing at forg- g temperatures by a ocess that scientifically stributes metal uni- rmly throughout the alls of the fitting for

FLOW EFFICIENCY

Uniform, gradual reduction of diameter from face to face of the fitting ...without abrupt change of diameter to impede flow...and full effective center line radius help maintain pressures and provide maximum flow

EASY TO INSTALL

Ladish Reducing Elbows save time and simplify installation by eliminating the extra weld necessary when separate elbow and reducer are used. The smooth, unbroken exterior also helps simplify application

Controlled Quality FITTINGS

LADISH CO.

CUDAHY, WISCONSIN
MILWAUKEE SUBURB
DISTRICT OFFICES:

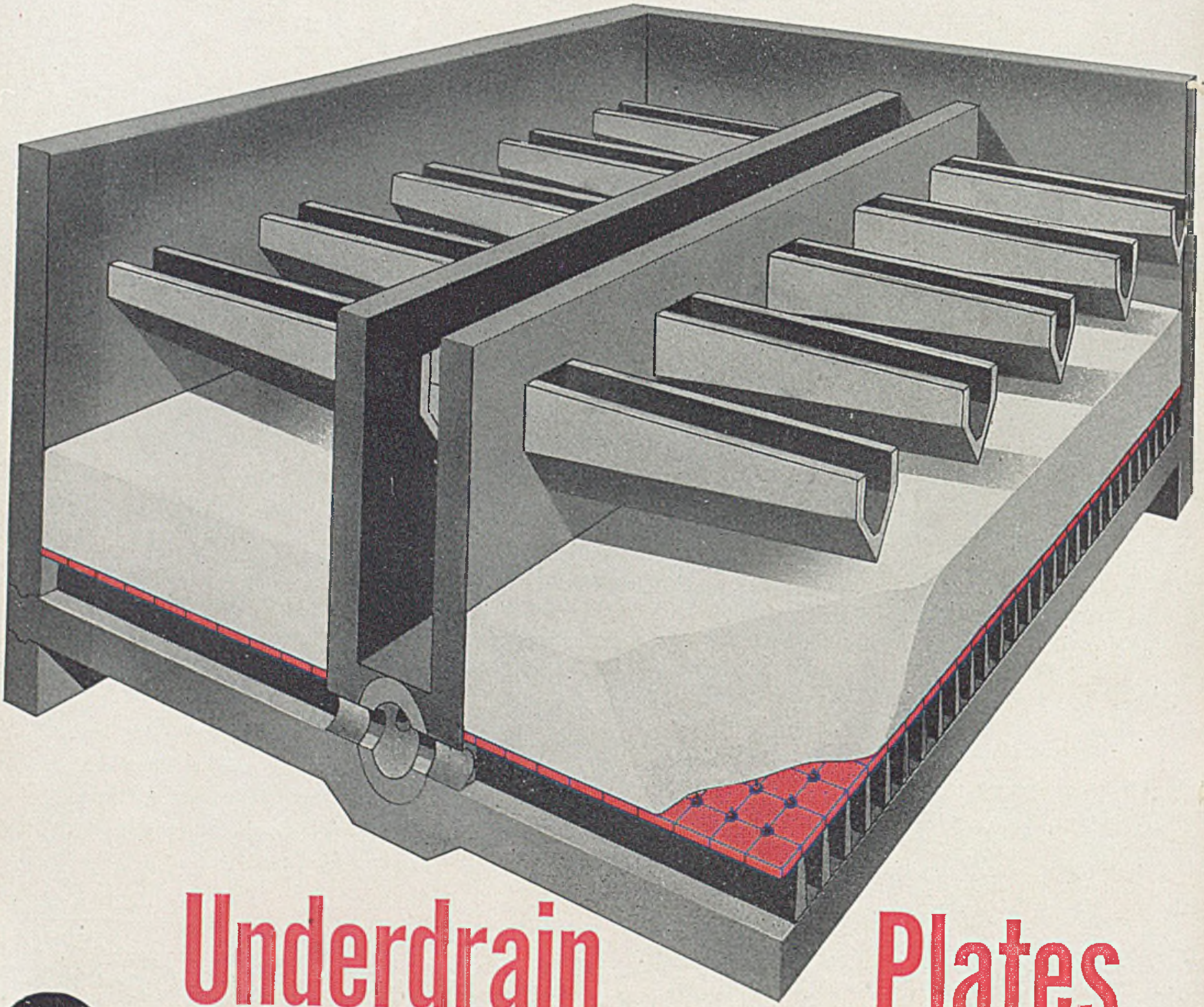
Simplicity Keynotes THIS Underdrain System

SIMPLE TO INSTALL. The ALOXITE aluminum oxide porous plate underdrain system is adaptable to large or small gravity and pressure units. It can be fitted into both new and old structures.

SIMPLE TO OPERATE. With all graded gravel eliminated, there is no displacement of filter bed. Filtration is more efficient. Backwashing is always complete and uniform. This operation usually requires less water and is accomplished in shorter time. Filtering and backwash operating heads, too, are reduced.

SIMPLE TO MAINTAIN. There is only one material to handle. The costly and tedious job of regrading sand and gravel is avoided. If required, bottom inspection is made quickly and easily. Repairs and replacements of spray nozzles, laterals, etc., are unnecessary as such metal parts are not required.

Our engineers will gladly explain, in more detail, how you might profit by utilizing the ALOXITE underdrain system. Immediate attention will be given your inquiries directed to Department E-117, The Carborundum Company, Refractories Division, Perth Amboy, N. J.



Underdrain Plates

BY **CARBORUNDUM**
TRADE MARK

"Carborundum" and "Aloxite" are registered trademarks which indicate manufacture by The

CELANESE NOW OFFERS CP ACETONE

ANOTHER CELANESE* CHEMICAL AVAILABLE TO INDUSTRY

elanese CP Acetone is now available in tank car or
rum quantities for immediate shipment. Increased pro-
uction makes possible the availability of this reagent
rade Acetone.

pecifications:

Acetone Content	99.5 min.
. Gr. 20/20°C.	0.7915—0.7930
stillation Range °C.	1°C. incl. 56.1°
olor APHA	5 max.
Acid as acetic	.002% max.
kalinity as NH_3	1 ppm max.
on-volatile	Max. .001 gr. per 100 cc sample
rmanganate time	2 hours min.
dehydes	None
ater	Less than 0.5% (miscible with 19 vol. 60° Be' gasoline at 20°C.)

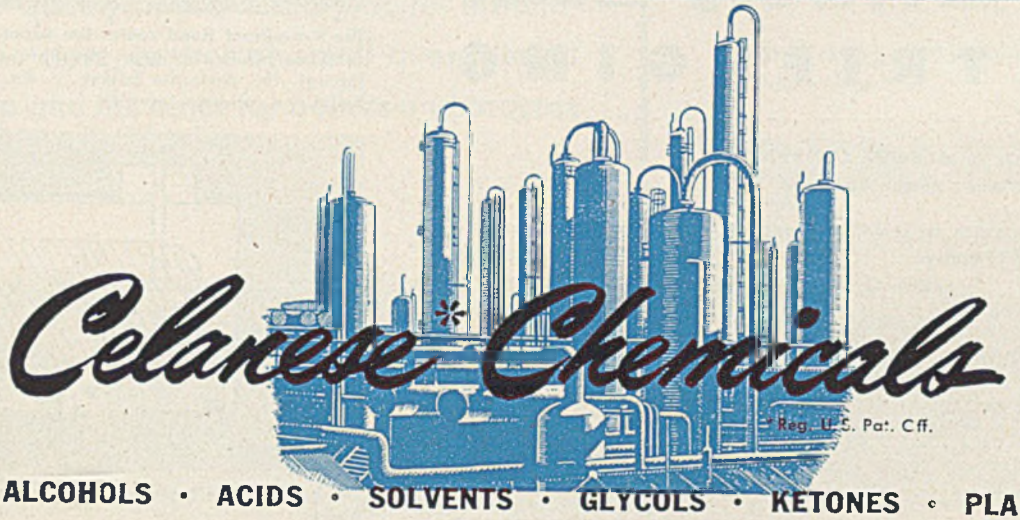
r samples and any additional technical data desired,
ite to Celanese Chemical Corporation, a division of
lanese Corporation of America, 180 Madison Ave-
e, New York 16, N.Y.

SEVEN NEW CHEMICALS

Here are the seven New Chemicals announced by Celanese in recent months. Some of them are already in volume production.

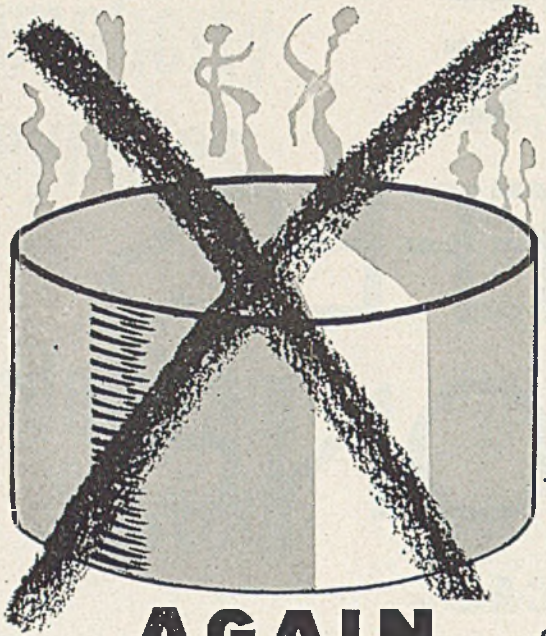
Normal Propyl Alcohol
Propionaldehyde
Methylal
Tetrahydrofuran
Methyl Ethyl Ketone
Butyl Alcohols
Methyl Pentanediol

Perhaps some of these new chemicals will be useful in further development of your processes and plans. Write us about your problems and Celanese Research and Technical Service will go to work for you.



*Reg. U.S. Pat. Off.

DEHYDES · ALCOHOLS · ACIDS · SOLVENTS · GLYCOLS · KETONES · PLASTICIZERS



Wanted: a profitable method for quickly separating a solid from a valuable, volatile solvent without any loss through evaporation.

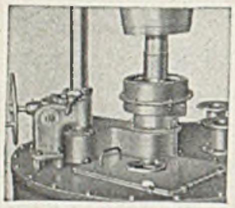
AGAIN . . . *the answer is centrifuging*

This is another example of how AT&M Centrifugals save time, money and space in the chemical processing field. Yet this case history represents only one of many profitable uses of centrifuging.

Whatever your processing problem, it may pay you to get a confidential cost comparison between your present method and centrifuging from an AT&M representative. Such qualified engineering experience is available to you at all times without charge or obligation.

Use the coupon below for specific information on how centrifuging can give you greater savings in time, money and space.

AMERICAN TOOL AND MACHINE COMPANY, 1421 Hyde Park Ave., Boston 36, Mass., 30C Church St., New York 7, N. Y.



AN AT&M PLUS

Processors cheered when AT&M came out with the radically different *Fume-Proof Hood.*

For, this Fume-Proof Hood answered the complex problems of sealing in gases while allowing complete rotating freedom for the spindle.

SAVE TIME, SPACE AND COSTS WITH

A.T. *and* M.

CENTRIFUGING

AMERICAN TOOL & MACHINE COMPANY
1421 Hyde Park Ave., Boston 36, Mass.

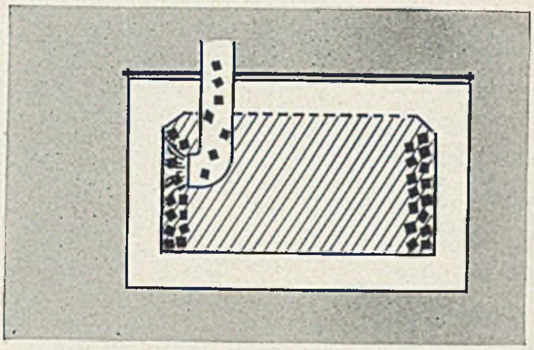
Please send information on centrifuging applied to the following processes:
☐ Extraction ☐ Filtration ☐ Dehydration ☐ Coating ☐ Precipitation
☐ Sedimentation ☐ Impregnation

Write here any other process......................................

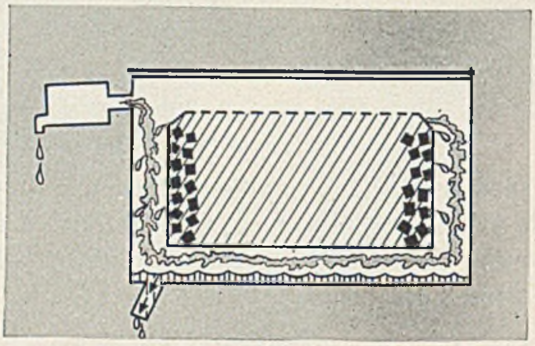
Name......................................

Company......................................

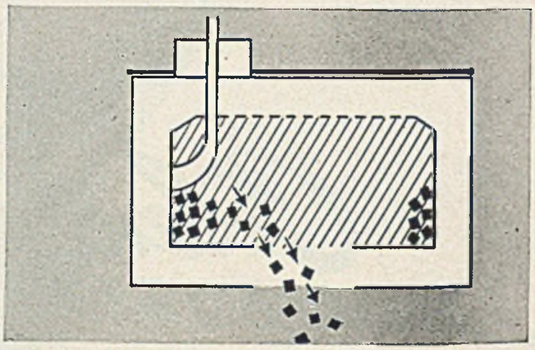
Address......................................



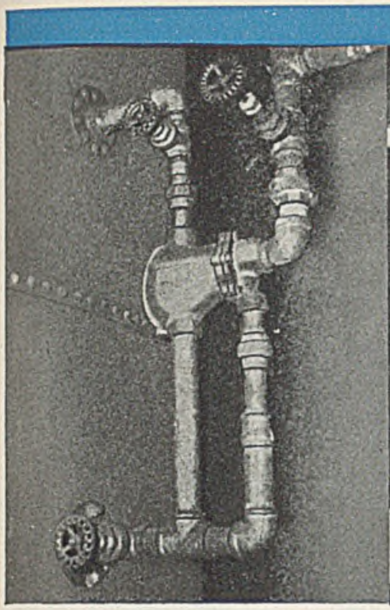
To separate the solid from the volatile solvent, AT&M installed a centrifugal with Fume-Proof Hood and perforate basket.



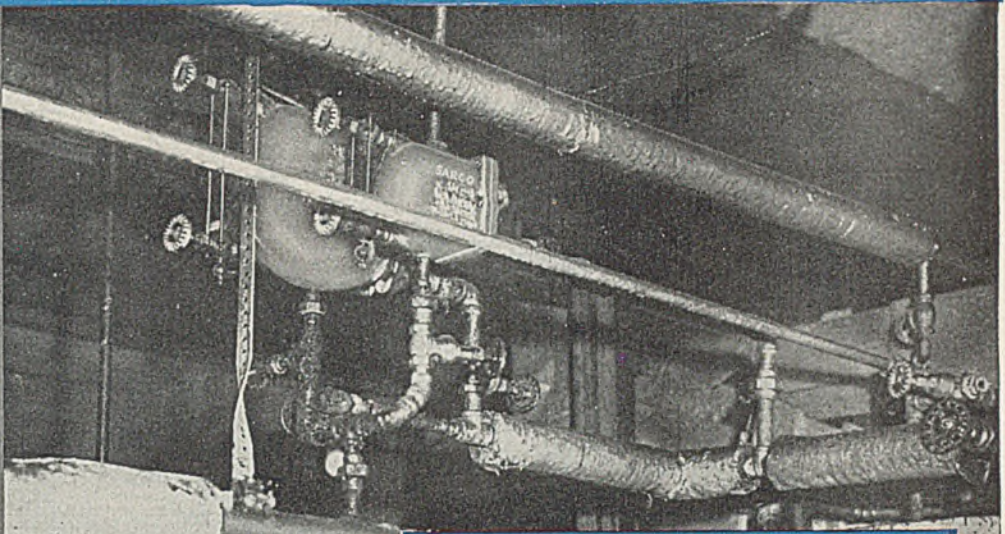
The Fume-Proof Hood routes the vaporous solvent to the condenser while centrifugal force throws the liquid solvent through the perforate basket . . . for 100% recovery of liquid and vaporous solvent.



The built-up cake is plowed out through the bottom of the basket.

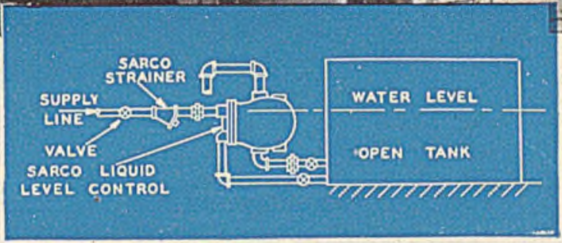


ON HOT WATER TANK



ON FOOD PROCESS TANK

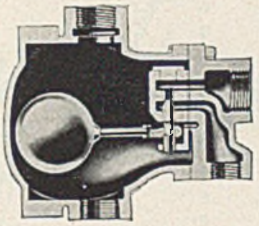
SARCO LIQUID LEVEL CONTROL

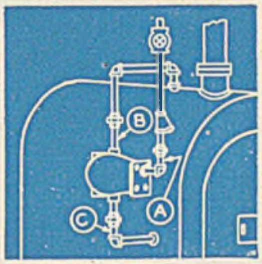


Sarco liquid level controller maintaining water level in an open tank.

The hook-ups on this page show how easy it is to control the liquid level in tanks and boilers with a product that costs little more than a good steam trap. In fact, the Sarco Liquid Level Control is an adaptation of the Sarco Float-Thermostatic Steam Trap which has been known for its reliability for more than a quarter of a century.

Whenever the float valve cannot be located inside the tank, Sarco liquid level controls solve the problem at low cost. Two types available: One for quality house heating boiler installations, for close control of small quantities of make-up and the other for boilers and process tanks. Catalog 450.





ON BOILER

SARCO TEMPERATURE CONTROLS

TR-21 Control for tanks.

KR-14 Control for ducts.

LSI Electric Control for plating, food, chemical processes.

TR-40 Cooling Control for compressors, condensers, degreasers.

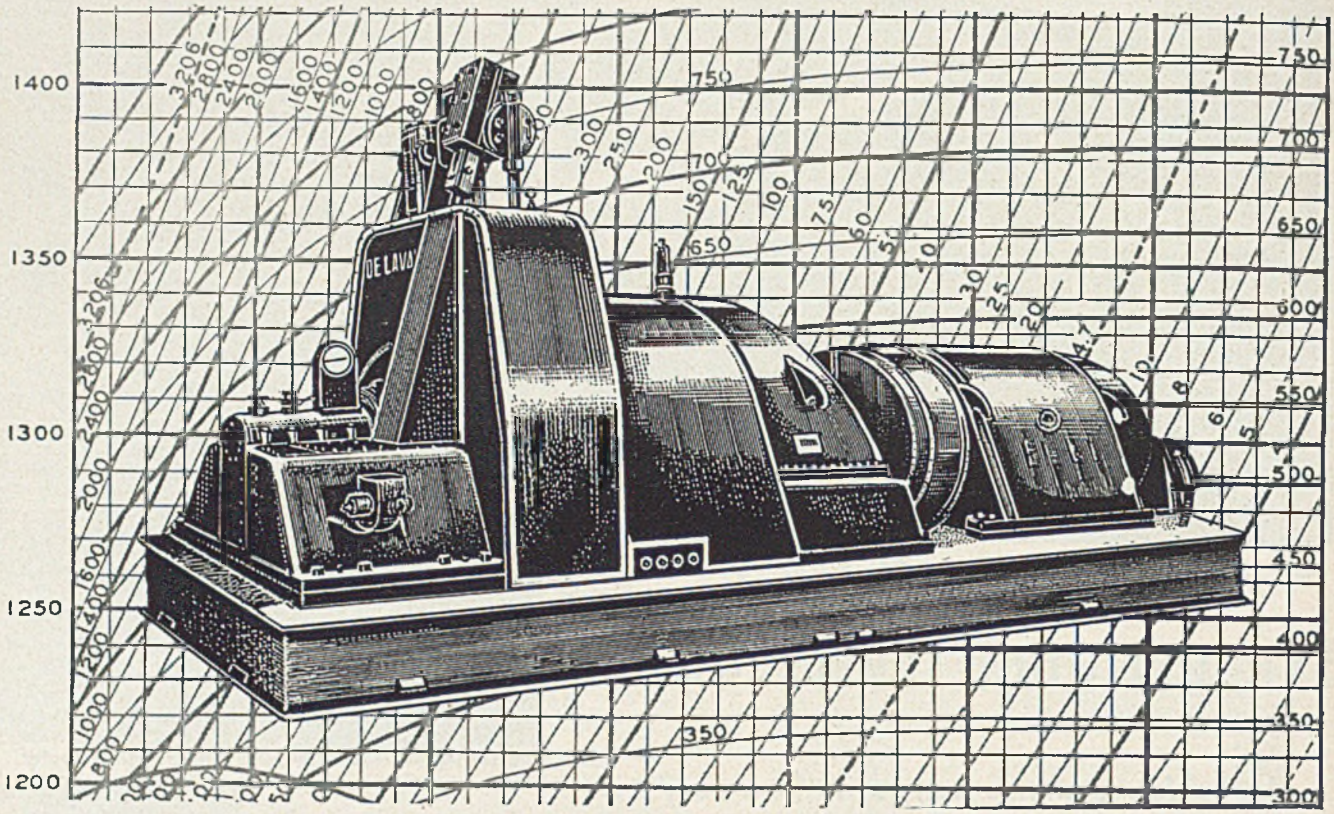
87-Trap-control — for outdoor tanks steam lines.

Water Blenders for Diesels, showers, process heating and cooling, and brine

150

SARCO SAVES STEAM

SARCO COMPANY, INC.
Represented in Principal Cities
475 FIFTH AVE., NEW YORK 17, N. Y.
SARCO CANADA, LTD., TORONTO 1, ONTARIO



SKIM THE POWER CREAM

from process steam

If you use appreciable quantities of steam consider the economy of generating all or a part of your own power by allowing the steam to expand through a De Laval Turbine before delivery to the heating or processing system.

De Laval Turbines can be furnished with automatic controls designed to make exhaust steam available in the quantities and at the pressures required to meet the demands of plant operation and the requirements of thermo-dynamic economy.

May we have the privilege of submitting cost figures based upon the installation of a De Laval turbine selected to meet your plant requirements?

T-7

DE LAVAL

DE LAVAL STEAM TURBINE CO., TRENTON 2, N. J.

Atlanta • Boston • Charlotte • Chicago • Cleveland • Denver • Detroit • Helena • Houston • Kansas City
Los Angeles • New Orleans • New York • Philadelphia • Pittsburgh • Rochester • Salt Lake City
San Francisco • Seattle • St. Paul • Tulsa • Washington, D. C. • Edmonton • Toronto • Vancouver • Winnipeg

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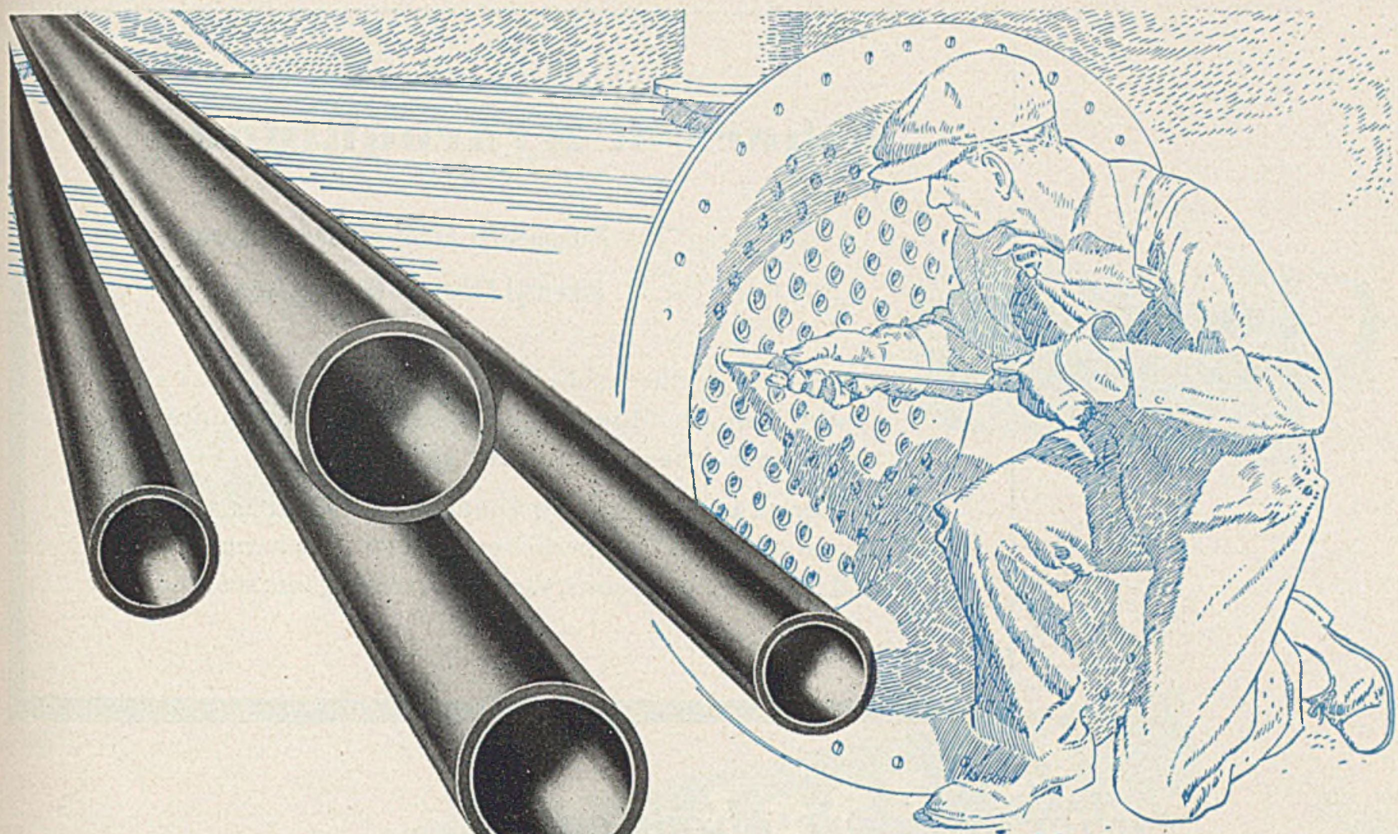
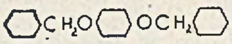


Ethers of Hydroquinone

Monobenzyl Ether of Hydroquinone



Dibenzyl Ether of Hydroquinone

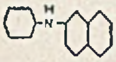
Good-rite
CHEMICALS

Monobenzyl ether of hydroquinone may be used as an antioxidant, stabilizer, or plasticizer in pharmaceuticals, paints, varnishes, and organic synthesis.

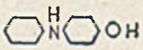
Dibenzyl ether of hydroquinone may be used as a high boiling solvent for perfumes, cosmetics, pharmaceuticals, plasticizers, paints, varnishes, and organic synthesis.

Other organic chemicals

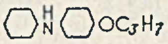
Secondary Aromatic Amines



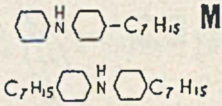
Phenyl B-Naphthylamine



p-Hydroxy Diphenylamine

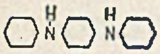


p-Isopropoxy Diphenylamine

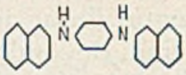


Mixed Mono and Diheptyl Diphenylamines

Di-secondary Aromatic Amines

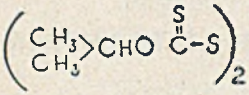


Diphenyl p-Phenylenediamine

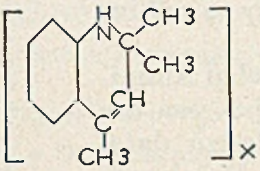


Di B-Naphthyl p-Phenylenediamine

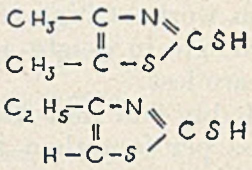
Miscellaneous



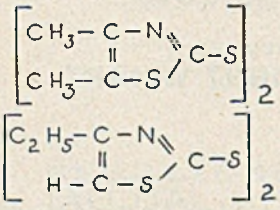
Di-Isopropyl Dixanthogen



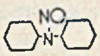
Trimethyl Dihydro Quinoline Polymer



Mixed Ethyl and Dimethyl Mercaptothiazoles



Mixed Aliphatic Thiazyl Disulfides



N-Nitroso Diphenylamine

All materials listed here are available in commercial quantities. Prices and technical information are available on request. Please write Dept. CC-11, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio.

B. F. Goodrich Chemical Company

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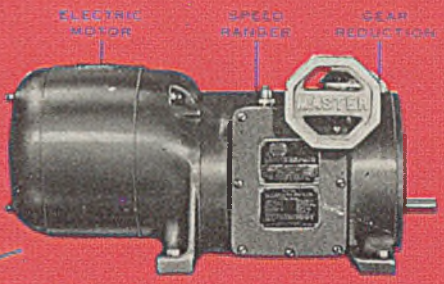
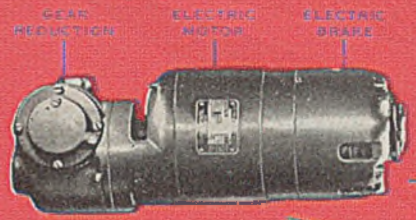
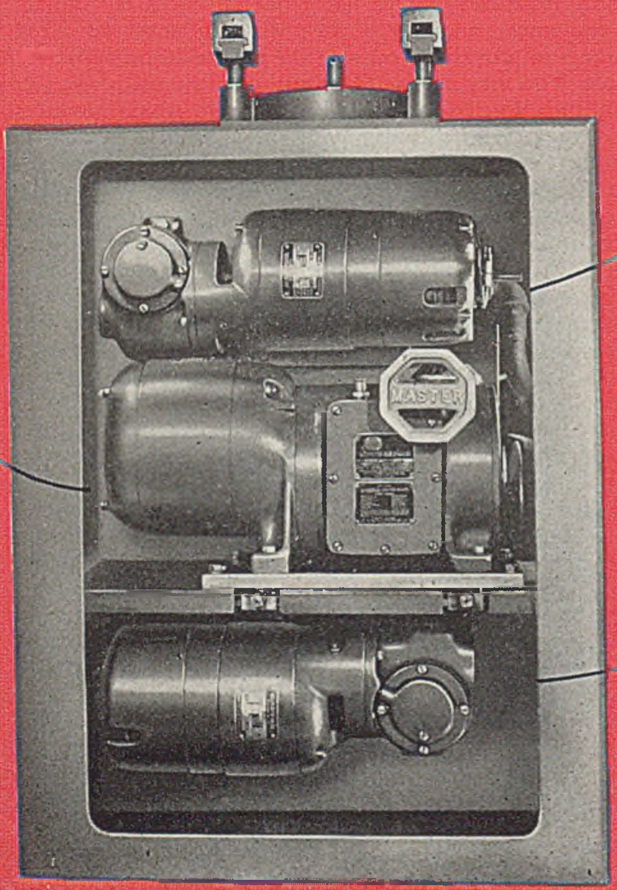
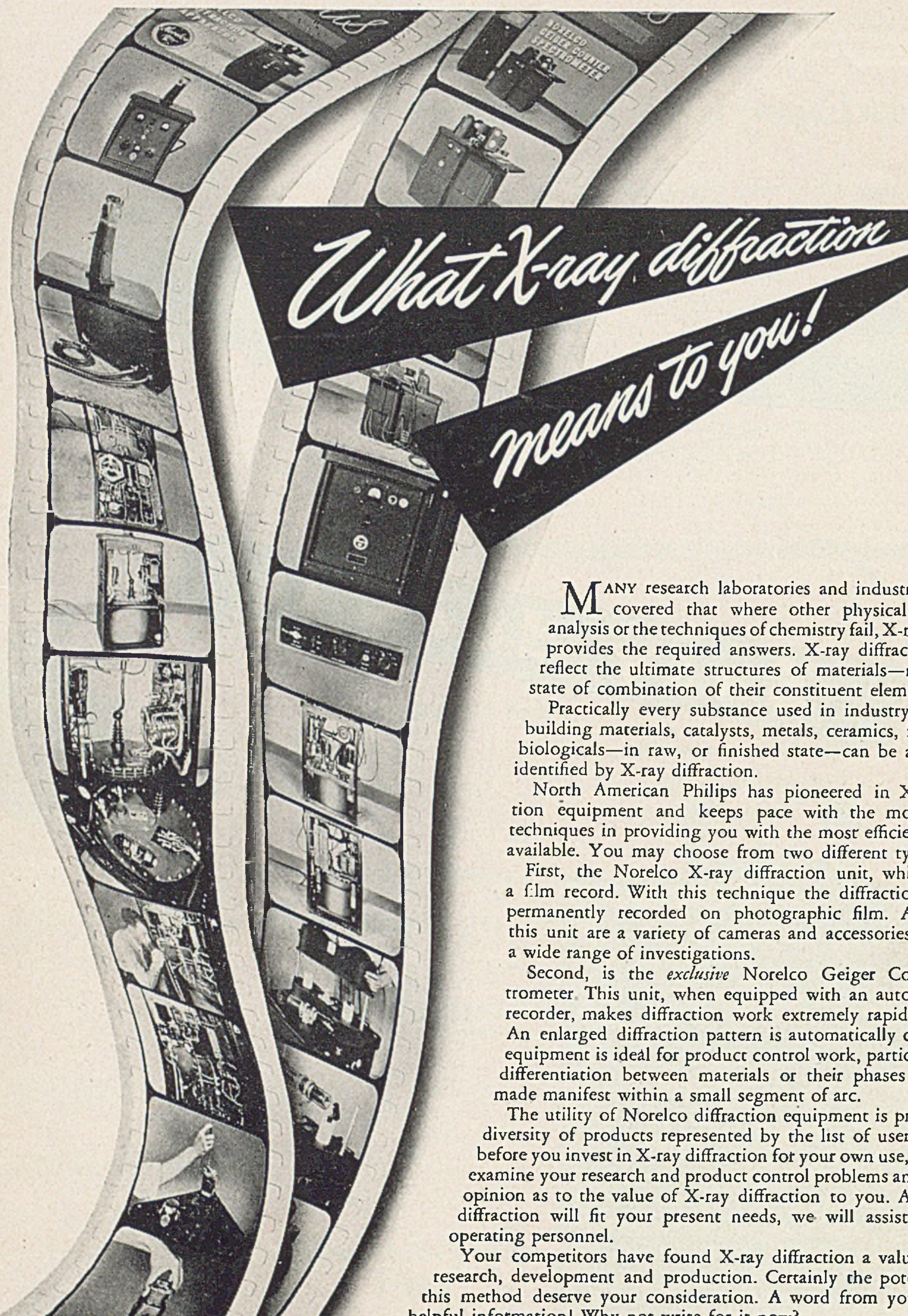

ELECTRIC MOTOR
SPEED RANGER
GEAR REDUCTION
MASTER


GEAR REDUCTION
ELECTRIC MOTOR
ELECTRIC BRAKE


MASTER



Many research laboratories and industries have discovered that where other physical methods of analysis or the techniques of chemistry fail, X-ray diffraction provides the required answers. X-ray diffraction patterns reflect the ultimate structures of materials—revealing the state of combination of their constituent elements.

Practically every substance used in industry—chemicals, building materials, catalysts, metals, ceramics, foods, fibres, biologicals—in raw, or finished state—can be analyzed and identified by X-ray diffraction.

North American Philips has pioneered in X-ray diffraction equipment and keeps pace with the most advanced techniques in providing you with the most efficient apparatus available. You may choose from two different types.

First, the Norelco X-ray diffraction unit, which produces a film record. With this technique the diffraction pattern is permanently recorded on photographic film. Adaptable to this unit are a variety of cameras and accessories, permitting a wide range of investigations.

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The utility of Norelco diffraction equipment is proved by the diversity of products represented by the list of users. However, before you invest in X-ray diffraction for your own use, permit us to examine your research and product control problems and render our opinion as to the value of X-ray diffraction to you. And, if X-ray diffraction will fit your present needs, we will assist in training operating personnel.

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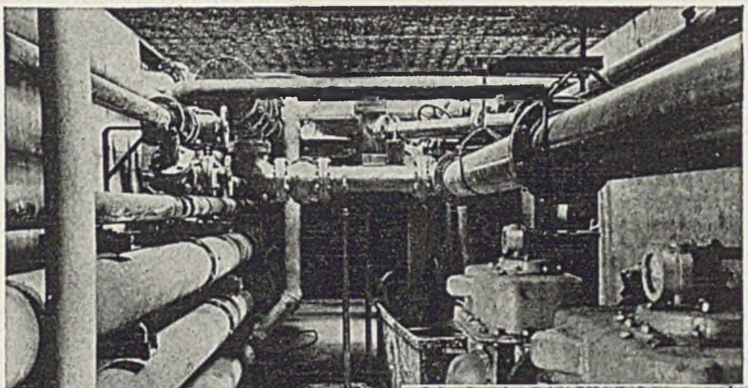
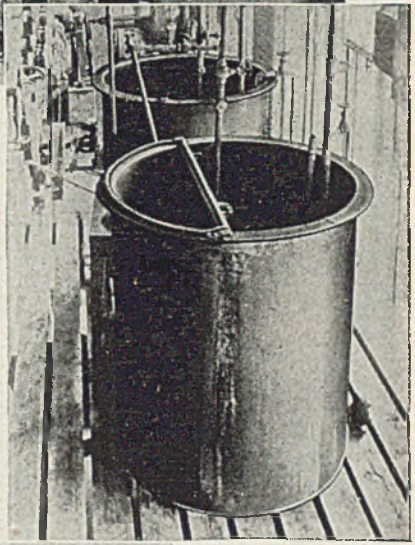
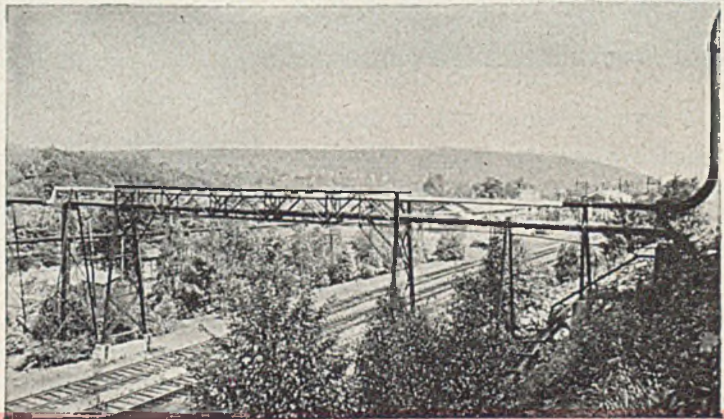


ACE rubber lined pipe, fittings, valves and tank, and ACE all-hard-rubber pipe and fittings are used in this one installation



Several of these ACE rubber lined tanks are used for caustic and bleach storage in one bleachery

Abrasive, acidulous water is handled by this ACE pipe lined with 1/4" soft rubber, in service more than 8 years



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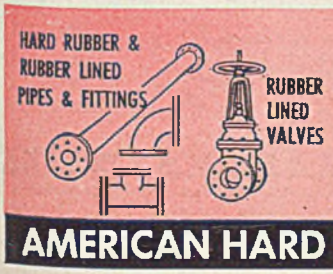

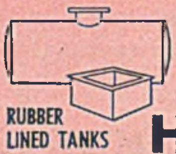

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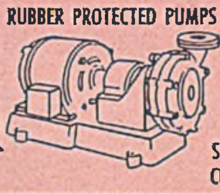

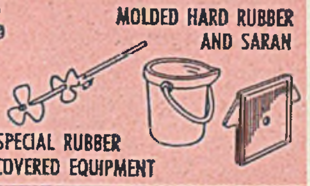

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YOUR TELEPHONE TRANSMITTER AND RECEIVER, *voice gateways to the telephone plant, are so essential to satisfactory service that they have been under study in Bell laboratories for seven decades.*

A TELEPHONE RECEIVER is a complex system of electrical and mechanical elements. Its coils, magnets, diaphragm and cap react on each other as they convert the electrical waves of your voice to sound waves. What is the best size for the holes in the ear cap? Will 1/1000th inch greater thickness help a receiver diaphragm to carry your telephone voice more clearly? One way to find out is to build numerous experimental receivers and test them.

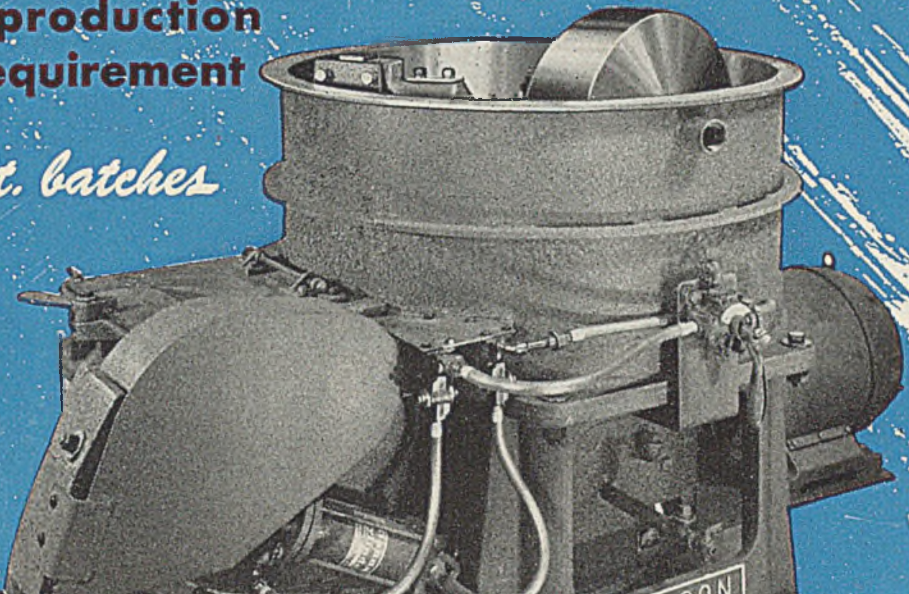
But Bell Laboratories have found a shorter way. They built an all-electrical replica, an "equivalent circuit" in which electrical resistance stands for air friction in the cap holes; capacitance corresponds inversely to the stiffness of the diaphragm. Over-all performance of this circuit can be quickly measured and design changes economically explored. Later, a model can be built for final check.

The "equivalent circuit" was pioneered by Bell Telephone Laboratories 25 years ago. It is a useful tool in many Laboratories developments—saving time, saving the cost of machine-tooled models, encouraging experimentation. It is one more example of the way Bell scientists get down to fundamentals as telephone progress continues—and service keeps on improving for all subscribers.

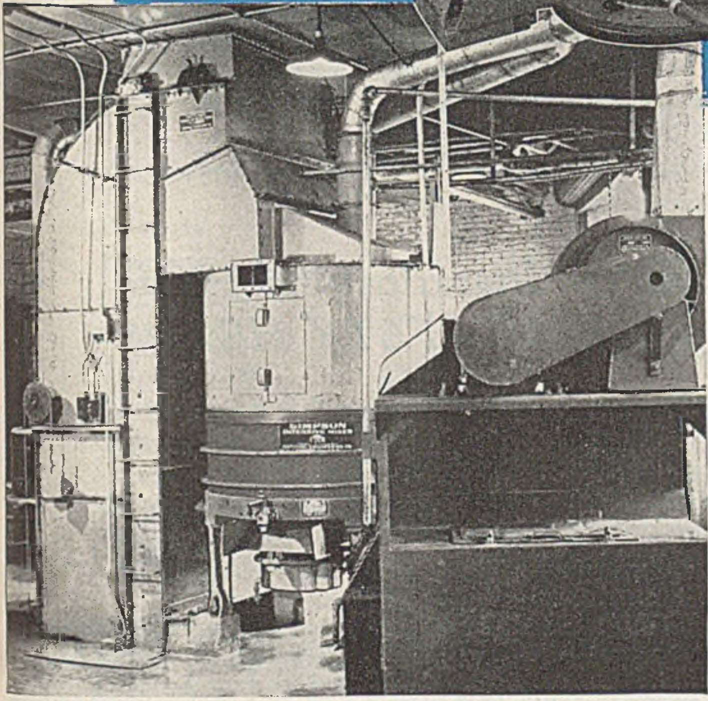
BELL TELEPHONE LABORATORIES

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

there are SIMPSON *Intensive* MIXER models for every "special" application or straight production mixing requirement up to *50 cu. ft. batches*



RIGHT: Specially designed Simpson Mixer Model O, built for experimental work at a large chemical plant.



ABOVE: Typical "standard" production size Simpson Mixer, equipped with a totally enclosed loader, and combination dust and cooling hood for handling dusty, corrosive or poisonous materials.

No matter what your chemical process mixing requirements may be . . . there is a SIMPSON Intensive MIXER model qualified to handle the job, within a range of capacities from 1/5 to 50 cubic feet per batch.

All models offer the superior "mulling" principle of controlled mixing, to blend all types of dry, semi-dry and plastic materials better, faster at lower cost. In addition, SIMPSON MIXERS are available with all necessary equipment for use as reaction vessels, where reactions, heating, cooling, etc., can be completely controlled.

Ask to have a National Engineer show you how Simpson Intensive Mixers can solve your most complex mixing problems, resulting in higher production, lower costs.

SIMPSON *Intensive Mixers*

NATIONAL ENGINEERING COMPANY

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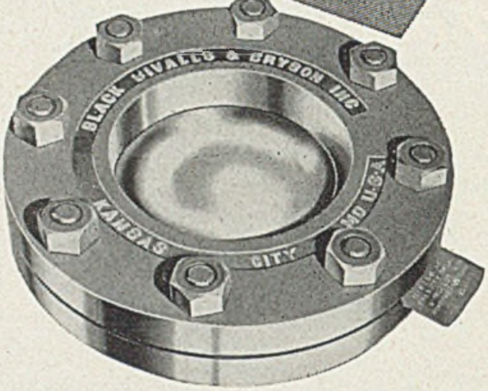
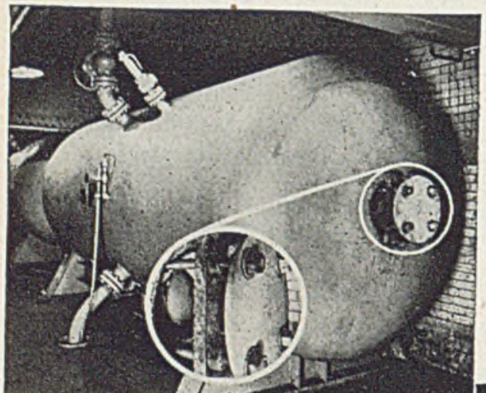
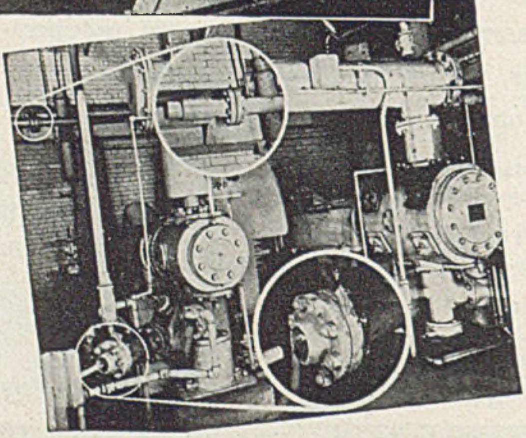
COMPRESSED AIR EXPLOSIONS?

There's Complete Protection Against Over-Pressure in BS & B SAFETY HEADS



● Don't scoff . . . compressed air systems do explode! Insurance company records offer proof. Vaporized oil-air mixtures touched off by a fleck of hot carbon, leaky discharge valves allowing hot air to be drawn back into the system, clogged intake filters overheating compressors . . . all these mean trouble. Inter and after coolers eliminate many dangers . . . relief valves handle normal pressure rises. But it takes SAFETY HEADS for that positive margin of safety. Yes, sir SAFETY HEADS act instantly, even to high speed pressure waves! Provide full, pipe-size unrestricted relief opening.





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No other pressure relief device offers such complete protection with such economy. No other device can approach the relief capacity of a SAFETY HEAD in a given diameter. The simple rupture diaphragm bursts in tension at pre-determined pressure and temperature. You'll be amazed at their versatility . . . 5 to 25,000 psi . . . a size for every need. Quickly and easily replaced.

Your plant, like the Central New York Power Plant at Oswego, pictured at left, can profit from the protection of SAFETY HEADS. Write today for complete information and specifications. Address the Special Products Division; Black, Sivalls & Bryson, Inc.; Power and Light Building, Kansas City 6, Missouri.

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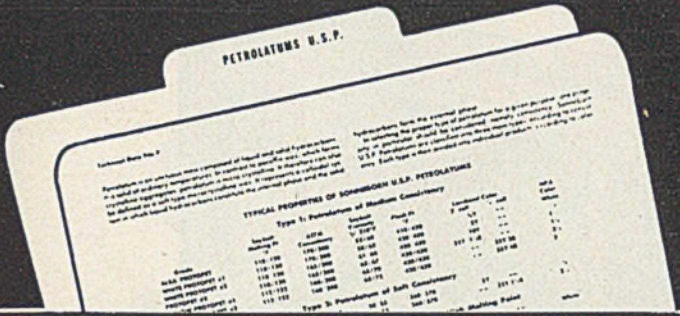

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(indicate use or business on line above)
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Company__________
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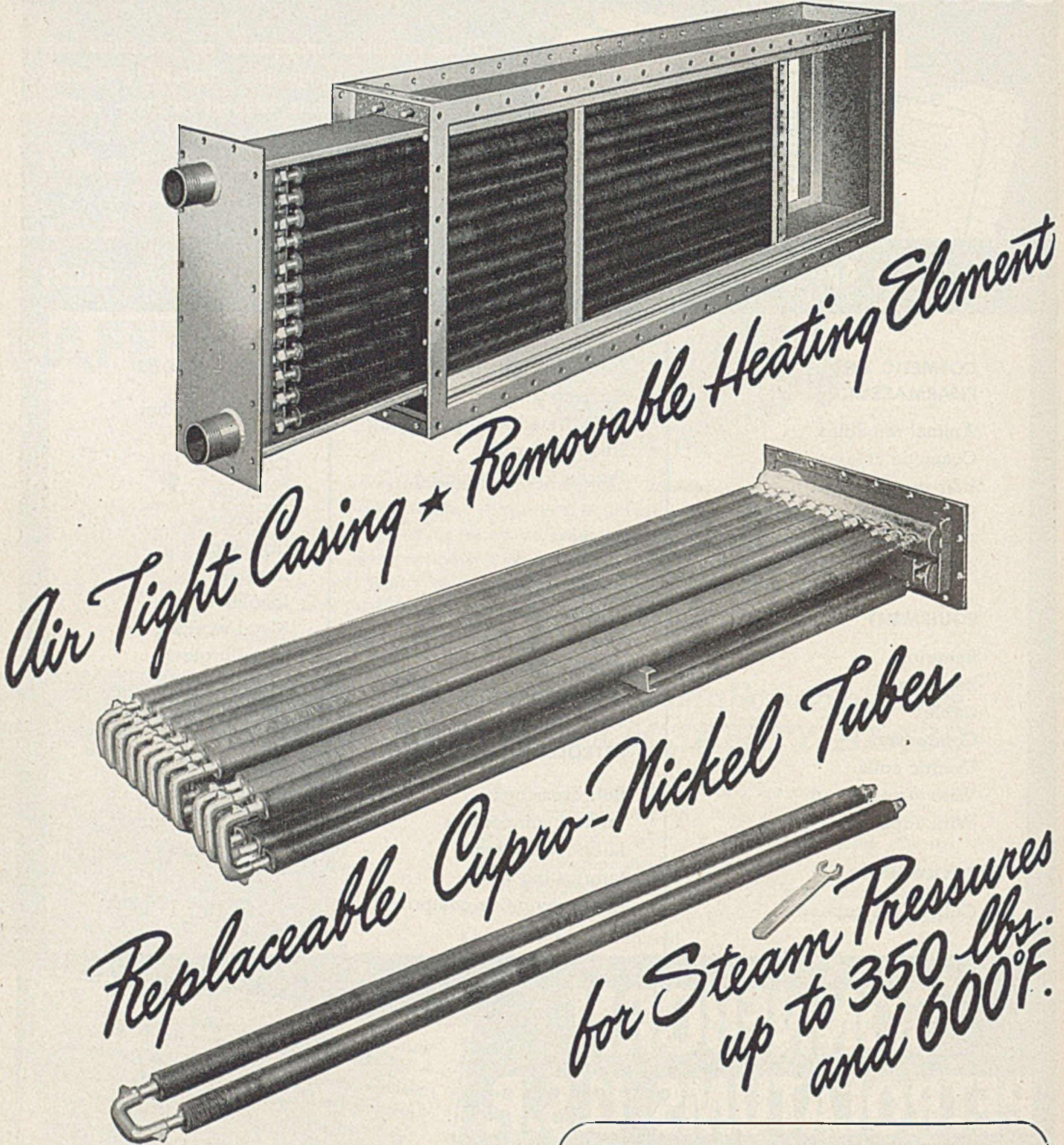
City__________ Zone____ State____



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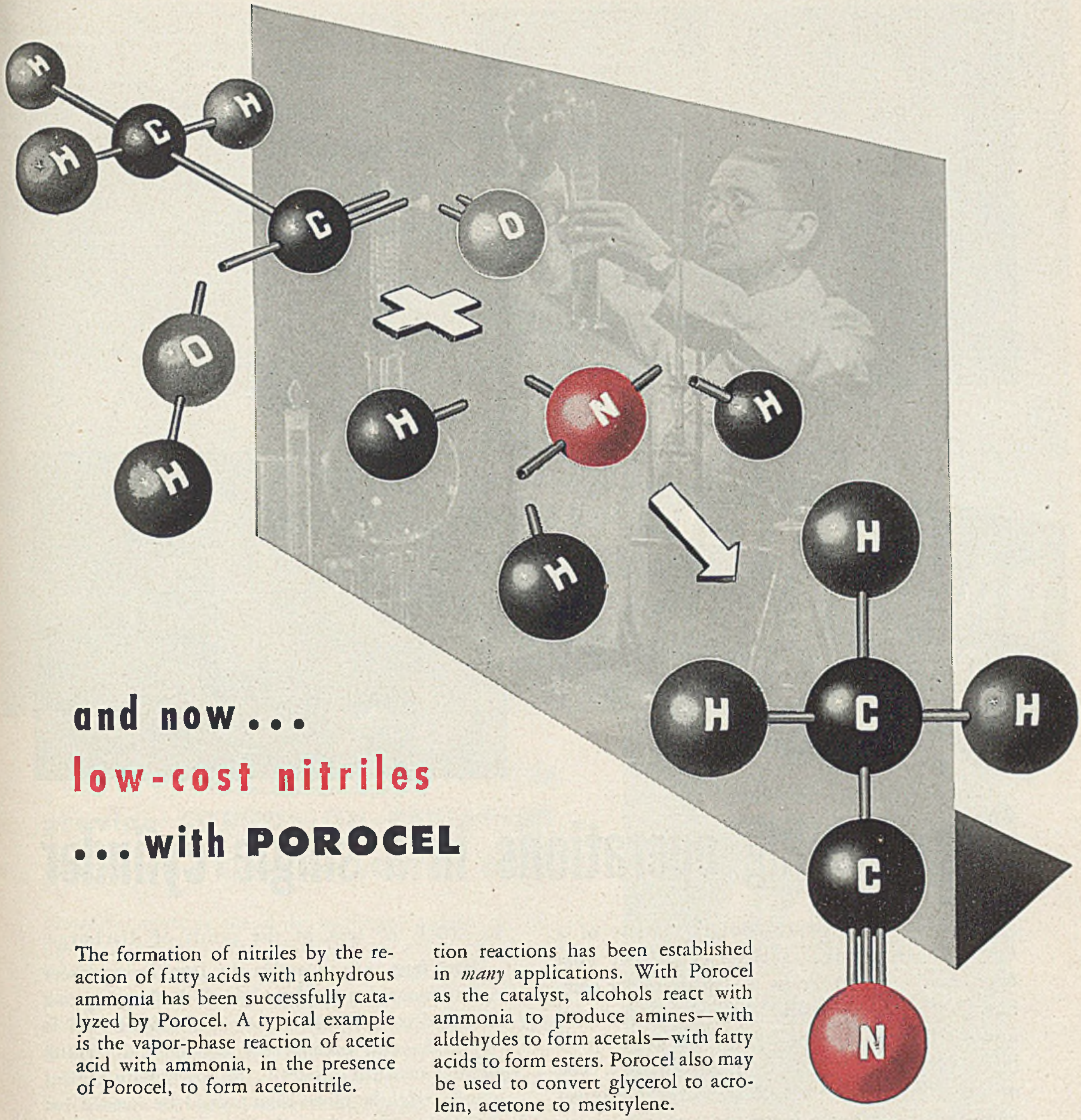

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. . . with POROCEL

The formation of nitriles by the reaction of fatty acids with anhydrous ammonia has been successfully catalyzed by Porocel. A typical example is the vapor-phase reaction of acetic acid with ammonia, in the presence of Porocel, to form acetonitrile.

Common to all such reactions are Porocel's cost-saving advantages—benefits accruing from continuous processing, and added savings made possible by the low initial cost of Porocel. Still further economies result from the ruggedness of this bauxite catalyst—its ability to stand up under severe conditions of temperature, flow, regeneration and handling.

Porocel's ability to promote dehydration reactions has been established in *many* applications. With Porocel as the catalyst, alcohols react with ammonia to produce amines—with aldehydes to form acetals—with fatty acids to form esters. Porocel also may be used to convert glycerol to acrolein, acetone to mesitylene.

Finding a way to make low-cost nitriles is a good example of the work our research staff is doing in its constant study of the catalytic action of Porocel. And the facts it has assembled are at your disposal, without obligation, to help you improve your own process or reduce costs. Outline the facts to: *Attapulgus Clay Company (Exclusive Sales Agent), Dept. C, 210 West Washington Square, Philadelphia 5, Pa.*

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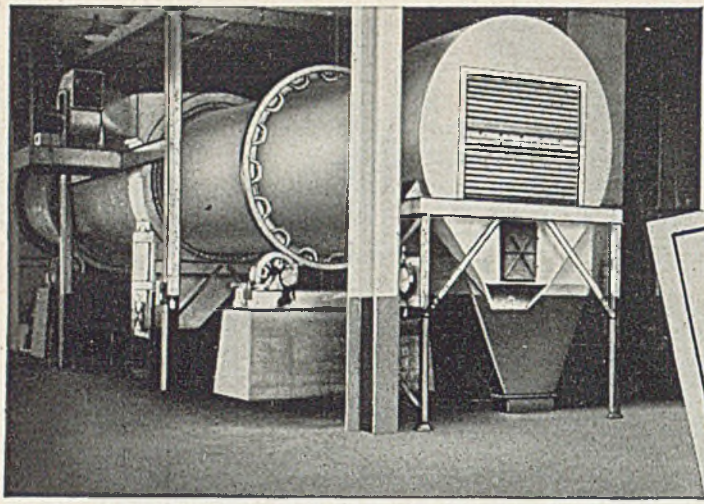

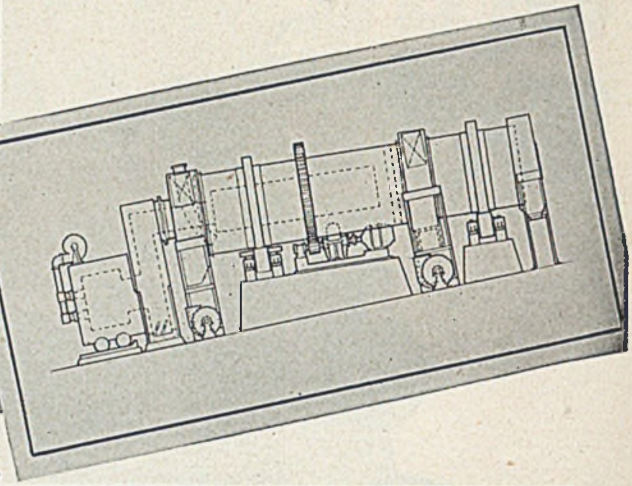

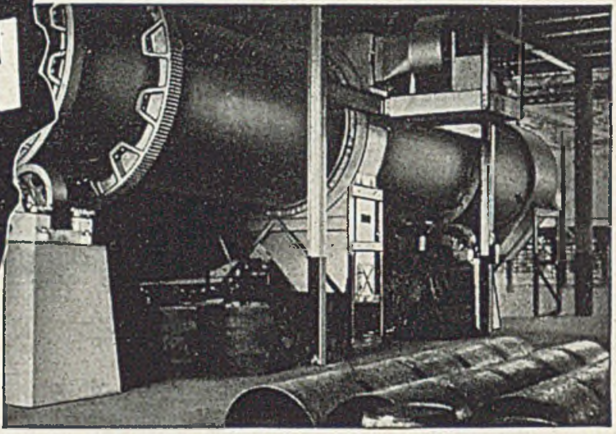

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..2 processing operations in a single cylinder

● Bartlett-Snow dryer-coolers consist of a Bartlett-Snow Style "H" indirect-direct heat dryer, and a Bartlett-Snow rotary air cooler combined into a single shell. Material is introduced into the feed end of the dryer,— and gives up all but a very small amount of its moisture. The material then passes through a specially designed lock—which—without involving any moving or complicated parts—permits the material but not the hot air and flue gases to pass into the "cooler" end. Here, in the cooling section, the material loses the balance of its moisture, and also enough sensible heat to bring the temperature down to 110°F. or less, at the point of discharge.

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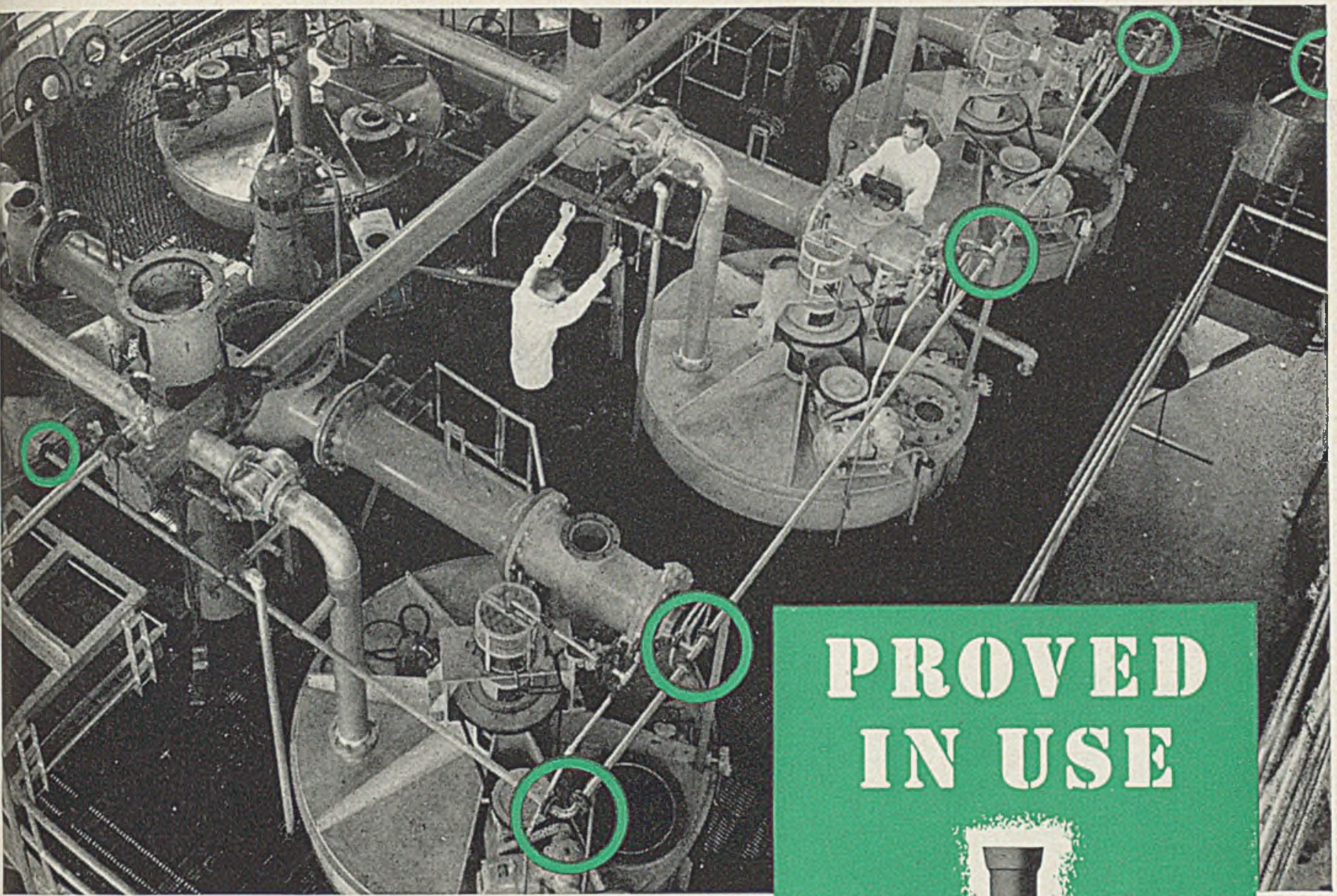

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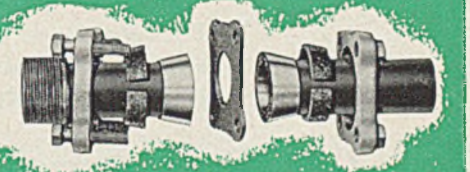
Tri-Clover Stainless Steel Conical End fittings are available in a complete line of ells, tees, crosses, returns, reducers, etc., from 1" thru 10" O. D. Shown below is the fast method of assembling, through leak tight flanges and simple gaskets, for pressures to 250 psi.



Be sure to see the Tri-Clover Exhibit at the New York Chemical Exposition . . . BOOTHS 567-568.

Tri-Clover *Conical End* Fittings provide CORROSION-RESISTANT Conveying Lines at LOWER COST

Illustrated above is one of the increasing number of large liquid conveying line installations assembled with Tri-Clover stainless steel type 316 Conical End fittings throughout. This installation, at the Plymouth, Fla., plant of Vacuum Foods, Inc., has attracted wide interest because of advanced engineering techniques employed.

Through the use of Tri-Clover Flanged Type Conical End fittings and stainless steel light gauge tubing, companies like this are realizing tremendous savings in engineering and installation costs. In addition, they are assured of longer fitting and line life, freedom from leakage, and complete protection against product contamination.

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TRIALLOY AND STAINLESS STEEL SANITARY FITTINGS, VALVES, PUMPS, TUBING, SPECIALTIES

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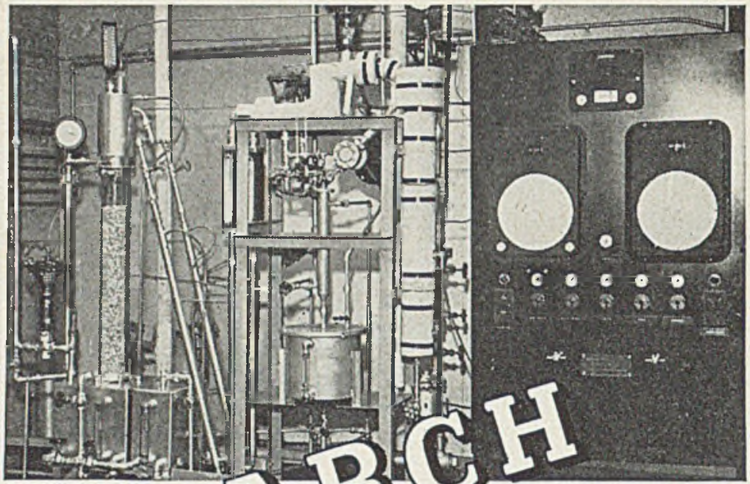
THE Complete LINE



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helps industry save over

1 BILLION POUNDS

of solvents annually

"Columbia" Activated Carbon in recovery plants now installed or being supplied can annually recover 1,250,000,000 pounds of solvents worth over 100 million dollars. This saving is made possible by special types of activated carbon and engineering features of recovery plants. Our research staff continues to seek improved solvent recovery carbons and processes.

To continue improving the equipment we design and supply for solvent recovery, we have installed an automatically controlled experimental pilot plant. This pilot plant duplicates large scale plant processes, thus giving accurate data for:

The evaluation of solvent recovery carbons—The perfection of new processes—The testing of materials of construction—Improvement of equipment design—The development of special operating methods.

Research in production and application of vapor adsorbent carbons continues to lead to new developments—meaning increased savings to you. Ask us about your adsorbent problems.

We supply vapor adsorbent carbons for use as catalysts and catalyst carriers; also, for air deodorization, gas purification, and other applications. Write for our newly revised booklet SOLVENT RECOVERY, F-4410.

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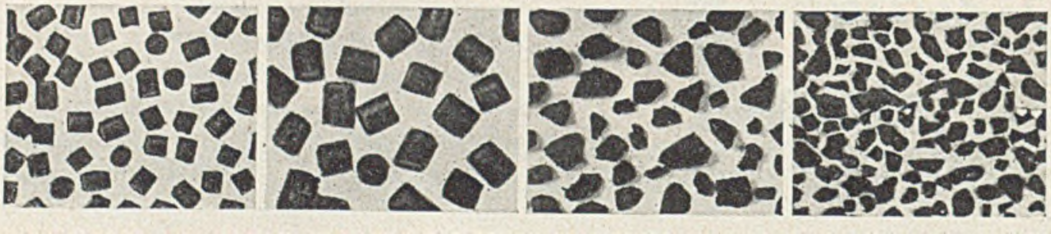

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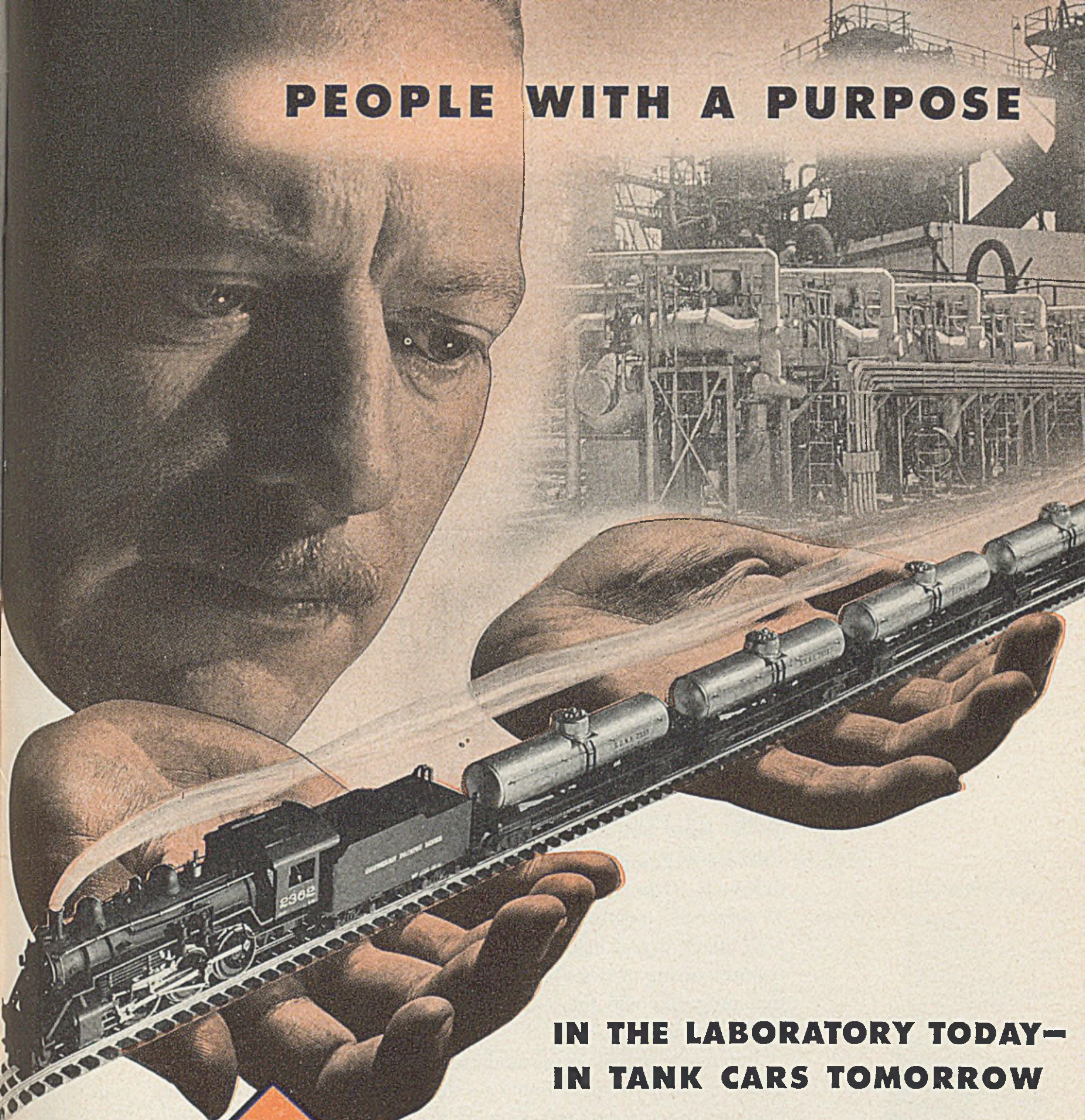

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Before an Oronite product is offered to industry, you can be sure it has proven its value and performance in Oronite laboratories. Here, each new industrial chemical is subjected to rigorous tests; examined and re-examined in the light of analysis and research.

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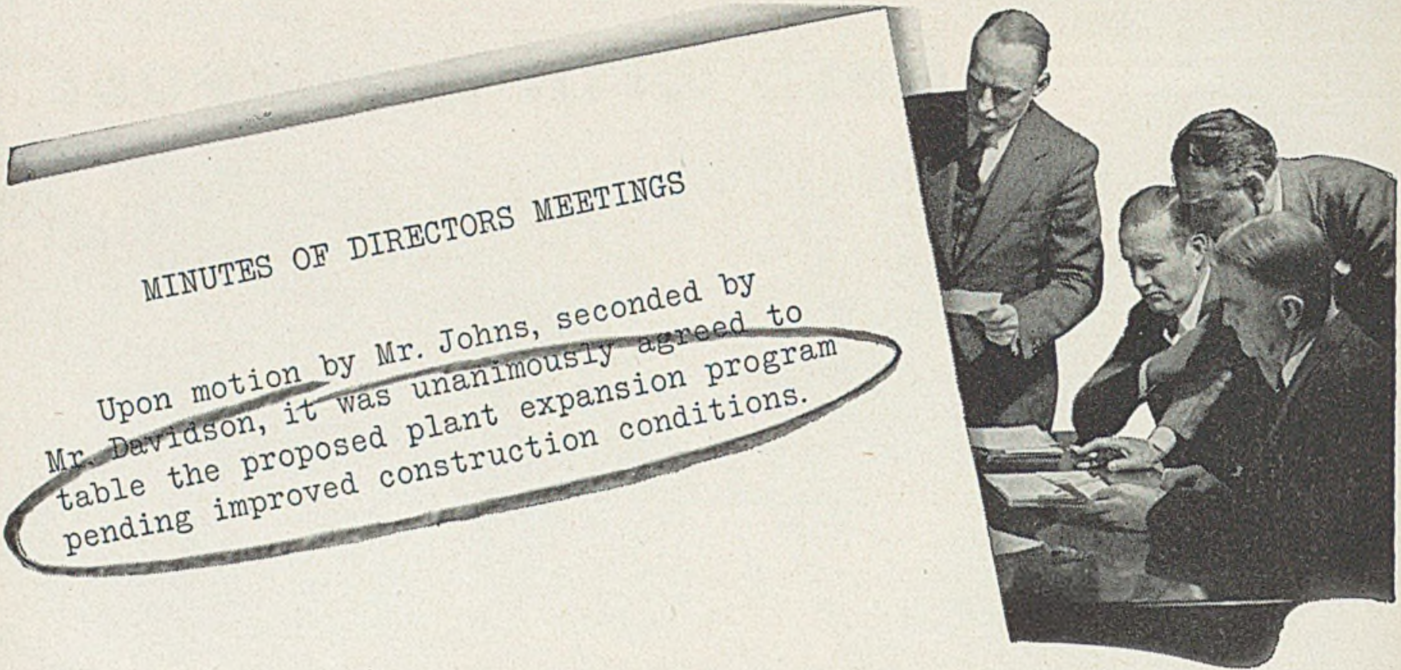

MINUTES OF DIRECTORS MEETINGS

Upon motion by Mr. Johns, seconded by
Mr. Davidson, it was unanimously agreed to
table the proposed plant expansion program
pending improved construction conditions.

You don't *have* to do that, Gentlemen...

INVESTIGATE READY-BUILT, READY-TO-OCCUPY PRODUCTION FACILITIES AVAILABLE NOW

To be sure, building materials *are* still short. Equipment deliveries *are* delayed. Other new-construction "headaches" continue to interfere with plant expansion plans, branch manufacturing or distribution relocation programs and the establishment of new enterprises.

But many industrialists and management executives have found a practical way to carry out their plans. They have solved their problems by purchase or lease of Government-owned industrial facilities . . . at money-saving prices.

Hundreds of good, usable, strategically-located plants and properties are available now. Small-town plants down South, big-city establishments in the Midwest, land and buildings on Atlantic, Pacific and Gulf coasts. One or more of these may be just right for you, or readily and economically adaptable to your needs.

So, before you "table" your plans, investigate the facilities ready and waiting for you to bid on today. Check the offerings listed in the new Plantfinder—consult our nearest office for further information.

NEW PLANTFINDER—FREE... Describes immediately available properties—lists others soon to be made available—indexed, cross-indexed for your convenience. Write for free copy—to the address listed below, on your company letterhead, please.

WAR ASSETS ADMINISTRATION
OFFICE OF REAL PROPERTY DISPOSAL

GOVERNMENT WAA SURPLUS

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SEE I★P★E for Special & Standard Process Plants and Equipment

THIS GREEN STRIPE

...the I★P★E Seal of Warranty on equipment

- ***Built***—to last
- ***Built*** —of warranted materials fitted to *your* needs
- ***Built***—to precise I★P★E standards
- ***Built***—to advanced engineering and design specifications
- ***Built***—to do more with less outage

ENGINEERED TO YOUR REQUIREMENTS

SEE 1

ENGINEERING. I★P★E equipment—both complete plants and individual units—incorporates advanced engineering. Result: equipment created *functionally* to fit your *own* process, simplified plant layout, and in many instances, a better product. This broad engineering experience has resulted in major improvements in standard equipment used by the process industries. I★P★E technological skills can, and do, incorporate both engineering and design improvements, especially where special equipment has been "tailored" to your particular manufacturing process.

SEE 2

DESIGN. Advanced design improvements are an important feature of I★P★E process equipment. I★P★E designers strip equipment down to fundamentals, adding only those design improvements that add greater efficiency. This means lower maintenance cost, less trouble shooting, longer equipment life and less outage!

If Production Is Holding Up Your Orders— Remember I★P★E Delivers Equipment on Time

MANUFACTURERS ARE being flooded with orders in these days of reconversion . . . particularly the chemical process industries. Even if full time production finds you unable to keep up with the avalanche of orders, consider this . . . let I★P★E analyze your production process . . . make suggestions that will help to step up your output through the addition of new process equipment.

MANY NATIONAL MANUFACTURERS have been able to increase production within a short period by calling in I★P★E as *Process Equipment Counsel.* Each I★P★E installation recommended is handled as a specific problem, geared solely to your product, rate of production and physical conditions encountered. The delivery of recommended equipment *will be made on time!* I★P★E has been the first to design certain types of chemical processing equipment that have become the standard for the industry. We have "tackled" and solved engineering problems attempted by few other manufacturers.

I★P★E's STAFF is at your disposal without obligation. Why not write, 'phone or wire today?

See I★P★E for

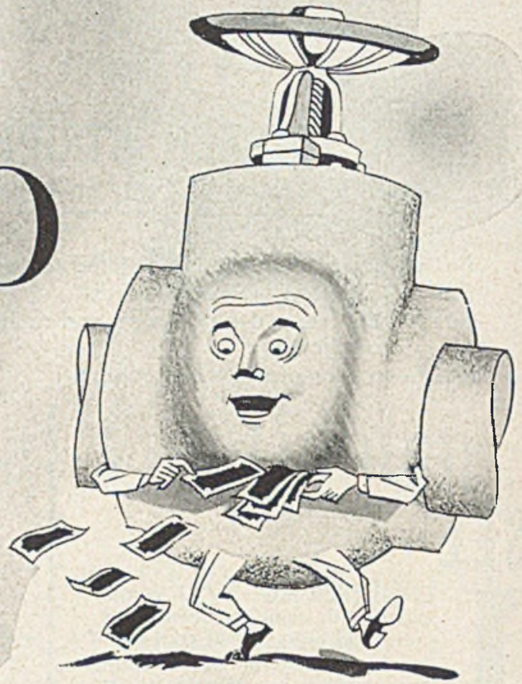
- Agitators
- Agitator Drives
- Autoclaves
- Chemical Process Equipment
- Complete Process Plants
- Condensers
- Conical Dry Blenders
- Continuous Processing Units
- Dowtherm Kettles
- Digesters
- Dissolvers
- Electric Kettles
- Extruders
- Gas Absorbers
- Grease Mixers
- Heat Exchangers
- Horizontal Mixers
- Jacketed Processing Units
- Kettles
- Mixers
- Nitrators
- Paint Mixers
- Paste Mixers
- Side Entering Agitators
- Soap Crutchers
- Special Process Machinery
- Special Valves
- Stills
- Sulfonators
- Synthetic Resin Plants
- Turbine Agitated Units
- Vacuum Kettles & Mixing Equipment

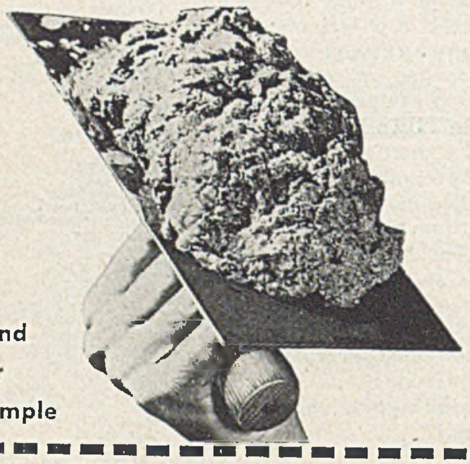
I★P★E
precision engineered design

"Special and Standard Process Equipment Engineered to Your Requirements"

INDUSTRIAL PROCESS ENGINEERS

5207 HUDSON AVENUE, WEST NEW YORK, N. J.



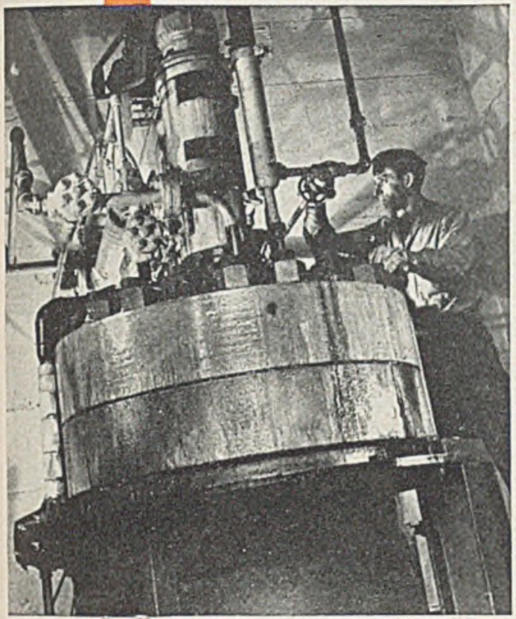


Hooker Cyclohexanol and Methyl Cyclohexanol

Solvents
Plasticizers
Homogenizing Agents

FOR

Lacquers
Coatings
Resins



Hooker high pressure autoclaves in which hydrogenations are carried out receive periodic inspection and careful maintenance.

HERE ARE TWO SPECIAL PRODUCTS worthy of investigation in your compounding and application of resins and plastics.

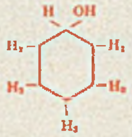
Cyclohexanol and Methyl Cyclohexanol have excellent solvent and plasticizing properties for many natural and synthetic resins. Cyclohexanol is particularly well adapted as a solvent for various oils, gums and waxes used in lacquer manufacture. It blends well with more volatile solvents and has excellent homogenizing ability. It is also compatible with a variety of resins which may be used in coating composition.

Methyl Cyclohexanol is an excellent solvent for waxes and resins, particularly the cellulose esters and ethers. Its low volatility and good emulsifying properties indicate a wide usefulness in the coating composition field.

Principal physical characteristics are listed below. Additional information is contained in Hooker Technical data sheets. When writing for more information please use your business letterhead.

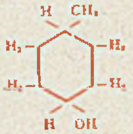
PHYSICAL DATA

Cyclohexanol
$C_6H_{11}OH$



Mol. Wt.	100.1
Sp. Gr., 25°/15.5°C	0.945
R. I., n20/D	1.4654
Flash Point	68°C
F. R. High Grade	18° to 22°C
Tech Grade	0° to 5°C
B. R. High Grade (100%)	159° to 163°C
Tech Grade (95%)	155° to 165°C

Methyl Cyclohexanol
$CH_3CH_{10}OH$



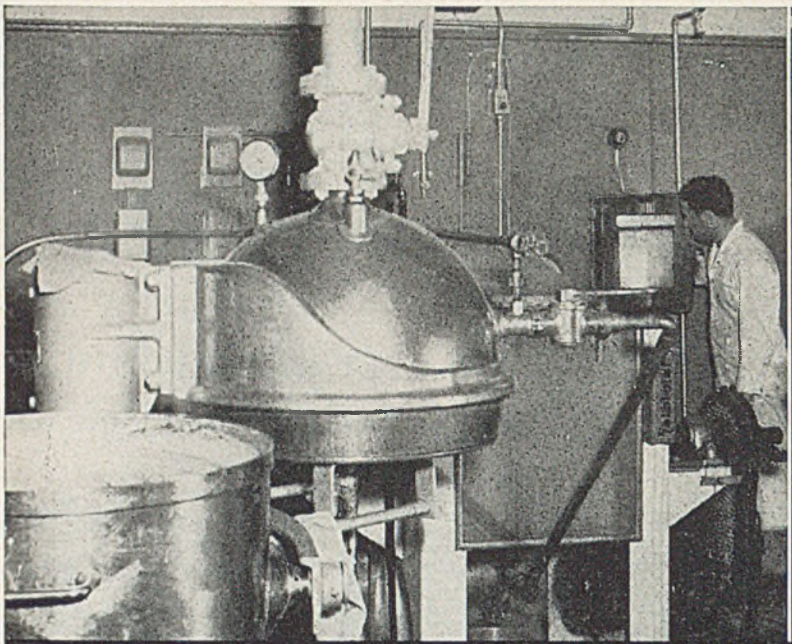
Mol. Wt.	114.1
Sp. Gr., 15.5°/15.5°	0.924
R. I., n20/D	1.461
Flash and Fire Points	71°C
F. R.	about 20°C
B. R. (100%)	155° to 180°C

HOOKER ELECTROCHEMICAL COMPANY

9 Forty-Seventh St., Niagara Falls, N. Y.
New York, N. Y. Wilmington, Calif. Tacoma, Wash.

HOOKER CHEMICALS

Caustic Soda Paradichlorbenzene Muriatic Acid Chlorine Sodium Sulfide Sodium Sulfhydrate



Micromax Records Cooking Temperatures
Vick Chemical Co.

Speedomax Recording 200-600 F
Gulf Research Corp.

Recorders and Controllers for "EVERYBODY"

Did you ever try this way of selecting the correct Recorders or Controllers for a process?

First step is an analysis of basic requirements (with our help, if you wish) to include such factors as:

Type of Control action if any — on-and-off; fully proportioning; manual based on instrument readings.

Type of Control mechanism — pneumatic or electric.

Type of instrument — recording or non-recording; single-point or multiple; round-chart or strip; speed of response.

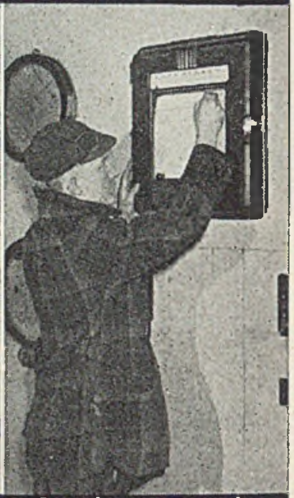
Inherent characteristics of the process, which help determine the correct instrumentation.

Meeting Industry's Need for Stable Control

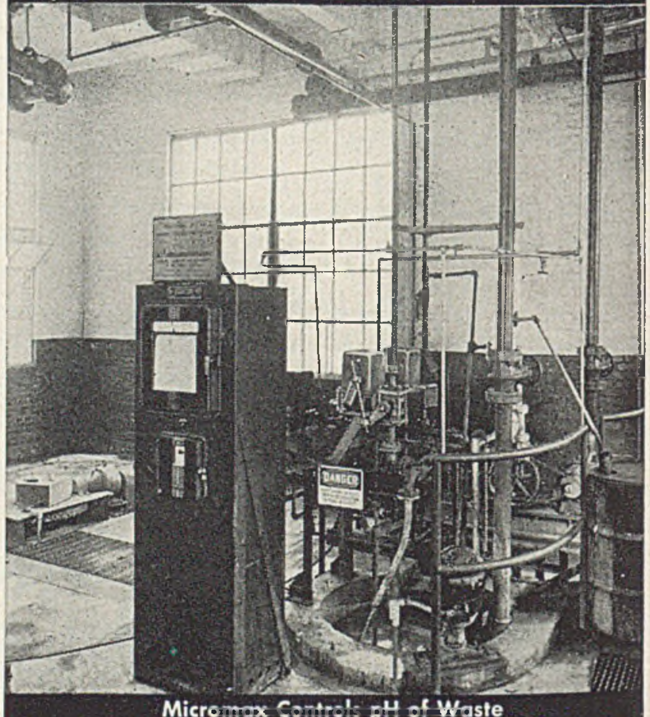
For any combination of requirements which may appear, Micromax and/or Speedomax instruments meet the need — exactly and completely. And they do more — they contribute a highly *stable, continuous* control, which helps your plant maintain production continuously.

This quality of stability of course includes accuracy, but stability's real value is to *make accuracy useful.* Stability means "no interference" by weather, temperature, vibration, dust, electric fields, etc. Stability enables Micromax and/or Speedomax to meet the needs of almost "everybody." For details write Leeds & Northrup Co., 4920 Stenton Ave., Phila. 44, Pa.

Micromax Controllers
Hoffmann-La Roche Inc.



Speedomax Recorder
Alan Wood Steel Co.



Micromax Controls pH of Waste
Bakelite Corp.

LEEDS & NORTHRUP

MEASURING INSTRUMENTS · AUTOMATIC CONTROLS · TELEMETERS
HEAT-TREATING FURNACES

Jrl. Ad ND4 (1a)

ANNOUNCING A NEW AND LARGER

Size Range

STAINLESS STEEL MECHANICAL AND PRESSURE TUBING

These are common sizes. A limited number of other sizes can be made by welding direct to size, and intermediate sizes can be made by cold drawing. Wall thicknesses heavier than those shown may be obtained in most sizes. Many geometric shapes other than round can be supplied with limits of a 9½" periphery.

OUTSIDE DIAMETER	GAUGE RANGE	OUTSIDE DIAMETER	GAUGE RANGE
⅜"	16-22	1½"	10-20
7/16"	16-22	1⅝"	10-20
½"	14-22	1¾"	10-20
⅝"	14-21	1⅞"	10-20
11/16"	14-21	2"	9-20
¾"	13-20	2⅛"	9-20
⅞"	12-20	2¼"	9-20
1"	11-20	2⅜"	8-20
1 1/16"	11-20	2½"	8-20
1⅛"	11-20	2⅝"	8-18
1¼"	11-20	2¾"	8-18
1 5/16"	11-20	2⅞"	8-18
1⅜"	11-20	3"	8-18

The above sizes are available in types 304, 309S, 310, 316, 317, 347, 430 and 446.

Type 302 is available in a limited range of sizes for ornamental use only.

STAINLESS STEEL PIPE

NOMINAL PIPE SIZE	OUTSIDE DIAMETER	SCHEDULE 40 STANDARD PIPE WALL THICKNESS	SCHEDULE 10 LIGHT WALL PIPE WALL THICKNESS
⅛"	.405	.068	.049
¼"	.540	.088	.065
⅜"	.675	.091	.065
½"	.840	.109	.083
¾"	1.050	.113	.083
1"	1.315	.133	.109
1¼"	1.660	.140	.109
1½"	1.900	.145	.109
2"	2.375	.154	.109

The above Pipe Sizes are available in the Chrome-Nickel analyses of Enduro Stainless Steel.

OF ELECTRUNITE

STAINLESS STEEL TUBING

...made of Republic Enduro

Now, whatever your requirements for stainless steel tubing, you'll find the answer in ELECTRUNITE Tubing made of time-tested Republic ENDURO.

In addition to the many standard tubing sizes, ELECTRUNITE *is available* in a range of much-in-demand Standard and "Schedule 10" pipe sizes—made by the same superior forming and welding process which distinguishes all ELECTRUNITE Stainless Steel Tubing.

Complete information is available upon request. Call your nearest Steel and Tubes district office, or write for full details.

REPUBLIC STEEL CORPORATION
STEEL AND TUBES DIVISION • CLEVELAND 8, OHIO
Export Dept.: Chrysler Bldg., New York 17, N.Y.

REPUBLIC STEEL
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Republic
ELECTRUNITE
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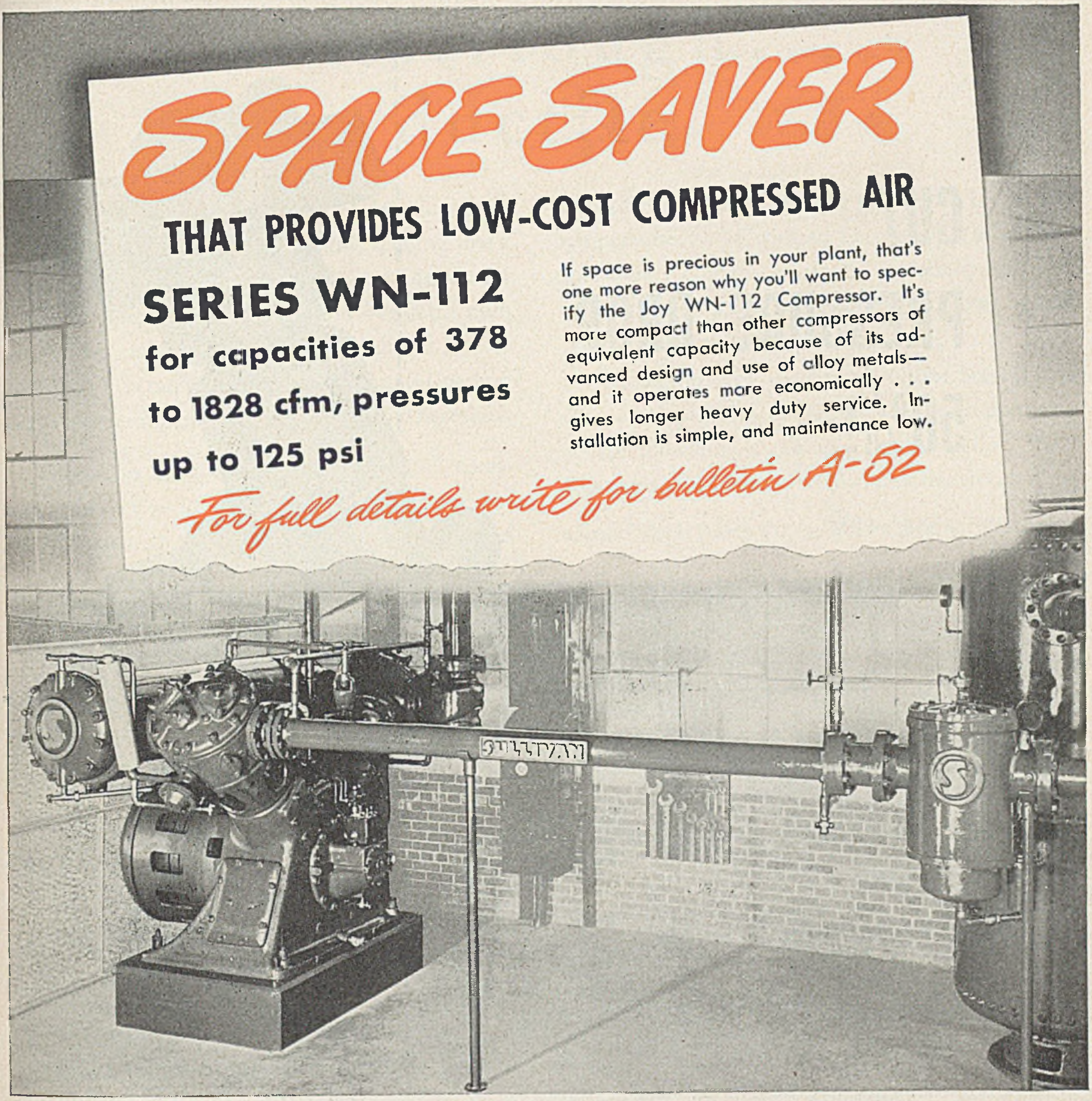
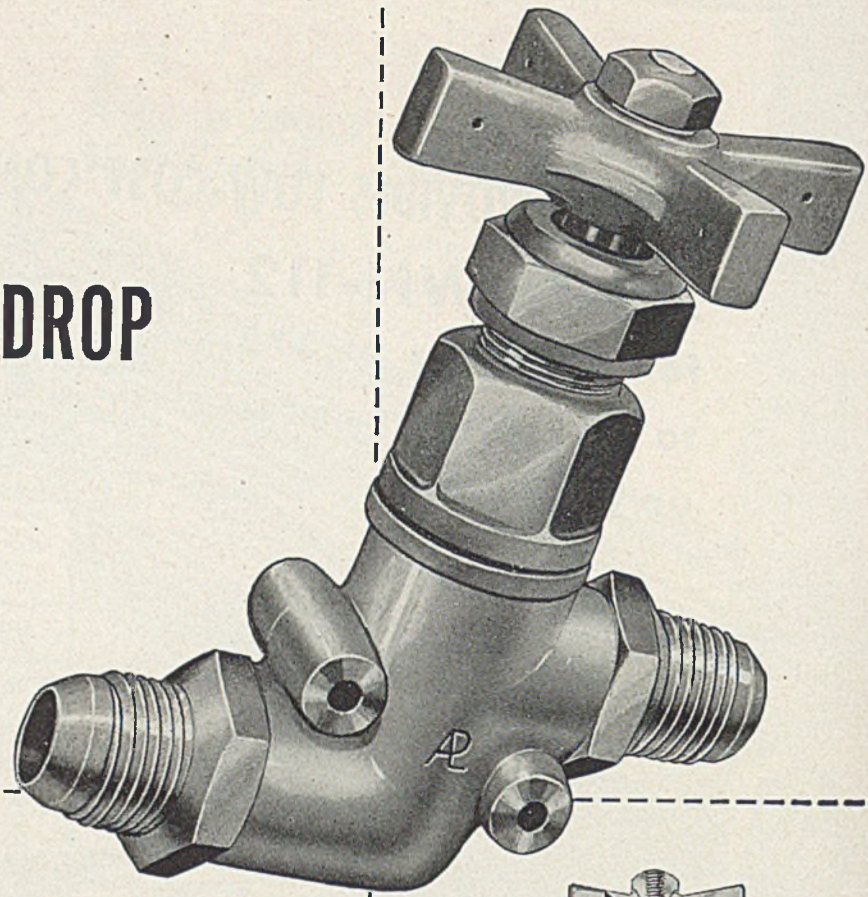
STAINLESS STEEL TUBING




Consult a Joy Engineer

CUT PRESSURE DROP 50%!



Operating tests prove you can reduce pressure drop in your hydraulic or fluid transmission systems by installing PARKER Globe Valves.

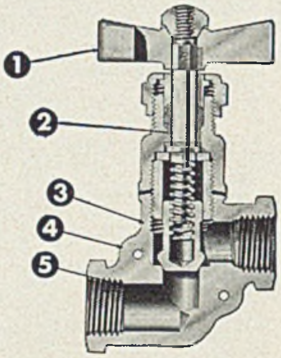
The secret is free flow. The offset body design eliminates pockets and intricate chambers that trap liquids and gases. The result is smoother flow—less turbulence—and less pressure drop—by as much as 50%.

PARKER Needle Valves also keep pressure drop low. You can install these Globe and Needle valves directly into the circuit. Models are available in various combinations of tube ends and pipe threads, thus eliminating awkward adapters that block flow—add weight—and take up valuable space.

If you're interested in pressure-tight systems for moving liquids and gases, you'll want more information about these *precision*-made PARKER Valves. Write for Bulletin A52.

THE PARKER APPLIANCE COMPANY
17325 Euclid Avenue · Cleveland 12, Ohio
Plants: Cleveland and Los Angeles
Offices: New York, Cleveland, Chicago, Los Angeles, Dallas, Atlanta
Distributors in Principal Cities

Parker
TUBE FITTINGS • VALVES



WHY PARKER GLOBE VALVES GIVE TROUBLE-FREE SERVICE

1—Prong handle provides easy grip.

2—Stem is non-rising type—permits easy installation where space is limited.

3—Forged brass body is small, flat, thin, strong.

4—Mounting lugs are forged into the body.

5—Offset design provides smooth, free flow.

★

PARKER offers manufacturers a complete line of precision-made industrial valves for small diameter tubing systems.

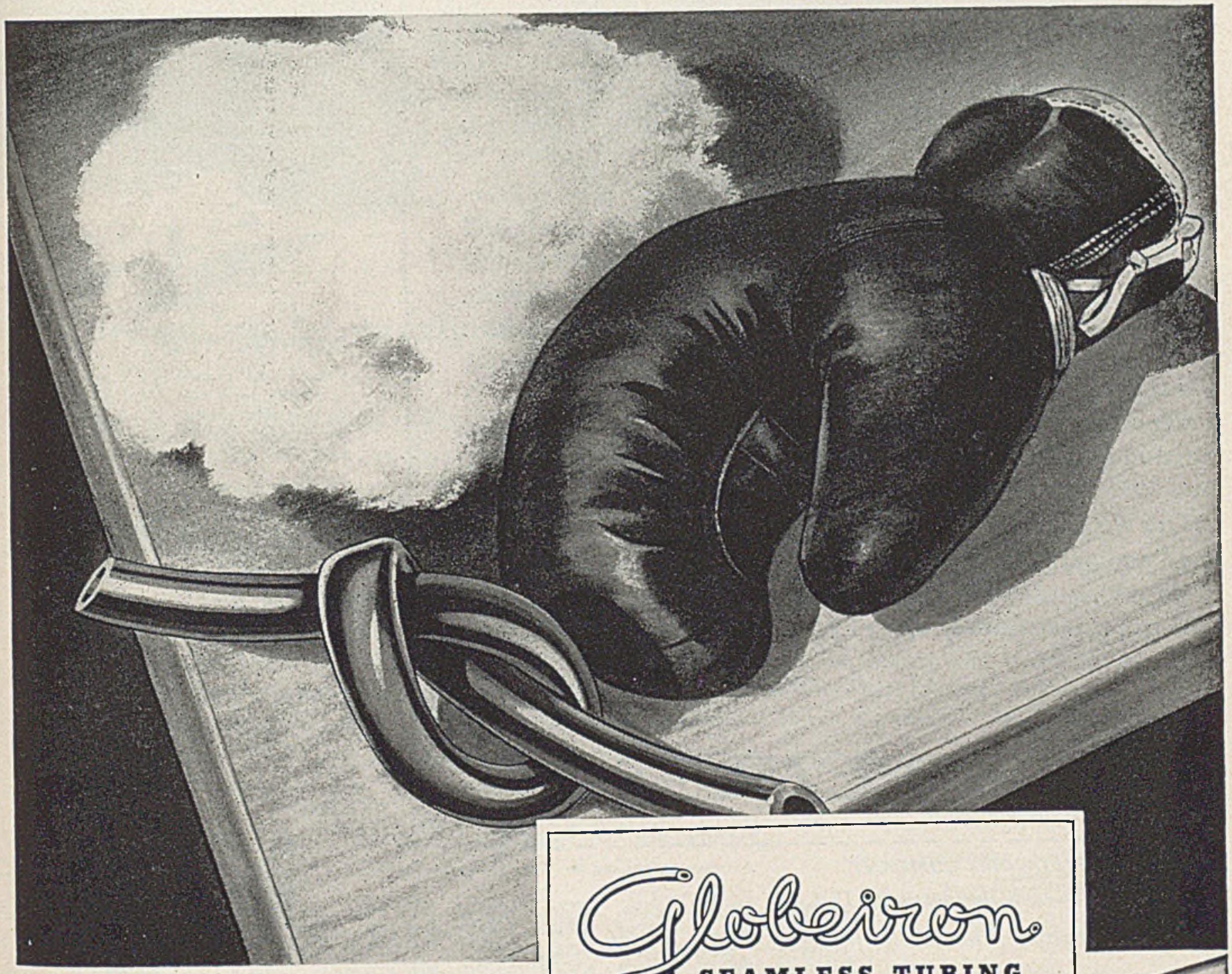
Soft . . . tough . . . ductile

SOFT . . . tough . . . ductile — that's Globeiron high purity ingot iron seamless tubing. Tubing that's ideal for severe forming operations—cold or hot. Its metal structure is uniquely uniform — almost pure ferrite. Its magnetic permeability is almost that of pure iron. You can weld it with any common method — no pre-heating or other precautions are necessary.

Globeiron is superior to many steels in corrosion resistance — in any applications wherever corrosive attack is accelerated by segregations and impurities in steels. It may be hot-worked in any temperature range without becoming brittle. Pressure tube requirements, where uniformity, ductility and purity of metal are essential, can best be met with Globeiron seamless tubing.

Globeiron is a product of Globe Steel Tubes Co. — a specialized, dependable manufacturing source for seamless tubing in carbon, alloy, stainless steels, and Gloweld welded stainless steel tubing.

Globe Steel Tubes Co. • Milwaukee 4, Wisconsin.



Globeiron
SEAMLESS TUBING

Write for Globeiron Bulletins
Nos. 109A and 113

HAVE YOU INVESTIGATED VINSOL

a low-cost thermoplastic resin with many uses

IF you're looking for both economy and versatility in a resin —it's Hercules Vinsol®!

Low in cost and immediately available, this resin contributes many unique properties to a wide variety of compositions. Vinsol's properties include insolubility in petroleum hydrocarbons, and incompatibility with most petroleum oils and waxes. It is soluble in alcohol, esters, cyclic hydrocarbons, and chlorinated solvents.

Vinsol is compatible with cellulose acetate, nitrocellulose, and ethyl cellulose. It may be dispersed in natural rubber and most synthetic rubbers. Compatibility with zein makes it ideal as a component of shellac substitutes. Combined with lignin, it imparts improved flow. Vinsol can be made soluble with many vegetable oils by cooking Vinsol-vegetable oil to varnish-making temperatures.

Vinsol may be saponified with sodium or potassium hydroxide to form water-soluble soaps. It may be esterified with alcohols, or condensed with formaldehyde.

This economical thermoplastic resin is available in lump, flake, and pulverized form. It is also available in emulsion form of 40 per cent solids content. For more complete technical details, or for assistance in applying Vinsol, return coupon below.

HERCULES

HERCULES POWDER COMPANY
INCORPORATED
904 King Street, Wilmington 99, Del.

*I am interested in Vinsol Resin for:*______________________

____

*Name*______________________________

*Company*______________________________

*Street*______________________________

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These and Other Industries use Vinsol Resin

PLASTICS...

Modifier for ethyl cellulose, shellac, vinyl resins for phonograph records. Modifier and extender for phenol-aldehyde resins in molding powders, and as binders for rock wool insulation batts and laminated plastics.

PAPER...

Stiffener and modifier for heavy paper and paperboard . . . binder for lignin-like building boards made from fiber or cellulose products.

CONSTRUCTION...

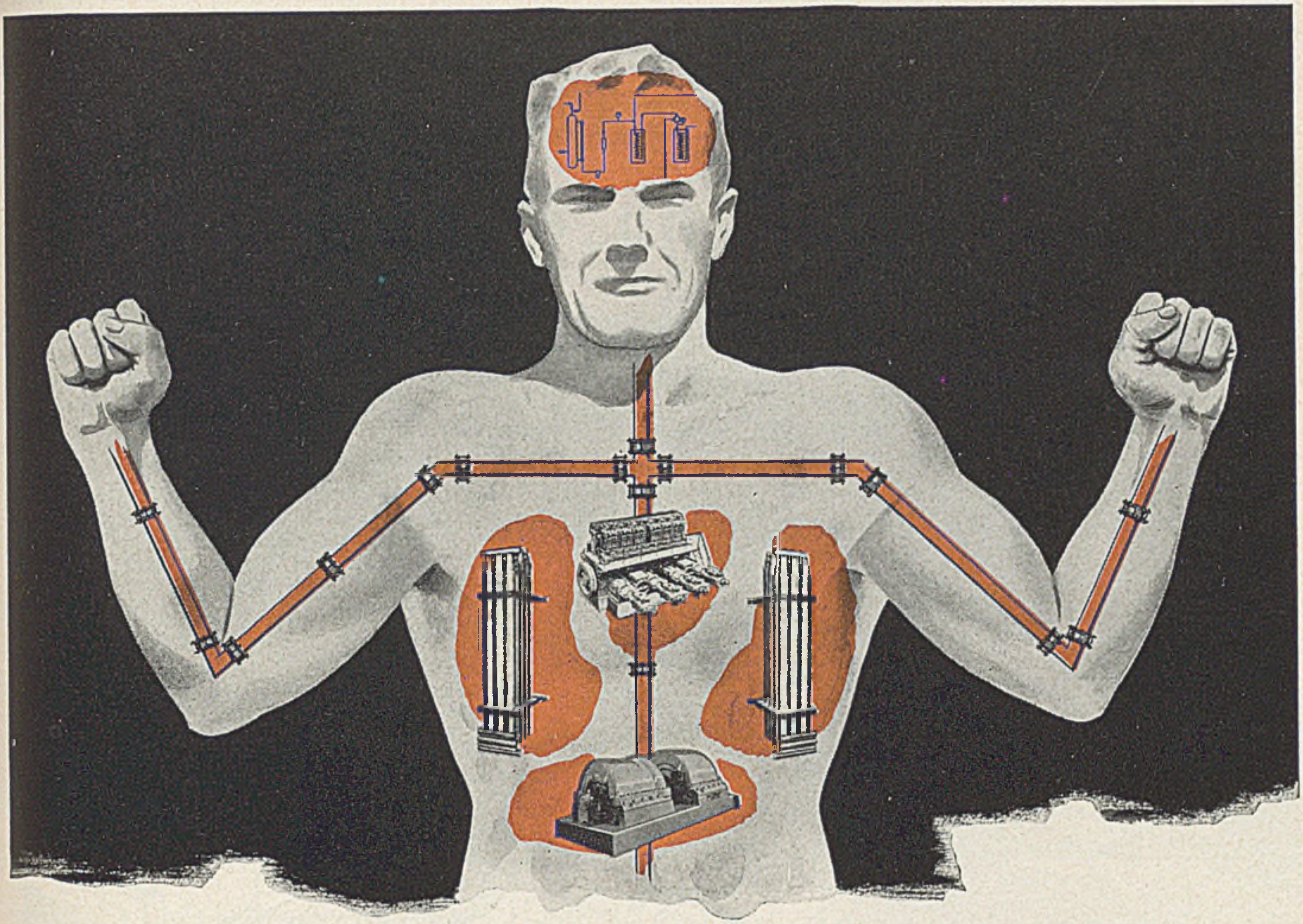
Vinsol and Vinsol NVX are used as emulsifiers and stabilizers for asphalt emulsions . . . air-entraining agents for Portland cement, masonry cement.

PROTECTIVE COATINGS...

Gives spirit varnishes, from cherry to mahogany, color without the use of dyes . . . low-cost ingredient for dark-colored nitrocellulose lacquers.

ADHESIVES...

Economical ingredient for linoleum and floor tile cements . . . in



Breathing is merely the oldest use for OXYGEN

● Today, industrialists expect to turn coal into gasoline, to make city fuel gas more efficiently, to reduce tremendously the time required for making steel—with oxygen.

Now that it's cheap enough.

Up to now oxygen has cost about $75.00 a ton.* Dresser Industries is engineering and equipping plants to produce oxygen at $5.00 a ton. Even less for larger plants. That's 95% pure. Or 99.5% pure!

Through Stacey-Dresser Engineering, Dresser Industries lays out the brains, but through six other member companies Dresser builds, also, the actual bones and muscle that determine the payoff of your investment: the compressors, engines, air inter & aftercoolers, reversing exchangers, regenerators, expanders, reboilers, pumps, and the numerous less spectacular components. For years many of these have been standard products of Dresser members.

What would you like to know about high purity oxygen—fantastically cheap? Dresser Industries, Inc., Terminal Tower, Cleveland 13, Ohio.

Ton O_2=24,000 cu. ft. standard conditions.

Creative Engineering FOR INDUSTRY
with special emphasis on oil, gas and chemistry

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INDUSTRIES, INC.

BOVAIRD & SEYFANG Mfg. Co.
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CLARK Bros. Co., Inc.
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DAY & NIGHT Mfg. Co.
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DRESSER Mfg. Division
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DRESSER Mfg. Company, Limited
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INTERNATIONAL Derrick & Equipment Co.,
Columbus, Marietta & Delaware, Ohio;
Beaumont, Texas; Torrance, Calif.

KOBE, Inc.,
Huntington Park, Calif.

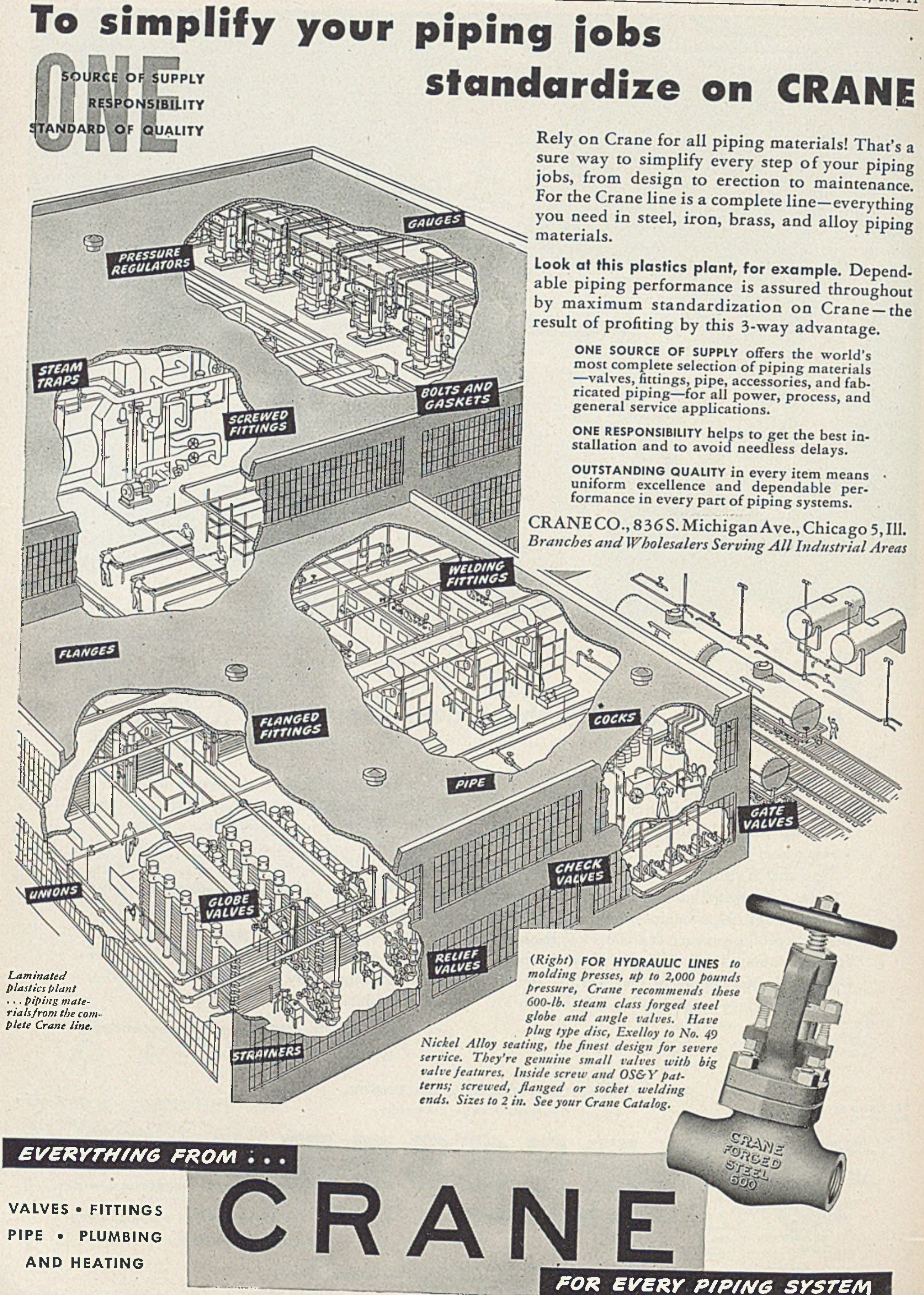
PACIFIC Pumps, Inc., Huntington Park, Calif.

PAYNE Furnace Co., Beverly Hills, Calif.

ROOTS-CONNERSVILLE Blower Corp.
Connersville, Ind.

SECURITY Engineering Co., Inc.
Whittier, Calif.

STACEY BROS. Gas Construction Company
Cincinnati, Ohio
Stacey-Dresser Engineering Division
Cleveland, Ohio



To simplify your piping jobs standardize on CRANE

ONE
SOURCE OF SUPPLY
RESPONSIBILITY
STANDARD OF QUALITY

Rely on Crane for all piping materials! That's a sure way to simplify every step of your piping jobs, from design to erection to maintenance. For the Crane line is a complete line—everything you need in steel, iron, brass, and alloy piping materials.

Look at this plastics plant, for example. Dependable piping performance is assured throughout by maximum standardization on Crane—the result of profiting by this 3-way advantage.

ONE SOURCE OF SUPPLY offers the world's most complete selection of piping materials—valves, fittings, pipe, accessories, and fabricated piping—for all power, process, and general service applications.

ONE RESPONSIBILITY helps to get the best installation and to avoid needless delays.

OUTSTANDING QUALITY in every item means uniform excellence and dependable performance in every part of piping systems.

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

Laminated plastics plant . . . piping materials from the complete Crane line.

(Right) **FOR HYDRAULIC LINES** *to molding presses, up to 2,000 pounds pressure, Crane recommends these 600-lb. steam class forged steel globe and angle valves. Have plug type disc, Exelloy to No. 49 Nickel Alloy seating, the finest design for severe service. They're genuine small valves with big valve features. Inside screw and OS&Y patterns; screwed, flanged or socket welding ends. Sizes to 2 in. See your Crane Catalog.*

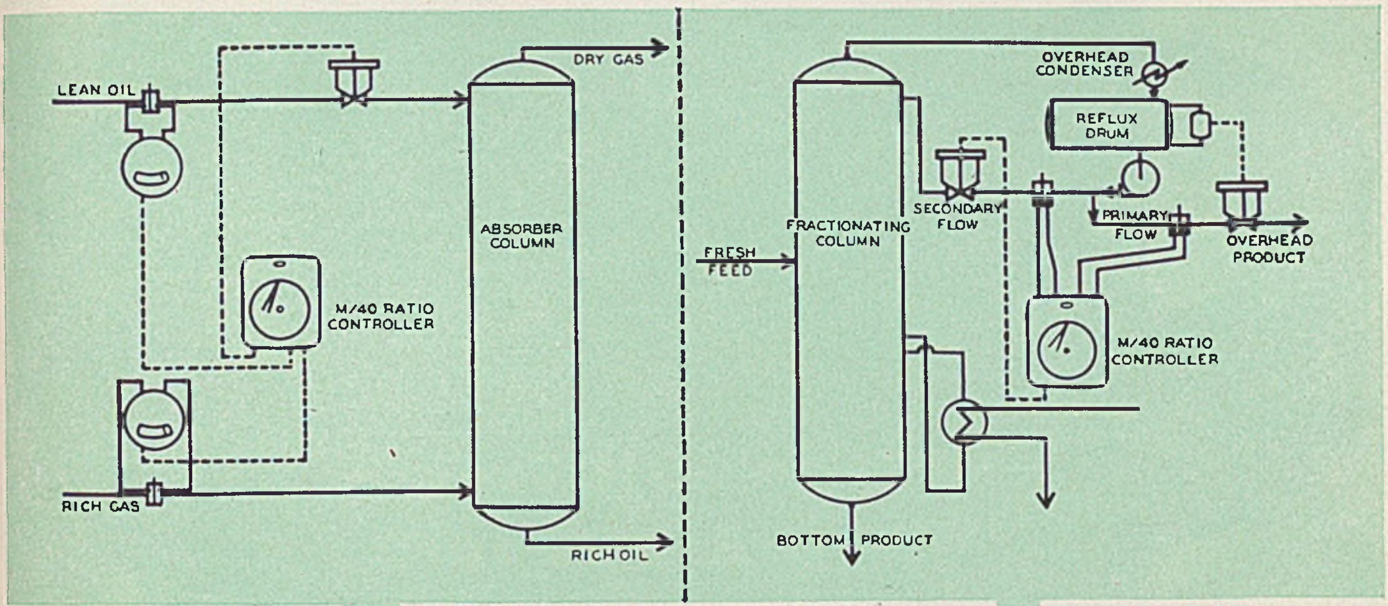
EVERYTHING FROM . . .

CRANE

VALVES • FITTINGS
PIPE • PLUMBING
AND HEATING

FOR EVERY PIPING SYSTEM

HERE'S *Automatic* HEAT ECONOMY PLUS CLOSER QUALITY CONTROL..



with FOXBORO Automatic Flow-Ratio Controllers on the Job . . .

REG. U. S. PAT. OFF.

BY CONTROLLING the flow of a liquid or gas in unvarying, continuous ratio to that of another, processes such as those illustrated can be streamlined to peak efficiency. Every change in the flow of the primary fluid is reflected by a proportional change in the secondary fluid flow, thereby maintaining a constant ratio between the two. The operation is precise, instantaneous, and completely automatic. Liquid level, pressure, and other process variables may similarly be ratio-controlled. (Controllers are also available to ratio more than one secondary flow to a common primary flow.)

The Foxboro Flow-Ratio Controller offers unique advantages both in its measuring system and its M-40 control mechanism. Its combination of accuracy, sensitivity, and simplicity is unrivalled.

The ratio mechanism has been specifically designed to maintain set ratios accurately through the whole range of the instrument. The desired ratio is easily obtained by turning a calibrated thumb wheel visible through the chart plate. The mechanism is a compact, rugged unit that fits into any Model 40 Controller.

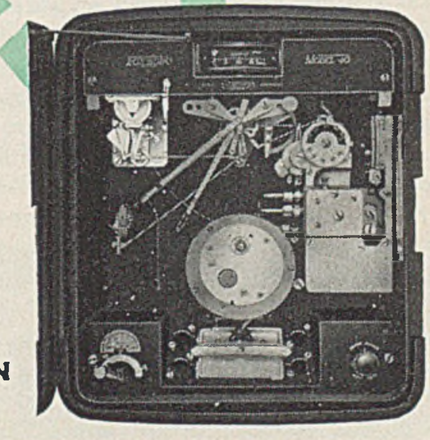
Write for detailed information. **The Foxboro Company, 40 Neponset Avenue, Foxboro, Massachusetts, U. S. A.**

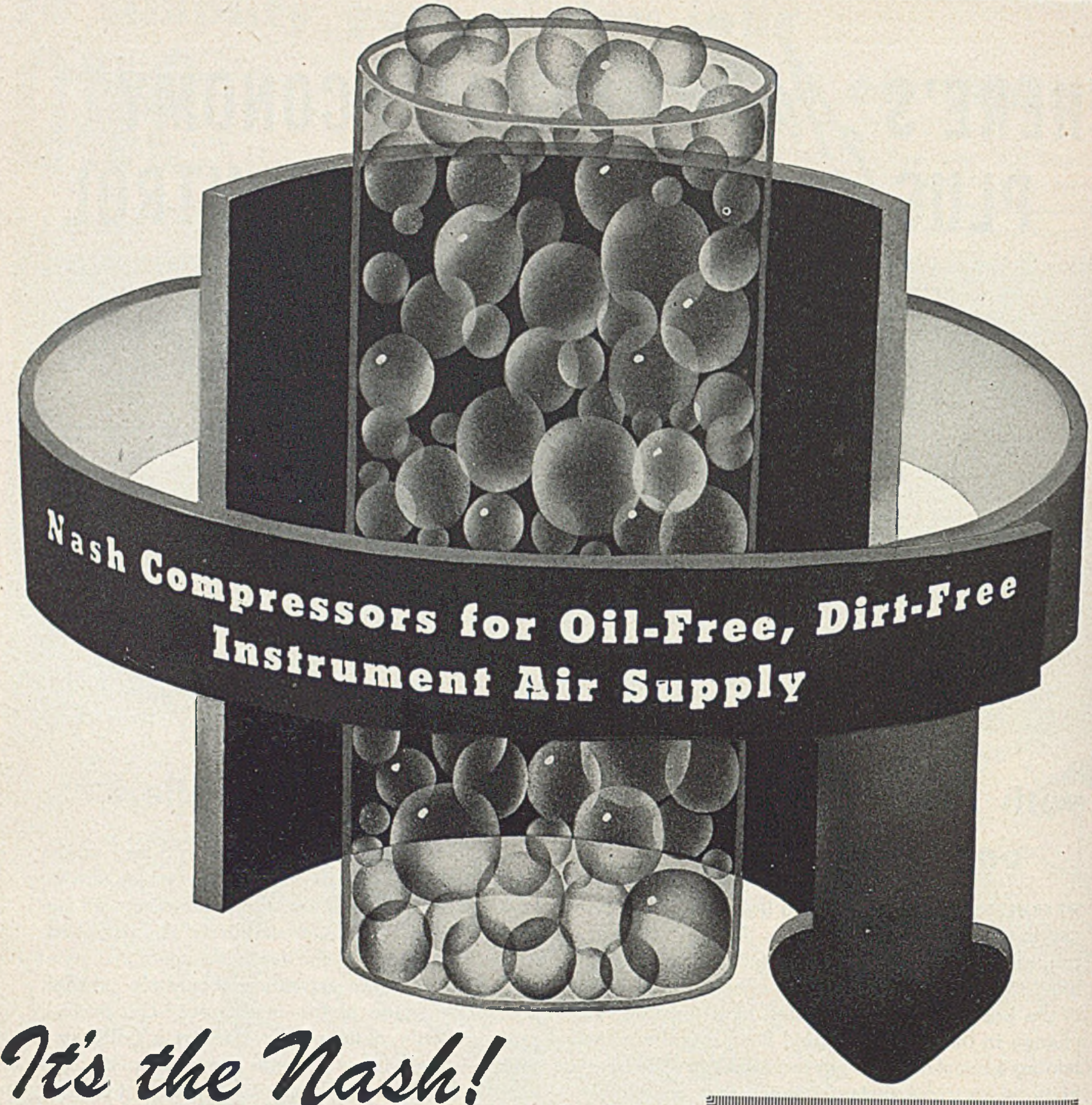
FOXBORO
REG. U. S. PAT. OFF.

M·40

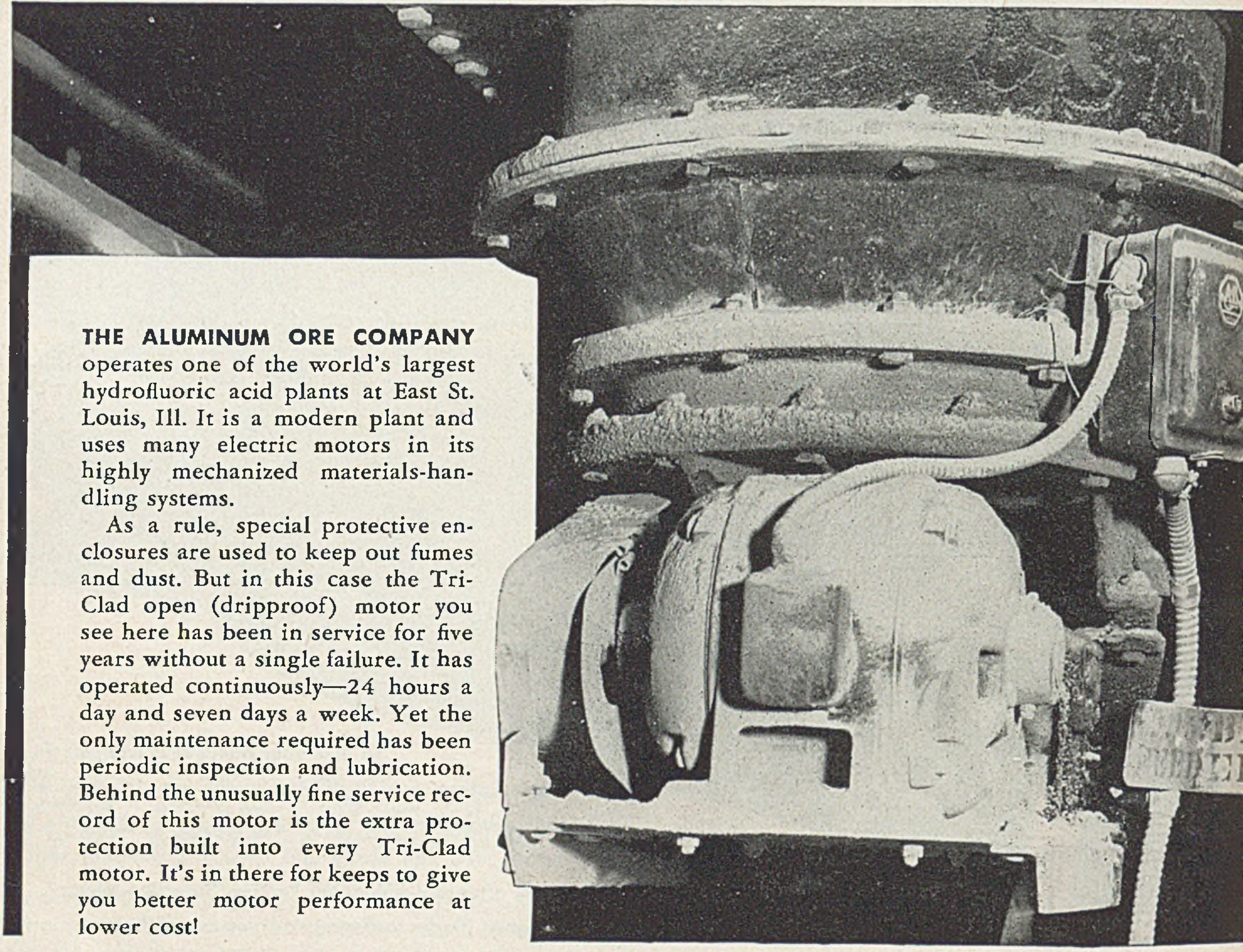
FLOW-RATIO CONTROLLER

THE ONLY CONTROLLER WITH *Permaligned* CONSTRUCTION




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

4 MILLION HP



THE ALUMINUM ORE COMPANY operates one of the world's largest hydrofluoric acid plants at East St. Louis, Ill. It is a modern plant and uses many electric motors in its highly mechanized materials-handling systems.

As a rule, special protective enclosures are used to keep out fumes and dust. But in this case the Tri-Clad open (dripproof) motor you see here has been in service for five years without a single failure. It has operated continuously—24 hours a day and seven days a week. Yet the only maintenance required has been periodic inspection and lubrication. Behind the unusually fine service record of this motor is the extra protection built into every Tri-Clad motor. It's in there for keeps to give you better motor performance at lower cost!

The toughest TRI-CLAD ever built!

REG. U.S. PAT. OFF.

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

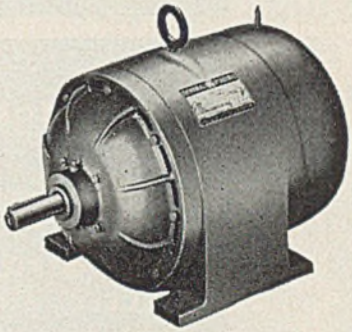
- A cast-iron, double-wall frame which completely encloses and protects the windings and punchings.
- A non-shrinking compound around motor leads which protects motor interior from dust and moisture.
- A rotating labyrinth seal which further protects the motor interior from damage by foreign matter.

CONFIRMS IT!

FOR TOUGH MOTOR JOBS, YOU CAN'T BEAT

TRI/CLAD

EXTRA PROTECTION



To date, a million and a half Tri-Clad motors, with a total output of over 4-million horsepower, have been purchased by American industry!

In every kind of plant from steel mill to dairy, these motors are proof beyond doubt that you can't beat Tri-Clad extra protection for tough motor applications. Even on jobs where special protective enclosures would ordinarily have been specified, Tri-Clad open motors, applied during the war years, have stood up to heat, dust, and dampness, operating smoothly and efficiently for years with only minimum maintenance.

Today, the Tri-Clad family includes many different types and sizes. But whatever your selection, the Tri-Clad motor nameplate is still your best assurance of a high return on your motor dollar. *Apparatus Department, General Electric Company, Schenectady 5, N. Y.*

EXTRA PROTECTION . . AGAINST PHYSICAL DAMAGE!

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

EXTRA PROTECTION . . AGAINST ELECTRICAL BREAKDOWN!

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

EXTRA PROTECTION . . AGAINST OPERATING WEAR AND TEAR!

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

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

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- EXPLOSION-PROOF

GENERAL ELECTRIC

750-287

From LABORATORY to FULL SCALE PRODUCTION

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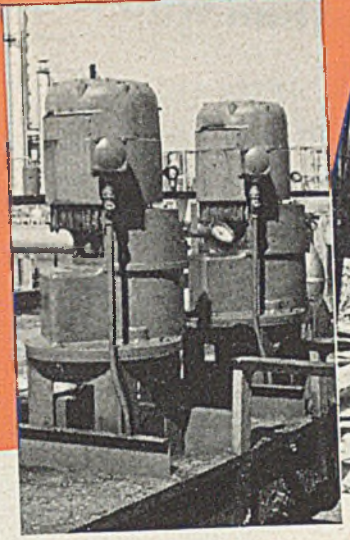
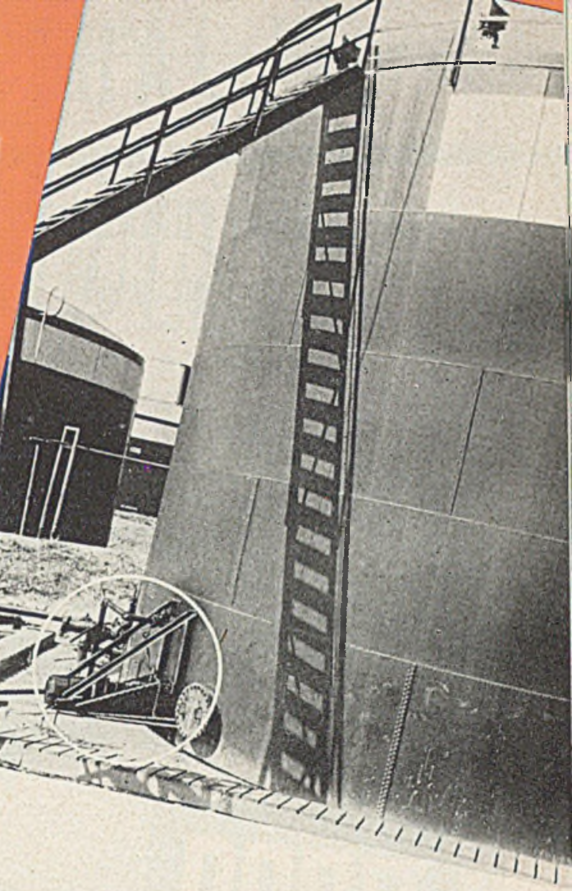
Process Adapted Agitation





300 cc to 5 gallons
Laboratory mixers are invaluable for pre-pilot plant experiments, small production batches, dissolving chemicals, etc. Illustrated above is a laboratory mixer used on a one-liter beaker.

5 to 3000 gallons
Lightnin Portable Mixers are used for both continuous and batch operations. The upper illustration shows mixer in a standard 600 gallon wooden tank. Lower installation shows use as a continuous flash mixer for industrial waste disposal.

25 to 50,000 gallons
Top Entering Mixers answer requirements for open tanks and for mixing in pressure or vacuum tanks. Above is a Top Entering-Turbine installation showing part of a series of mixers each handling about 10,000 gallons.

1,000 to 5,000,000 gallons
Side Entering Mixers are for use on large tanks, for tanks where tops must be kept clear or where head room is limited. This small gasoline blending tank is equipped with only a 5 HP mixer, blending all components in 1 to 2 hrs.

There's a vast difference in the problem of mixing 300 cc and 5,000,000 gallons of liquid and there is just as much difference in the equipment to do the job. Mixing Equipment Company can supply mixers to answer the requirements of these widely divergent quantities and all quantities in between. And every piece of equipment is specifically recommended for each individual job!

Mixing Equipment Company Engineers are prepared to help you apply Process Adapted Agitation to any operation involving the controlled recirculation of liquids to produce physical changes, as included in the following table. Mixing Equipment Company studies each individual operation, giving full consideration to size and shape of tank, power consumption, viscosity and specific gravity of fluids, time element and all other factors effecting the results. Recommendations are backed by over a quarter of a century of experience and development—exclusively in the field of liquid agitation.

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1062 Garson Ave., Rochester 9, N. Y.

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- ☐ B-68 and 68B Permanently Mounted Mixers for Pressure Vessels and Open Tanks
- ☐ B-75—Portable Mixers (*Electric and Air Driven*)
- ☐ B-77—Laboratory Mixers
- ☐ Mi-11—Operating Data Sheet

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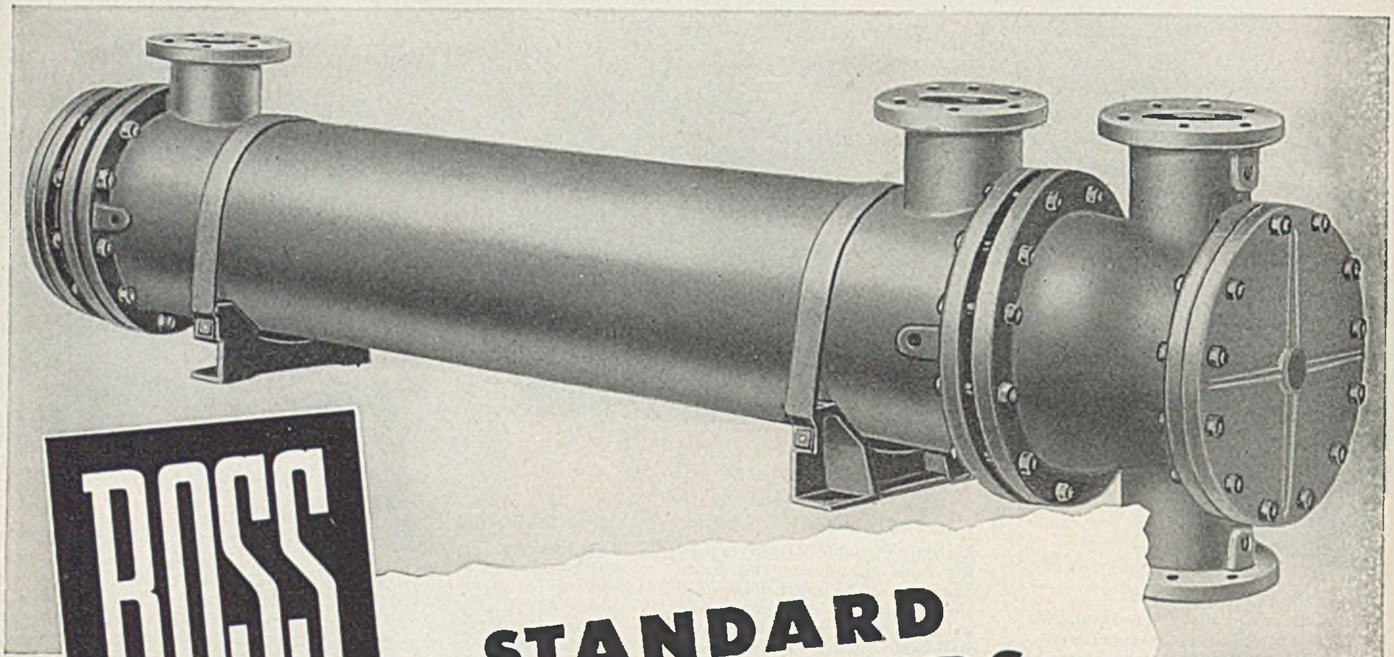
why more cooling requirements and more operating conditions are served than with any other make



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You'd think, then, that practically *ANY INDUSTRY,* requiring circulation of oil, water and other fluids for heat removal, would have little choice to make. That's right! Both machinery builders using coolers as original equipment, as well as industrial consumers making their own installations, show a great preference for this all-purpose Ross unit. They continually select the "CP" design, knowing that both normal and special problems of installation, operation and maintenance can be regularly served without the need for high cost, special engineering and fabrication.

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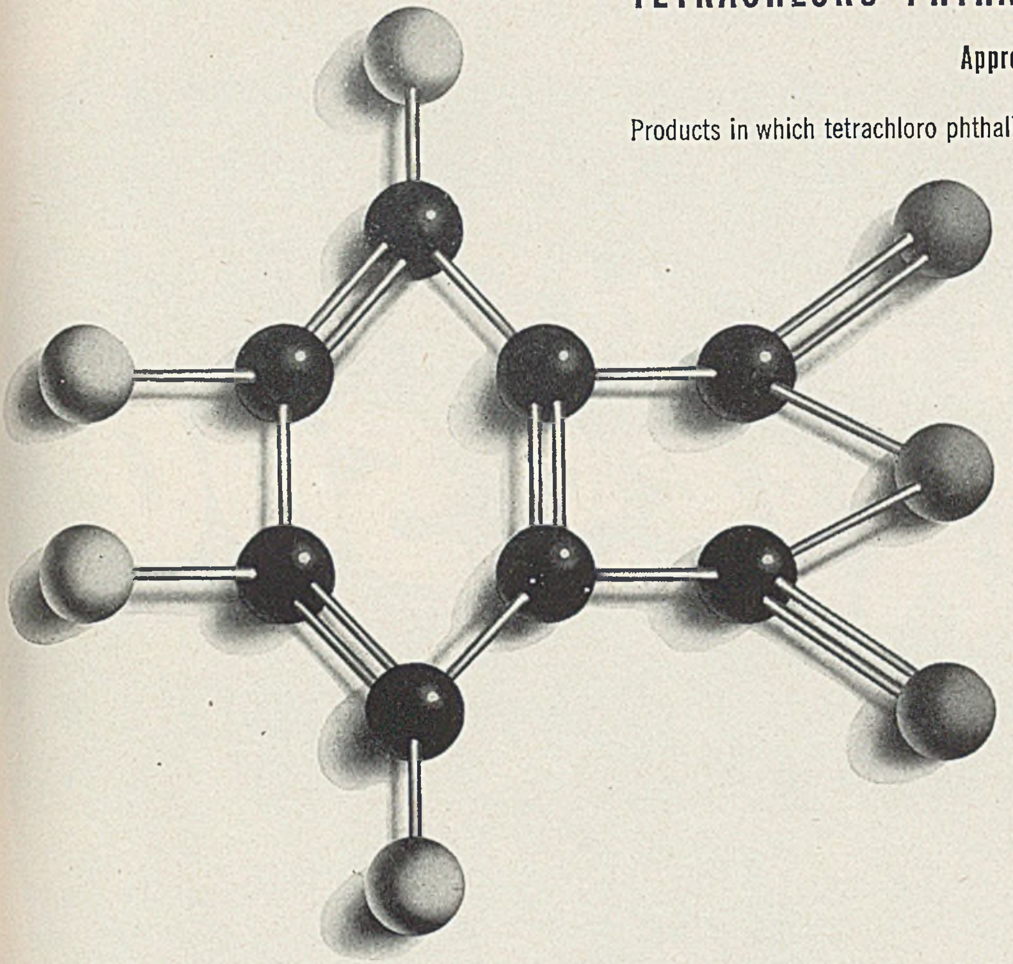
Approx. 50% chlorine



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- Lubricants
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- fluorescein
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- phenolphthalein

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Tetrachloro phthalic acid hydrate

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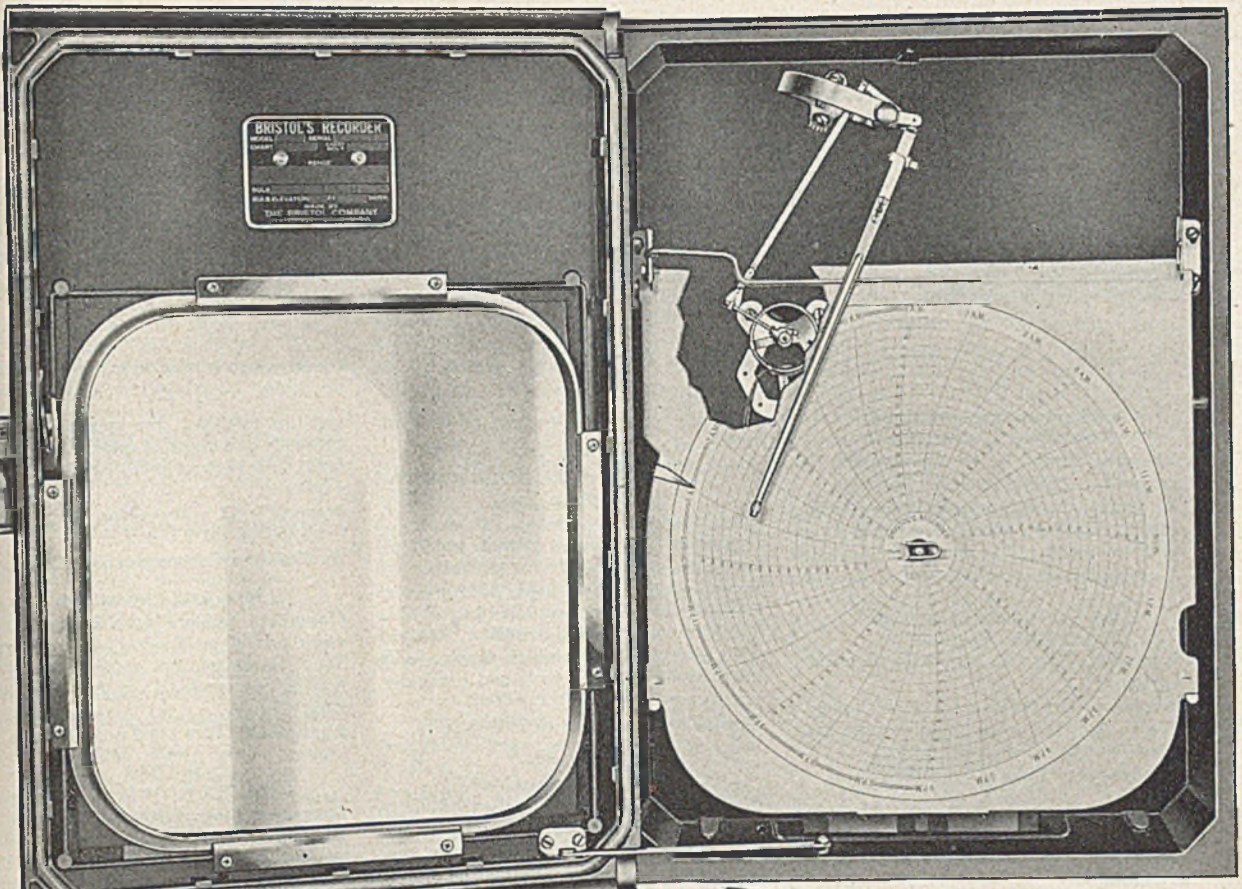
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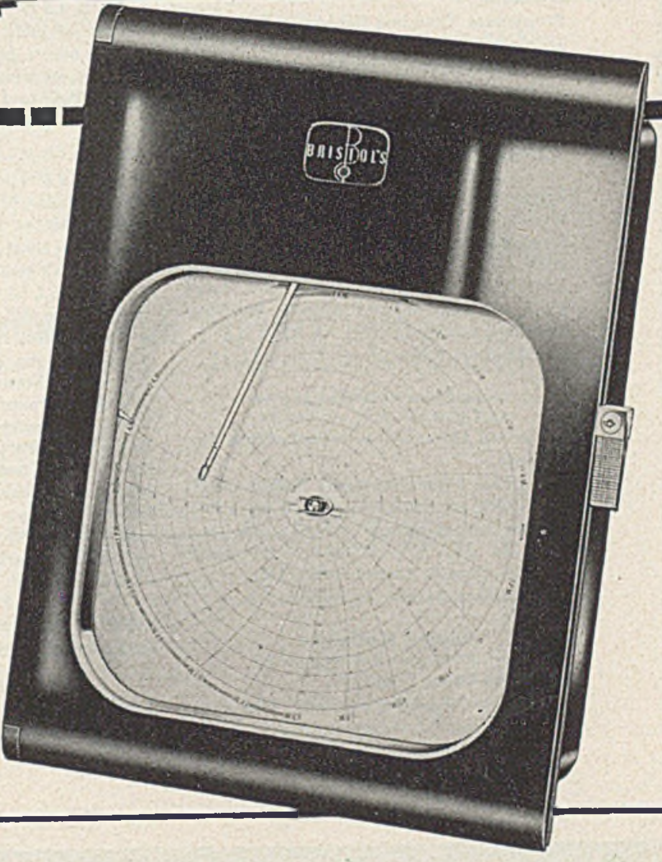
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Among the 28 new Monsanto chemicals and plastics described here, you are likely to find a number of new ideas that can be profitably applied to your business — now, or later.

For your convenience, each of these new Monsanto products is briefly described in terms of suggested uses, properties and availability... Also, each product is numbered (A-1, A-2, etc.) for easy identification and reference in asking for further information — either on the coupon on the opposite page or on your letterhead.

Your request will receive prompt attention — whether it applies to any of the products listed here, or to any other Monsanto chemicals and plastics that may help reduce your production costs, improve your product, its performance or sales.

ortho-Chlorobenzoic Acid

$Cl.C_6H_4COOH$ Mol. wt., 156.57

Suggested Uses: As an intermediate for synthesis.

Properties: Crystalline solid. Melting point, 140°C. Sublimes. Soluble in ethanol, ether and hot water.

Availability: Research quantities. (A-1)

para-Chlorobenzoic Acid

$Cl.C_6H_4COOH$ Mol. wt., 156.57

Suggested Uses: As an intermediate for synthesis.

Properties: Crystalline solid. Melting point, 235°C. Sublimes. Soluble in ethanol and ether. Sparingly soluble in water.

Availability: Research quantities. (A-2)

meta-Chloroethylbenzene

$Cl.C_6H_4C_2H_5$ Mol. wt., 140.61

Suggested Uses: As an intermediate for synthesis.

Properties: Colorless liquid. Boiling point 181–186°C. Refractive index, n25/D 1.5170. Soluble in the usual organic solvents. Insoluble in water.

Availability: Research quantities. (A-3)

ortho-Chloroethylbenzene

$Cl.C_6H_4C_2H_5$ Mol. wt., 140.61

Suggested Uses: As an intermediate for synthesis.

Properties: Colorless liquid. Boiling point, 80°C @ 30 mm. Refractive index, n25/D 1.5190. Sp. gr., 1.055 @ 25°/25°. Soluble in the usual organic solvents. Insoluble in water.

Availability: Research quantities. (A-4)

para-Chloroethylbenzene

$Cl.C_6H_4C_2H_5$ Mol. wt., 140.61

Suggested Uses: As an intermediate for synthesis.

Properties: Colorless liquid. Boiling point, 179–180°C. and 84.5°C. @ 30 mm. Refractive index, n25/D 1.5152. Sp. gr., 1.044 @ 25°/25°. Soluble in the usual organic solvents. Insoluble in water.

Availability: Research quantities. (A-5)

Copper Phthalate

$C_6H_4(COO)_2Cu$ Mol. wt., 227.65

Suggested Uses: Fungicide.

Properties: Fine blue powder. Bulk density, 25#/cu. ft. Assay, minimum 95%. Insoluble in common organic solvents or water.

Availability: Pilot plant quantities. (A-6)

Diethyl Phosphite

$(C_2H_5)_2HPO_3$ Mol. wt., 138.11

Suggested Uses: As a solvent, paint remover and intermediate for synthesis.

Properties: Colorless liquid. Boiling point, 92°C. @ 30 mm. Sp. gr. 1.0912 @ 0°/0°. Refractive index, n 25/D 1.4055. Miscible with most organic solvents except long chain aliphatics. Soluble in and gradually hydrolyzes in water.

Availability: Research quantities. (A-7)

Hibitite* L

$C_{27}H_{45}NO_{10}S_2$ Mol. wt., 607.77

Suggested Uses: Metal pickling inhibitor.

Properties: Brown liquid. Boiling point, 1.2% wt. loss @ 200°/5 mm. Sp. gr., 1.16 @ 15° C./15° C. Refractive index, n 20/D 1.5275. Assay, 95% (minimum). Limited solubility in dilute mineral acids, and diethyl ether. Soluble in ethanol, acetone, dioxane, benzene, $CHCL_3$ and CCl_4. Insoluble in H_2O and petroleum ether.

Availability: Pilot plant quantities. (A-8)

Lustrex

Suggested Uses: Opens up an entirely new group of uses for plastics, permitting them to be immersed in boiling water.

Properties: Heat resistant polystyrene. Injection molding temp. 350°–620°F. Molding pressure p.s.i. 10,000 and up. Sp. gr., 1.05. Flexural strength, p.s.i. 1200–14,000. Flexural deflection, inches, 0.15–0.25. Impact strength, ft. lbs. per inch (unnotched) 3.2–3.6. Heat distortion temp. °C. (Air bath) 87–88½. Dielectric constant, 1 megacycle, 2.5–2.7. Power factor, 1 megacycle. 0.0001–0.0005. Water absorption, % (24 hrs.) 0.04–0.05. Chemical resistance, no effect from weak acids and bases or strong bases. Strong oxidizing acids attack. Soluble in ester, aromatics, higher alcohols, chlorinated hydrocarbons. Color possibilities, almost unlimited. Usually can be molded in cycles up to 30% faster than that required for ordinary polystyrene.

Availability: Commercial quantities. (A-9)

Mertone WB-2

Suggested Uses: For use as a precoat on paper to be subsequently coated with light-sensitive solutions. The precoat increases brilliancy and depth of color after development, and reduces wastage due to overexposure.

Properties: A milky white silica aquasol (15% SiO_2), pH 9.0–9.5.

Availability: Commercial quantities. (A-10)

Mim Acid Phosphate

Properties: Mixture composed mainly of mono and di acid phosphates of methyl isobutyl carbinol. Sp. gr., 1.05 @ 25° C. Acidity, 300 mg KOH per gm. Light brown syrupy liquid.

Availability: Pilot plant production. (A-11)

N-1540

$C_{27}H_{22}O_2N_4S_6$ Mol. wt., 626.87

Suggested Uses: Rubber accelerator.

Properties: Cream colored powder. Melting range, 223–227°C. Sp. gr., 1.46. Assay, not less than 95%. Very slightly soluble or insoluble in ethyl alcohol, butyl alcohol, ethyl acetate, acetone, chloroform, carbon tetrachloride, carbon bisulfide, benzene, toluene, ether and naphtha. Soluble in hot chlorobenzene and o-dichlorobenzene.

Availability: Pilot plant quantities. (A-12)

N-3411

$C_{19}H_{21}NO$ Mol. wt., 279.37

Suggested Uses: Antioxidant for GR-S Latex.

Properties: Gray powder. Melting point, 124°C. Sp. gr. 1.133. Assay, 98%. Soluble in acetone, benzene, toluene.

Availability: Pilot plant quantities. (A-13)

Santocel* C

Suggested Uses: Used as a flatting agent to produce matte finishes in coatings of all types (lacquers, varnishes, vinyl resin coatings and resin dispersions); as a bodying agent for printing inks and non-aqueous liquids; as a bulking agent and free-flowing aid for dry powders; as an insecticide for stored grain insects; to aid in application of rubber cements; and as a reinforcing agent in rubber compounding.

Properties: Dry bulk density, 6 pounds per cubic foot. Sp. gr., 2.2. Index of refraction, 1.464. pH, 3.5 to 4.0. SiO_2, 89.5% to 91.5%. Oil absorption, too high for conventional test methods. Average particle size, 3 to 5 microns in diameter.

Availability: Commercial quantities. (A-14)

News of Monsanto Chemicals for the Process Industries...November, 1947

Santolite* HLA

Suggested Uses: In lacquers makes films that are clear, colorless and of good gloss and adhesion. Decreases water permeability and increases tensile strength.

Properties: Aryl sulfonamide—formaldehyde condensation resin. A clear, hard brittle, nearly colorless resin. Refractive index (25 gm. resin in 75 gm. normal butyl acetate) approximately 1.43 @ 25°C.

Availability: Commercial quantities.(A-15)

Sodium Phosphite, Di (Anhydrous)

Na_2HPO_3 Mol. wt., 125.98

Suggested Uses: As a mild reducing agent in neutral solution humectant, detergent additives.

Properties: Melting point, decomposes @ 130°C. pH 2% solution, 7.0. White crystalline hygroscopic powder. Assay, 63–65% H_3PO_3.

Availability: Laboratory quantities.(A-16)

Sodium Phosphite, Hemibasic

$NaH_2PO_3.H_3PO_3$ Mol. wt., 186.00

Suggested Uses: Convenient source of phosphoric acid in solid form.

Properties: Melting point, 156°C. pH 2% solution, 1.9 White crystalline powder, slightly hygroscopic. Assay, 87/% H_3PO_3.

Availability: Laboratory quantities.(A-17)

Sodium Phosphite, Mono (Anhydrous)

NaH_2PO_3 Mol. wt., 103.99

Suggested Uses: As a mild reducing agent, humectant, detergent, additive.

Properties: Melting point, decomposes 250°C. pH 2% solution, 3.9. White crystalline hygroscopic powder. Assay, 76–78% H_3PO_3.

Availability: Laboratory quantities.(A-13)

Tetraethyl Pyrophosphate

Suggested Uses: Insecticide.

Properties: Pure product has probable formula $(C_2H_5)_4\ P_2O_7$. Technical product is mixture of this and related esters. Light, straw colored, mobile liquid. Sp. gr., approximately 1.2. Completely miscible with polar and aromatic solvents and immiscible with paraffinic hydrocarbons. Has a high degree of biological activity, apparently through the inhibition of cholinesterase. Gradually hydrolyzes in presence of water, with accompanying decrease in toxicity.

Availability: Experimental quantities to qualified testing agencies.(A-19)

meta-Tolylene Diisocyanate

$CH_3.C_6H_3(NCO)_2$ Mol. wt., 174.15

Suggested Uses: Organic synthesis, textile-treating processes, polymers and plasticizers.

Properties: Boiling range, 82–85°C. @ 1 mm. Melting range, 19.6–21.8°C. Odor, medicinal. Color, clear, colorless to yellow.

Availability: Pilot plant quantities.(A-20)

meta-Toluic Acid

$CH_3.C_6H_4COOH$ Mol. wt., 136.14

Suggested Uses: As an intermediate for synthesis.

Properties: Crystalline solid. Melting point, 111–113°C. Boiling point, 263°C. Sp. gr., 1.054 @ 112° / 4°C. Very soluble in ethanol and ether. Soluble in 1170 parts of water at 15°C. and in 60 parts of water at 100°C. Is volatile with steam. Sublimes.

Availability: Research quantities. (A-21)

ortho-Toluic Acid

$CH_3.C_6H_4COOH$ Mol. wt., 136.14

Suggested Uses: As an intermediate for synthesis.

Properties: Crystalline solid. Melting point, 107–108°C. Boiling point, 259°C. @ 751 mm. Sp. gr., 1.062 @ 115° / 4° C. Soluble in hot water, and benzene. Very soluble in ethanol. Is volatile with steam.

Availability: Research quantities. (A-22)

para-Toluic Acid

$CH_3.C_6H_4COOH$ Mol. wt., 136.14

Suggested Uses: As an intermediate for synthesis.

Properties: Crystalline solid. Melting point, 181°C. Boiling point, 274–275°C. Very soluble in methanol, ethanol and ether. Sparingly soluble in water. Is volatile with steam and sublimes.

Availability: Research quantities. (A-23)

Tributyl Phosphite

$(C_4H_9)_3PO_3$ Mol. wt., 250.32

Suggested Uses: As a stabilizer, antioxidant and intermediate for synthesis.

Properties: Colorless liquid. Boiling point, 121–123°C. @ 8 mm. Sp. gr., 0.9253 @ 20°/4°. Miscible with the usual organic solvents. Immiscible with water. Gradually hydrolyzes in contact with water.

Availability: Research quantities. (A-24)

Triethyl Phosphite

$(C_2H_5)_3PO_3$ Mol. wt., 166.15

Suggested Uses: Stabilizer, antioxidant, solvent and intermediate for synthesis.

Properties: Colorless liquid. Boiling point, 157°C. Sp. Gr., 0.9605 @ 17°/0°. Miscible with usual organic solvents. Immiscible with water. Gradually hydrolyzes in contact with water.

Availability: Research quantities. (A-25)

Sodium 2, 4-Dichlorophenoxyacetate

$Cl_2.C_6H_3OCH_2COONa.H_2O$ Mol. wt., 261.05

Suggested Uses: Herbicide.

Properties: White powder. Assay as monohydrate, 97.0% minimum. Total water, 5%–8.5%. Free alkali as NaOH, 0.2% maximum. Inorganic chloride as NaCl, 0.8% maximum. Water-insoluble matter, 0.1% maximum. Dichlorophenol, 0.1% maximum.

Availability: Commercial quantities.(A-26)

Phenylacetic Acid

$C_6H_5CH_2COOH$ Mol. wt., 136.14

Suggested Uses: Penicillin precursor, perfume base and pharmaceutical chemical.

Properties: Fine white crystals. Assay, 99.0%. Melting point, 76–77°C. Moisture, 0.2% maximum.

Availability: Commercial quantities.(A-27)

2,4-Dichlorophenoxyacetic Acid

$Cl_2.C_6H_3OCH_2COOH$ Mol. wt., 221.04

Suggested Uses: Herbicide.

Properties: Fine white powder. Assay, 99.0% minimum. Melting point, 138.0°C. minimum to start. Water, 0.5% maximum. Ash, 0.2% maximum. Dichlorophenol, 0.5% maximum.

Availability: Commercial quantities.(A-28)

*Reg. U. S. Pat. Off.

MONSANTO CHEMICAL COMPANY, 1705 South Second Street, St. Louis 4, Missouri. District Sales Offices: New York, Philadelphia, Chicago, Boston, Detroit, Cleveland, Cincinnati, Charlotte, Birmingham, Houston, Los Angeles, San Francisco, Seattle. In Canada: Monsanto (Canada) Limited, Montreal.

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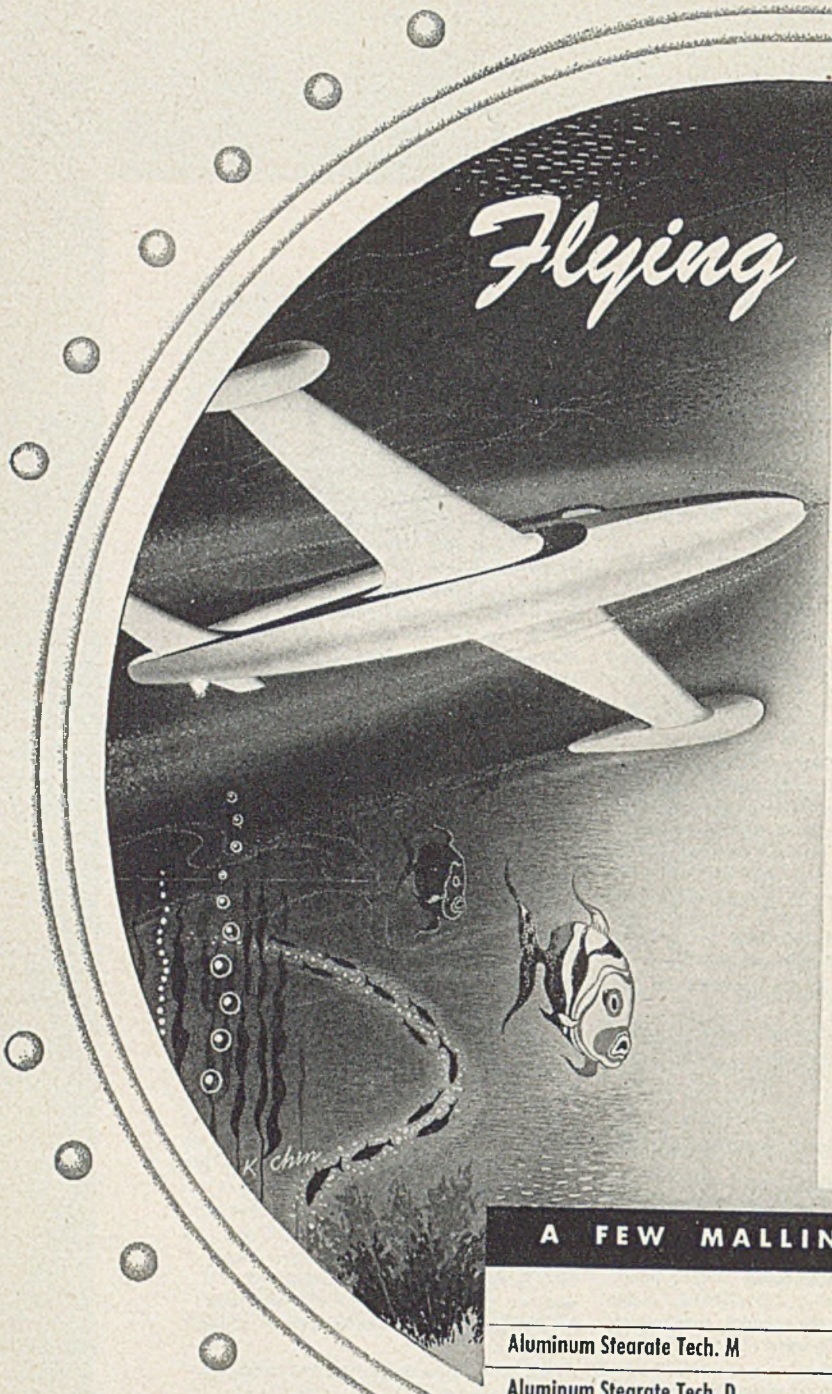

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Aircraft engineers have actually towed full scale airplanes under water—several fathoms down—in their search for better design and construction. Low speed in water was used to simulate high speed in air. Records automatically made of stresses and strains during the tests located weaknesses in the plane. Genius of the aircraft industry in developing punishing and revealing tests and in building its product to meet them are the foundation of its success.

Less spectacular but equally searching are the many tests which **Mallinckrodt stearates** meet. Superior, too, are the products developed by this constant searching for weakness, this constant striving toward perfection.

Valuable in a variety of applications—gelling, coating, lubricating, releasing and repelling moisture—**Mallinckrodt** stearates are made to exacting specifications. Uniform dependable purity characterizes each type and grade.

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Aluminum Stearate Tech. D	50-55	8.4-8.7	6-7	155-160
Aluminum Stearate Tech. D #5-48	45-50	8.7-8.9	6-7	155-160
Flatting Agent No. 22	60-65	8.4-8.7	9-10	145-150
Aluminum Stearate Fluffy	60-65	8.4-8.7	6-7	145-150
Aluminum Stearate Tech. TD	85-95	7.5-8.0	12.5-13.5	125-130
Aluminum Stearate Tech. T	60-65	6.0-6.5	24-25	105-110
Ammonium Stearate Tech.	30-35	-----	decomposes	decomposes
Calcium Stearate Impalpable Powd. Gr. A	130-150	8.8-9.3	0.5-1.0	145-150
Calcium Stearate Tech. Bulky Gr. A	130-150	8.8-9.3	0.5-2.5	145-150
Magnesium Stearate Impalp. Powd. Gr. A	115-130	7.5-8.0	0.5-1.0	125-130
Sodium Stearate Tech. Grade A	35-40	9.5-10.5	-----	175-180
Zinc Stearate Tech.	130-150	13-14	1-2	112-117
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As We See It . . .

Silicates and Silicones. This month organic silicon compounds turn up in the spotlight position. A two-session symposium at the Atlantic City A.C.S. meeting last spring, presented on the program of the Division of Industrial and Engineering Chemistry, is the source of the articles. Nine papers passed the review trial and make their appearance in the lead-off location. The first four are slanted toward industrial applications of the compounds. Cogan and Setterstrom appropriately start the series on page 1364 with a paper on the uses of ethyl silicates, which were the first organic silicon compounds to become commercially important. Miner, Bryan, Holysz, and Pedlow (page 1368) describe several *tert*-alkoxyaminosilanes and their utility in making materials water repellent. Doede and Panagrossi discuss silicone elastomers and their many interesting capabilities (page 1372), and on page 1376 Patterson discusses the use of silicone resins in protective and decorative finishes. The remaining articles are somewhat more specialized in scope. Iler and Pinkney (page 1379) describe preparation of polysilicic acid esters; Iler alone authors a second paper (page 1384) discussing some reactions of butoxychlorosilanes; Hunter *et al.* (page 1389) report properties of silicones on glass; Atkins, Murphy, and Saunders on page 1395 discuss the stability of silicone fluids; and Fox, Taylor, and Zisman describe surface active properties of the silicones on page 1401. With the symposium but not a part of it is the paper by Konkle, Selfridge, and Servais. It describes the resistance of a silicone rubber to aging and appears on page 1410.

Water, Water, Everywhere. The thirst of many an industrial process for just plain water is as great as that experienced by any poor shipwrecked sailor; but, as in the case of the sailor, the water readily available sometimes is a long way from being plain. Five papers this month discuss various aspects of the problems thus created for the process engineer. Bauman, Eichhorn, and Wirth (page 1453) tell of the several chemical methods that can be used to permit silica removal from boiler feed water by the ion exchange method. They find that cost of silica removal varies as a straight-line function of the silica content and conclude that the method is economic only where the silica content is 10 parts per million or less. Cost at this upper limit is approximately 50 dollars per million gallons for the required fluoride treatment and resin regeneration.

Our May 1947 issue on industrial wastes received a top award in *Industrial Marketing's* 1947 editorial achievement competition. We acknowledge with appreciation the able work of the many contributors who made that issue possible.

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Chemistry
For the best single issue
published during the twelve months
ending July 31, 1947 in the
tenth annual competition

Boiler feed water is also the central subject of the article by Tanzola, Reed, and Maguire. The current shortage of soda ash, the chemical normally used for softening raw water, has inspired their discussion of alternative methods for accomplishing the same result. The use of caustic soda, internal chemical treatment, hot-process lime-soda softeners, zeolite beds, and barium carbonate are discussed in turn, and the conditions favoring or militating against their use at a given plant are enumerated. The article appears on page 1440.

Burkardt and Imhoff report on page 1427 the results of a study of one type of damage that occurs when boiler water is not ideal in composition. In this instance the undesired result is a deposit on the blades of steam turbines.

Sheen contributes a useful treatise on page 1433 on the practical requirements in setting up an automatic pH control system. Flow sheets are given for a number of systems for water treatment, waste disposal, and process liquor control.

Undissolved solids in water and process liquors present another variant on our general theme of water process problems which is treated by Kominek in a discussion of the industrial applications of diatomite filters (page 1413). A satisfying number of data are given on comparative filtration rates and costs.

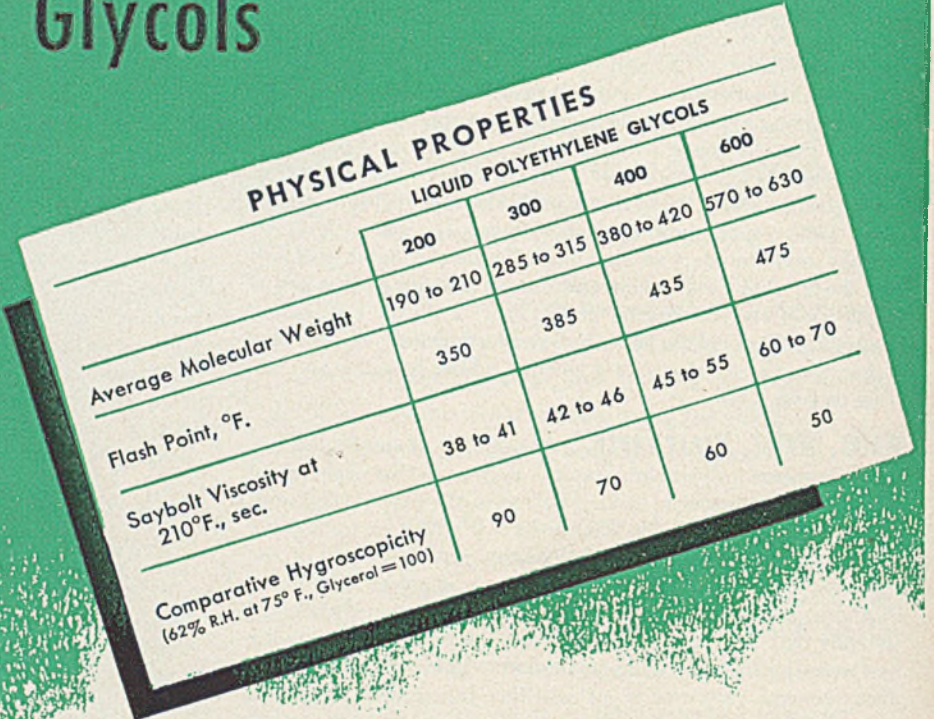
Debut at 79. In the organic chemical field, publication of a pair of essentially introductory papers about a compound originally prepared seventy-nine years ago is nearly as unusual as the "coming out" of a debutante that age would be. However, Lawlor does just that in this issue. The explanation is reasonable, however; only recently has the compound become available in commercial quantities. The first of his two papers (page 1419) describes its reactions and uses, and the second (page 1424) reports its properties and solubilities. Tetrachlorophthalic anhydride or its various derivatives are already suggested in the literature for use as laxatives, chemical indicators, pharmaceuticals, plastics, flameproof resins, plasticizers, dyes, lubricants, fillers for dusting powders, and as a component in a coating composition for motion picture screens!

THE COLUMNS feature, first, Brown's appreciative notice of the plant maintenance man, a frequently undervalued employee. Munch reports the recent convention of the Instrument Society of America and describes three new controllers. Fontana's column describes stress corrosion and includes illustrative photographs. Von Pechmann discusses principles and techniques of the industrial engineer in selling the plant employee on operating improvements.

D. O. Myatt

the answer to many product problems

Polyethylene Glycols



PHYSICAL PROPERTIES

	LIQUID POLYETHYLENE GLYCOLS			
	200	300	400	600
Average Molecular Weight	190 to 210	285 to 315	380 to 420	570 to 630
Flash Point, °F.	350	385	435	475
Saybolt Viscosity at 210°F., sec.	38 to 41	42 to 46	45 to 55	60 to 70
Comparative Hygroscopicity (62% R.H. at 75° F., Glycerol = 100)	90	70	60	50

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Some present uses of polyethylene glycols

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Mutual solvents—for zein and other proteins, dyestuffs, and essential oils.

Lubricants—water-soluble lubricants in warp sizes and yarn conditioners.

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INDUSTRIAL and ENGINEERING Chemistry

WALTER J. MURPHY, Editor

An Educator's Reply

Our July editorial, "Education for an Industrial Career," apparently touched on a subject of very lively interest. The original response from industrialists yielded a rich harvest of comment while the editorial was under development; many thoughtful replies came from the educators to whom it was addressed.

One prominent chemical engineer who also is dean of a school of engineering is among the correspondents. His letter, written from a different perspective, contains a number of points we believe should be kept in mind when the complex subject of technical education is under consideration. He comments as follows:

"1. Why is it that engineering, and science to a lesser degree, of all the professions is the only one that believes it can train a man adequately in four years? If our method has all the perfection that we believe it has, why do medicine, law, dentistry, and so forth require a greater number of years for training?

"2. What company has a program for promoting professional development or, let us say, extending the basic theoretical training among its technical men—exclusive of its training courses, which probably are not for professional development but for company indoctrination and job training.

"3. Do the opinions of the industrialists reflect the backgrounds of the individuals themselves? In the old-style curriculum for engineering and science none of the so-called social humanistics courses were offered. For instance, economics was not offered and such things as psychology were unknown. Later these individuals, as they became junior and senior executives, have wished that they had taken such courses. Are they reflecting this deficiency in their training?

"4. How many companies are willing to agree that the education should be complete enough to fulfill all the demands that they make? They desire the training of a man for a technical or precision job and then gradually promote him to an executive job where the requirements are entirely different and a different type of training would be preferred. This means that the old-style limited four-year education is no longer adequate.

"5. Why charge against a four-year course all the deficiencies of the entire educational system? I am referring especially to English. Competency in English has always been a debatable question, not only among engineers but others. Probably many of the deficiencies could be made up in college, but some of them are more deep-seated than that and are chargeable back to faulty English and deficiencies in the high, and even grade schools.

"6. This is more important still. How many of the critics revisit colleges where they have an opportunity to see what is actually being taught? Of course, the rest of the answer to this is that college trains only in fundamentals; the rest of it must come from experience. If a man does not know twenty years after he leaves college any more than he learned while there, he is surely a very poor engineer and is quite incapable as an executive."

A partial answer to our correspondent's comparison of the educational pattern for chemists and chemical engineers, as contrasted to that for the other professions, is given in several other comments we have received. These letters report increased scheduling of humanities courses in the chemical engineering curriculum, an indication that this lack in earlier curricula is being viewed as a deficiency. However, ever-increased pressure is being placed on the four-year curriculum, already almost intolerably overcrowded.

A four-year curriculum is obviously inadequate for providing the scientific fundamentals, specialized training in a particular field of applied science, plus what might be called executive training, a combination of humanities courses and such subjects as economics and business administration and law. The issue facing educator and industrialist is the optimum division of this educational responsibility among the school, the employer, and the individual.

It is encouraging that some American companies now consider desirable actual classroom instruction for technical employees to supplement their on-the-job training. Such instruction, however, usually will be on the specialized topics or advanced subjects in the company's field of activity. It appears logical to expect the employer rather than the educator to accept the basic responsibility for such specialized training, since the expense of providing it may be considered a legitimate investment in the greater future value of his employee. Where the employer defaults, the individual with initiative usually will supply the deficiency, for an obvious incentive exists. At the same time the colleges will always have the basic responsibility for giving the fledgling chemist or chemical engineer as complete a grounding in fundamentals as time and educational resources permit.

The question of technical *vs.* executive training is more complex. With rare exceptions, those technical graduates who move up to executive positions have no opportunity to apply the techniques of business administration until years after graduation. Logic would suggest that such formal training as will complement the latent abilities of a technical graduate should be given at company initiative and expense and should come just before the employee is in a position to apply them. On the other hand, the humanities, and such broad subjects in the social sciences as economics, are appropriate for the college.

Finally, another word about English and the widespread dissatisfaction with the ability of the technical graduate to express himself. The secondary and grade schools certainly share the responsibility for developing the student's ability to put thoughts into words. But the technical school has the specific additional obligation of teaching its students to view and to utilize technical expression as mathematics paraphrased. The poet uses the English language to bring his reader the moon in "a ghostly galleon tossed upon cloudy seas." For our profession the language stands ready to bear the sturdy freighter of the technical report from points distant in place or time, without loss or damage to its cargo of facts.

Members of the chemical profession differ from the majority in the other professions in that their careers are in our industries. Because of the chemical employee's need for highly specialized training superimposed on a broad, fundamental education, educator and industrialist alike have an unusually great stake in the educational process. A healthy situation exists when both realize its first-rank importance.

ORGANIC SILICON COMPOUNDS

Presented before the Division of Industrial and Engineering Chemistry
at the 111th Meeting of the American Chemical Society, Atlantic City, N. J.

ETHYL SILICATES

H. D. COGAN AND C. A. SETTERSTROM[1]

MELLON INSTITUTE, PITTSBURGH, PA.

THE esters of silicic acid are old-timers chemically (*7*) and may lack the glamor of the newer organic silicon compounds. Nevertheless, they are among the most important commercially, and serve many useful purposes. Some of the esters are of interest as heat transfer liquids (*16*) or as chemical intermediates (*14, 27*), but in general the organic silicates are of industrial importance because they are a convenient source of silica. Methyl silicate would be the logical ester for such applications because it contains the highest percentage of silicon, but exposure to the vapors under certain conditions causes a necrosis of the corneal cells which may lead even to blindness. The ethyl silicates, on the other hand, suffer from no serious toxicological handicaps (*39, 40*) and have become the esters of major industrial importance.

PHYSICAL PROPERTIES

Three types of ethyl silicate are available commercially. Tetraethyl orthosilicate, $(C_2H_5O)_4Si$, is a colorless liquid with a mild esterlike odor. Condensed ethyl silicate is a light brown liquid consisting predominantly of tetraethyl orthosilicate together with some polysilicates. Ethyl silicate 40 is a mixture of ethyl polysilicates. Its name comes from the fact that its available silica content is approximately 40%. Table I lists some of the physical properties of the tetraethyl orthosilicate. Table II gives specifications of the three types.

Tetraethyl orthosilicate is a distilled product of particular interest where high purity of the deposited silica is important. Condensed ethyl silicate and ethyl silicate 40, although undistilled, are of greater industrial importance because of lower initial cost and higher available silica content. Ethyl silicate 40 is the most economical; condensed ethyl silicate is of special interest as an investment binder for precision casting.

METHODS OF MANUFACTURE

In the usual batch process the esters are made by charging silicon tetrachloride to a glass-lined jacketed reactor and adding ethanol at some predetermined rate. The initial addition of ethanol is accompanied by vigorous evolution of hydrogen chloride and a dropping of the reactor temperature. When the theoretical amount of ethanol has been charged, the heat of reaction begins to outweigh the heat of vaporization of the hydrogen chloride, and the reactor temperature rises. After the alcohol has been added, the mixture must be stripped promptly to avoid formation of undesirable high boiling polymers. Variations in the stripping technique and in the subsequent hydrolysis, to obtain the partially condensed esters, affect the structure and size of the resultant polymers, with resultant variations in performance (*32, 35*).

In the continuous process carefully controlled feeding rates, together with integrated continuous stripping, hydrolysis, and distillation procedures, assure more consistent and uniform products than are possible by the batch process. These products, in turn, make possible the use of standardized techniques for deposition of silica.

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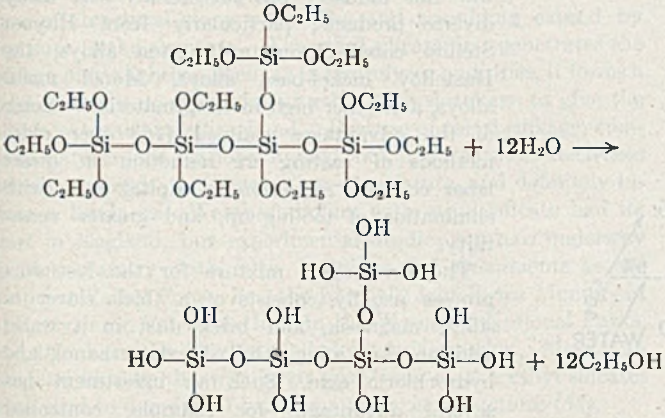
[1] Present address, Carbide & Carbon Chemicals Corporation, 30 East 42nd Street, New York, N. Y. The work reported here was carried out at Mellon Institute under a Multiple Industrial Fellowship of Carbide & Carbon Chemicals Corporation.

THE esters of silicic acid were the first organic silicon compounds to achieve commercial importance. Monomeric ethyl silicate and its polymers are large-tonnage industrial chemicals manufactured from silicon tetrachloride and ethanol by a continuous process which eliminates batch-to-batch variation. The important commercial applications hinge upon the ability of ethyl silicate to deposit silica from solution, so the techniques of hydrolysis and polymerization are important. Recent advances include the development of useful aqueous systems without mutual solvents, and the large-tonnage availability of a stable liquid polymer with an equivalent silica content of 40%. The ethyl silicates are used as adhesives for investments in precision casting, binders for ceramics, gelling agents for alcohol fuels, sources of finely divided amorphous silica, building stone impregnants for weatherproofing, and in the preparation of glass adherent lacquers.

METHODS OF HYDROLYSIS

All of the ethyl silicates hydrolyze slowly in the presence of water to yield silicic acids. These acids then undergo a simultaneous dehydration and polymerization which eventually yield an amorphous silica.

The hydrolysis of a typical molecule of ethyl silicate 40 can be pictured as follows:



$$\mathrm{C_2H_5O{-}\underset{C_2H_5O}{\overset{C_2H_5O}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OC_2H_5}{\overset{OC_2H_5}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OC_2H_5}{\overset{\overset{\overset{\overset{OC_2H_5}{|}}{C_2H_5O{-}Si{-}OC_2H_5}}{|}}{O}}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OC_2H_5}{\overset{OC_2H_5}{\underset{|}{\overset{|}{Si}}}}{-}OC_2H_5} + 12H_2O \longrightarrow$$

$$\mathrm{HO{-}\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OH}{\overset{\overset{\overset{\overset{OH}{|}}{HO{-}Si{-}OH}}{|}}{O}}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{OH}{\overset{OH}{\underset{|}{\overset{|}{Si}}}}{-}OH} + 12C_2H_5OH$$

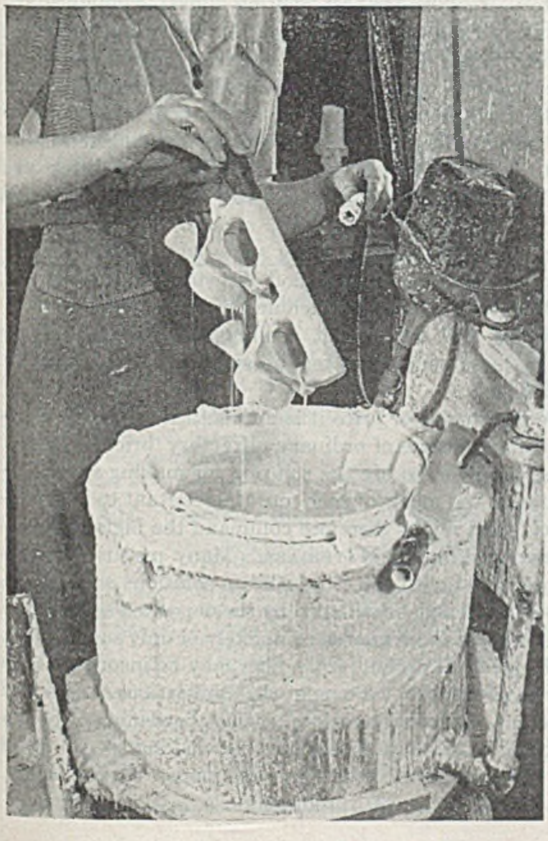
The complex silicic acid, in turn, reacts with other similar molecules or ester molecules, splits out water or alcohol, and polymerizes finally to yield an adhesive form of silica, $(SiO_2)_x$.

None of the ethyl silicates is miscible with water, but hydrolysis can be made to proceed fairly rapidly in an aqueous medium by using vigorous agitation or an emulsifying agent, and large amounts of a catalyst. For example, if 20 volumes of ethyl silicate 40 are vigorously mixed with 4 volumes of 5% hydrochloric acid, the mixture which is at first nonhomogeneous becomes clear in 5 to 10 minutes. After about an hour this silicate solution can be diluted with the desired amount of water. The addition of 76 volumes of water gives an opalescent solution, containing about 8% silica, which remains fluid for several days. Such solutions deposit adhesive silica, but are somewhat more susceptible to catalysis and to gelling than are the ethanol solutions described in the following paragraphs.

ALCOHOL SOLUTIONS

For many industrial uses a mutual solvent such as ethanol or isopropanol is employed. Figure 1 shows the solubility characteristics of the three-component system: ethyl silicate 40, water, and Synasol solvent. (Synasol consists of proprietary solvent based on Specially Denatured Alcohol Formula No. 1.) Similar diagrams for tetraethyl orthosilicate and "condensed" ethyl silicate have already been described in detail (*4*).

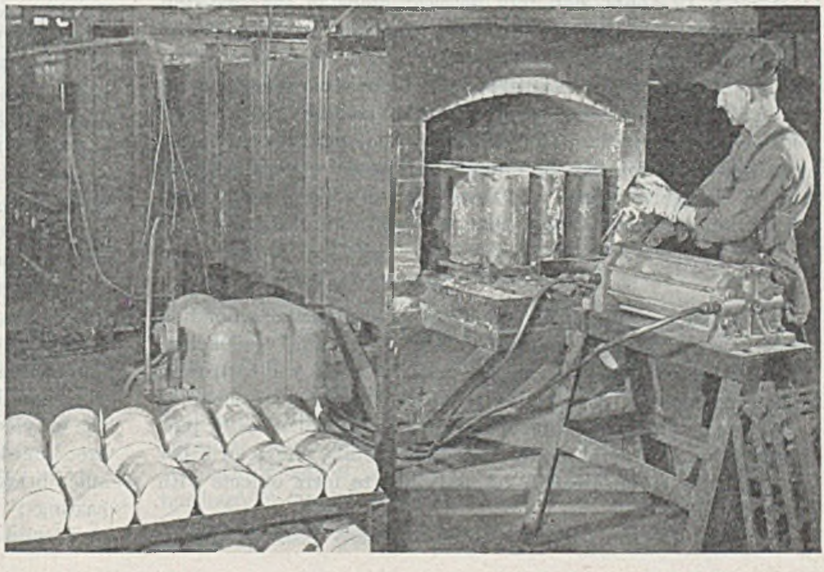
Line *BX* represents compositions containing the correct theoretical ratio of water to ethyl silicate 40 needed to give complete hydrolysis of the ester to SiO_2. Line *AX* represents useful compositions containing less than the theoretical water. In such systems a portion of the ester is converted only to a condensed resinous material which tends to improve the adhesive nature and to preserve some temporary flexibility of the silica film as the



Production of Molds for the Precision Casting of Stainless Steel Exhaust Couplings

At left the wax patterns are being dipped into a suspension of fine silica in a dilute medium containing ethyl silicate. The completed molds, shown below, with wax patterns set in the ethyl silicate investment, are loaded upside down in a continuous furnace to melt out the wax and further dry and set the investment.

COURTESY, HAYNES STELLITE COMPANY



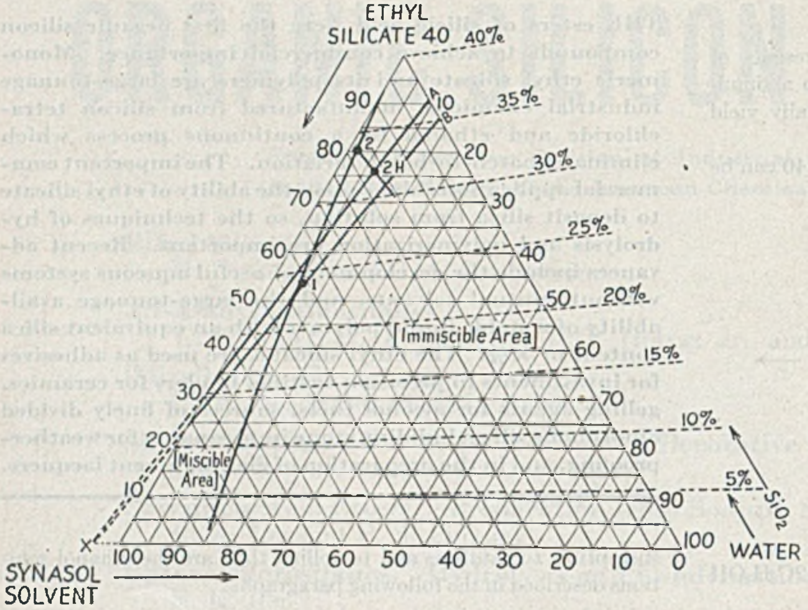


Figure 1. Solubility Characteristics of Three-Component System Ethyl Silicate 40–190-Proof Ethanol–Water

SiO_2 is given as percentage by weight; the other relations are by volume.

solvent evaporates. The relatively small amount of water required to complete the hydrolysis is subsequently absorbed from the surroundings.

The maximum possible silica content obtainable by a one-step hydrolysis is about 24% (indicated on chart at point 1). By first preparing a partially hydrolyzed solution from the ternary described by point 2, and subsequently adding enough water so the total constituents before reaction are described by point 2H, a stable solution containing 32% SiO_2 is obtained. Miscibility is achieved by allowing the components of the first step to react, form ethanol, and, in effect, shift the miscibility line to the right.

RATES OF REACTION

In a neutral solution the hydrolysis of ethyl silicate is very slow. In the presence of ammonia the reaction proceeds rapidly to form gels or gelatinous precipitates. Hydrolysis is more easily controlled when hydrogen chloride is employed, and it is common practice to use a concentration of 0.3 to 5.0% hydrogen chloride in the water for hydrolysis. Even with the 5% hydrogen chloride, however, it is necessary to allow the solutions to stand 8–12 hours, not only between steps in the two-step process, but also between the final mixing and use in both the one- and two-step methods.

The one-step solution can be stored only for several days before gelling. In the two-step procedure the partially hydrolyzed solution can be stored for an indefinite period, and the completely hydrolyzed solution can be stored as long as a week without marked change in viscosity. Deposition of silica occurs upon evaporation of the water and ethanol.

USES

One of the most important applications has been as a bonding agent for comminuted materials (*29*). The sticky, colloidal silicate dries to a hard, vitreouslike material which will withstand high temperatures, is insoluble in water, and has no chemical action upon the surrounding material. Ethyl silicate is of particular value as a mold binder in casting metals, alloys, or other materials that cannot readily be machined to form objects with exact dimensions.

The ethyl silicates have been used for many years as the investment binder in the so-called lost wax process (*6*, *8*, *10*, *25*, *28*, *29*). Prior to the war the products of this process were chiefly dentures and metal appliances for bone surgery. During the war huge quantities of buckets or blades for airplane turbosuperchargers were manufactured by this technique. Since the war this industry has successfully cast many diverse products, particularly from Haynes Stellite cobalt-chromium-tungsten alloys, the Hastelloy nickel-base alloys, Monel metal alloys, and other high melting materials. Some of the advantages claimed (*15*) over older methods of casting are reduction in direct labor charges, reduction in capital costs with elimination of tooling up, and greater versatility.

The investment mixture for the lost wax process usually consists of a thick slurry of silica, magnesia, and brick dust in a water solution containing ethyl silicate, ethanol, and hydrochloric acid. Such an investment has several advantages—for example, controlled cold setting, dimensional accuracy, tolerance of temperatures up to 1600° C., adequate and easily varied mechanical strength, and ready parting from the cast object.

The ethyl silicates have also been suggested as binders for the "semidry piece mold" method (*33*) where the wax model is eliminated and the mold is made directly from a master pattern. In investment casting the mold must be readily broken away, but in piece molding a stronger and harder mold is required. It is believed that these properties can be obtained by using higher percentages of one of the ethyl silicates.

Refractory Binders. Ceramiclike articles may be produced by a simple molding and drying process. Sillimanite, an aluminum silicate, for example, may be shaped in this way by using enough hydrolyzed ethyl silicate to yield 5% silica after baking (*36*). Other materials which can be bonded with ethyl silicate are: refractory crucibles for high melting alloys; refractory and acid-resistant brick and mortar; cold-set electrical insulators, porous silica articles; ferrochrome; activated carbon; sawdust, wood flour, bagasse, etc., to make insulating material; and asbestos electrical insulation. Some work has been done to determine the suitability of ethyl silicate for bonding refractory materials to produce refractory and acid-resistant brick and mortars. If pulverized silica is mixed with the hydrolyzed ethyl silicate and then allowed to air-dry, a hard, strong, slightly porous refractory and acid-resisting material is formed. Air-dried blocks produced by this method withstood a crushing load of over 2000 pounds per square inch and a temperature of 1500° C. On heating and subsequent cooling, the strength of the blocks was reduced somewhat, but no spalling or serious deterioration developed.

From the standpoint of price it is impractical to use ethyl silicate for the manufacture of ordinary refractory brick. It may be practical, however, to use the solution for making special refractory objects and mortar which must be resistant to high temperature acid, and might therefore command the higher price.

Impregnating Porous Materials. Many porous materials can be impregnated with the ethyl silicate solutions and thus be strengthened, hardened, or stiffened by the deposited silica. The porous body may be impregnated completely or only superficially. If a smooth surface is desired, some filler may be incorporated in the ethyl silicate solution. Some of the applications in this field are: hardening of foundry molds; surface hardening of porous silica brick and of graphite molds used for making special metal castings; stiffening of asbestos materials, paper, straw, leather, cork, and textile products; production of a polished water-resistant surface coating for porous articles such as stone, tile, and plaster (*37*).

Weatherproofing. The oldest application of ethyl silicate has been for the preservation of artistic and architectural stonework (*17*, *20*). Properly prepared solutions penetrate the pores of stone, brick, or concrete surfaces. Upon evaporation of the solvent, they deposit an adhesive silica which sets and acts as a hardening and bonding agent, and thereby increases the resistance of structural stone to spalling and crumbling caused by exposure to the elements. The ethyl silicate first penetrates the surface only slightly; then, as it hydrolyzes and dries, it forms a gelatinous silicate which dries further with shrinkage to give the ultimate tenacious silica bond. Because of the shrinkage, complete waterproofing is not obtained, but this treatment decreases porosity, retards the penetration of moisture, and definitely increases hardness. Weatherproofing with ethyl silicate had its start in England, but experimental studies are now underway in this country with such buildings and monuments as the chapel at Valley Forge, Pa., the Eternal Light Peace Monument at Gettysburg, Pa., adobe huts in the Wyoming National Parks, and the Kenneth Taylor Galleries at Nantucket, Mass. In England during the war large quantities of the ethyl silicates were used to dampproof brick emergency constructions (*35*).

Gels. Stable gels of liquids such as ethanol, isopropanol, and acetone can be prepared by the addition of ethyl silicate, water, and catalyst such as caustic soda (*30*). The ethyl silicate hydrolyzes to produce, and distribute uniformly throughout the liquid, a relatively stiff framework or body of silicic acid and silica. The resultant gels are tough, elastic, and highly resistant to deterioration by aging, and tenaciously retain the liquid within the gel body. Because these gels burn uniformly at an ignited surface without observable liquefaction, they are of particular value as solid fuels. During the war carload quantities of ethyl silicate were used to make isopropanol and ethanol solid fuels for the Marine Corps and the Office of the Quartermaster General. Because of more uniform burning, these fuels produced more usable heat than equivalent nitrocellulose gelled alcohols.

In preliminary studies ethyl silicate gels of dilute organic acids have shown some promise for the debridement of burns.

Films. So far it has not been possible to prepare films of ethyl silicate alone which do not suffer from the disadvantages of brittleness and lack of adhesion. Pigmented ethyl silicate solutions deposit films of greater adhesion. In order to obtain maximum adhesion, it is necessary to use laminar fillers such as finely divided mica. A typical formula is 10 parts of completely hydrolyzed ethyl silicate, 3 parts of finely divided mica, and 3 parts of pigments by weight. Pigments most suitable for use with ethyl silicate are generally those that are chemically inert, such as ochre, sienna, or chromium oxide (*18*, *19*). Titanium oxide is a good white, and carbon black can be used as a black pigment (*2*). Such paints formulated with ethyl silicate are extremely resistant to heat and chemical fumes, do not darken on aging, and are fire retardant. They may prove useful as decorative and protective coatings for furnace castings, infrared lamps, asbestos blocks, concrete, and other special surfaces where inflexibility and porosity are not deterrents. In England during the war large tonnages of the ethyl silicates were used to camouflage concrete surfaces, particularly when subject to abrasion (*35*).

Table I. Properties of Tetraethyl Orthosilicate

Molecular weight	208.30
Specific gravity at 20/20° C.	0.9356
Boiling point at 760 mm. Hg, ° C.	168.1
Vapor pressure at 20° C., mm. Hg	1.8
Freezing point, ° C.	−77
Viscosity at 20° C., centipoises	0.60
Refractive index, n_D^{20}	1.3832
Flash point (open cup), ° F.	125

Table II. Specifications of Commercial Material

	Tetraethyl Orthosilicate	Condensed Ethyl Silicate	Ethyl Silicate 40
Sp. gr. at 20/20° C.	0.933 to 0.938	0.920 to 0.950	1.050 to 1.070
Boiling range at 760 mm. Hg, ° C.	Below 160, not more than 5%; above 170, not more than 27.9%	Below 90, not more than 5%; above 210, not more than 15%	Below 80, none; below 110, not more than 5%
Available silica as SiO_2, %	Not less than 27.9	Not less than 30	38–42
Max. acidity as HCl, %	0.05	0.20	0.10
Av. wt./gal. at 20° C., lb.	7.78	7.78	8.82

Shaw recently reported from England that cellulose ether and ester coating compositions can be made fire resistant by the use of ethyl silicate–ammonium phosphate solutions (*34*). Ethyl silicate alone, however, is not particularly effective as a fire retardant for flammable materials because the deposited silica is infusible and nonvolatile.

Increasing Adhesion to Glass. In 1936 Van Hueckeroth (*41*) noted the usefulness of ethyl silicate in increasing the adhesion of cellulose nitrate lacquers to glass. Since that time ethyl silicate has also been employed to increase the adhesion of vinyl acetate (*22*), urea-formaldehyde (*38*), vinyl acetal, and vinyl butyral (*5*) resins. Sufficient ethyl silicate is used to supply 30 to 50 parts of silica per 100 parts of resin in a mixture, and is applied as an undercoat. The completely hydrolyzed solutions of any of the ethyl silicates may be used for this application.

Sizable quantities of ethyl silicate have been used as binders for, or components of, the fluorescent powders or phosphors coated on the inside of fluorescent tubes (*9*, *11*, *24*). In England thermometer gradations are filled with ethyl silicate bound pigments (*35*).

Source of Pure Silica. Recently there has been considerable interest in ethyl silicate as a source of "white carbon black" for the rubber industry. One company (*23*) announced a method of burning ethyl silicate and collecting the resultant silica which is a white, partly translucent powder meeting the specific requirements of particle shape and degree of division necessary for this application. The cost is such, however, that no large tonnage use is anticipated. Nevertheless, ethyl silicate will probably continue to be used as a reference standard for the production of white carbon black from more economical sources such as silicon tetrachloride (*21*), and as a source of specially purified material where high electrical resistance or some other property would justify a premium.

Ethyl silicate and other volatile silicon compounds, such as trichlorosilane, have also been found useful for the production of transparent and heat-resistant articles of silica (*12*, *13*). The silica deposited on burning is subsequently vitrified by heating at temperatures of from 1000° to 1450° C.

Corrosion Inhibitor. Both the Army (*1*) and Navy (*26*) have used important quantities of ethyl silicate as a component of a carbon-removal liquid for engine parts. The ethyl silicate is used together with coal tar oil, orthotoluidine or dipentene, diethanolamine or triethanolamine, oleic acid, ethylene glycol or propylene glycol, and phosphoric acid. It serves as a corrosion inhibitor, particularly for copper. Yudin (*42*) reported that vapors of ethyl silicate form an anticorrosive layer on iron, protecting against sodium chloride solutions and iodine vapor. Partially hydrolyzed ethyl silicate solutions have shown promise as corrosion inhibitors for aqueous alcohol heat transfer liquids (*3*)

Other Uses. The ethyl silicates have shown some promise in many other diverse processes such as tanning dehydrated or pretanned pelt (*31*), stiffening vinyl butyral resin sheeting, sealing porous rock formation in oil wells, defoaming petroleum oils, fireproofing pipe bowls, impregnating wood to confer insect resistance, preparing catalyst carriers, and increasing tensile strength of cotton yarns. They have also improved overnight hardness of long-oil rosin varnish, medium-oil phenolic varnish, and alkyd resin solutions (*2*).

PLASTICIZERS FOR SILICA

The uses of ethyl silicates could be multiplied several fold if the silica deposited on hydrolysis were more flexible. But silica is the result of tetrahedral linkage through each of the four oxygen atoms which surround the silicon, and such rigid polymers are not susceptible to the usual external plasticizers. The silicon resin chemists have solved inflexibility by blocking off one or two corners of the tetrahedron with nonhydrolyzable groups to obtain triangular or linear polymers. If such groups were also nonflammable, the resultant resins would be useful for additional important applications such as heat-resistant paints and high temperature insulation.

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RECEIVED February 19, 1947.

tert-ALKOXYAMINOSILANES

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THE preparation and properties of a number of *tert*-alkoxyaminosilanes are described. The major raw materials for the synthesis of many of these compounds are silicon tetrachloride, tertiary alcohols, and ammonia. The aminosilanes hydrolyze readily to give *tert*-alkoxysilanols which change on heating to hydrophobic resinous materials. They react with alcohols to give orthosilicates which are remarkably stable to hydrolysis. These aminosilanes will render water-repellent almost any surface with which they come in contact. A variety of materials, including textiles, paper, ceramics, road aggregate, and silica gel have been successfully treated.

THE majority of recent publications on the organic compounds of silicon have been concerned with the true organosilicon compounds, wherein the organic groups are attached through a carbon-silicon bond (*2, 3*). The present investigation, however, deals with a class of compounds which are different in structure and chemical properties from both the true organosilicon compounds and the well known silicon esters, such as ethyl orthosilicate (*1*). Broadly speaking, the compounds which make up this class are those in which at least one tertiary alkoxy group and at least one amino group are attached to the same silicon atom. A typical and important example is di-*tert*-butoxydiaminosilane, $(tert\text{-}C_4H_9O)_2Si(NH_2)_2$.

These compounds are made in a two-step synthesis from silicon tetrachloride, the desired alcohol or alcohols, and ammonia. For example, when it is desired that all the alkoxy groups be tertiary, the first step is the reaction of a selected tertiary alcohol with silicon tetrachloride in the presence of an acid acceptor such as pyridine. The resulting *tert*-alkoxychlorosilane, frequently without isolation or purification, is then converted to the corresponding aminosilane by treatment with ammonia under controlled temperature conditions. The properties of some *tert*-alkoxychlorosilanes are given in Table I.

The equations for the preparation of a di-*tert*-alkoxydiaminosilane are typical.

$$2tert\text{-ROH} + SiCl_4 + 2C_5H_5N \longrightarrow (tert\text{-RO})_2SiCl_2 + 2C_5H_5N\cdot HCl \tag{1}$$

$$(tert\text{-RO})_2SiCl_2 + 4NH_3 \longrightarrow (tert\text{-RO})_2Si(NH_2)_2 + 2NH_4Cl \tag{2}$$

By proper selection of the reactants and the reaction conditions it is possible to prepare a mono-, di-, or tri-*tert*-alkoxychlorosilane in good yield substantially free from the chlorosilanes having a lower or higher degree of substitution. The general method of

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preparation is also applicable to chlorosilanes which contain primary or secondary alkoxy groups in addition to the tertiary group or groups. Here the reaction with the tertiary alcohol is completed, and ordinarily the product is isolated, before addition of the other alcohol.

Table I. Properties of Some *tert*-Alkoxychlorosilanes

Compound	Boiling Range, ° C./Mm. Hg.	Density, G./Ml. at 20° C.	Chlorine Analysis Calcd.	Chlorine Analysis Found	Typical Yield, % of Theory
tert-Butoxytrichlorosilane	29–30/9	1.176	51.3	50.5	77[a]
tert-Amoxytrichlorosilane	30–32/3	1.166	48.0	47.5	74[a]
Methoxy-*tert*-butoxydichlorosilane	75–6/80	...	34.9	35.0	68[b]
Ethoxy-*tert*-butoxydichlorosilane	60–1/20	1.072	32.6	32.4	60[b]
Isopropoxy-*tert*-butoxydichlorosilane	64–6/17	1.023	30.7	30.2	42[b]
n-Butoxy-*tert*-butoxydichlorosilane	73–4/9	1.040	28.9	28.8	72[b]
sec-Butoxy-*tert*-butoxydichlorosilane	72–3/10	1.037	28.9	28.6	80[b]
Di-*tert*-butoxydichlorosilane	70/15	1.034	28.9	28.1	83[a]
Di-*tert*-amoxydichlorosilane	102/17	1.027	26.0	25.6	81[a]
Tri-*tert*-butoxychlorosilane	76–8/5	0.937	12.5	11.8	67[c]
Tri-*tert*-amoxychlorosilane	128–30/15	0.924	10.9	8.0[d]	58[c]

[a] Based on $SiCl_4$.
[b] Based on *tert*-butoxytrichlorosilane taking part in reaction. An excess was used.
[c] Based on $(tert\text{-}RO)_2SiCl_2$.
[d] Fading end point.

The type of product which results from the reaction of ammonia with a *tert*-alkoxychlorosilane depends to a considerable extent on the ratio of chlorine to silicon in the chlorosilane. The *tert*-alkoxytrichlorosilanes react with ammonia to give only resinous condensation products which, although initially soluble and fusible, continue to condense with the evolution of ammonia, and soon become insoluble and infusible. The monochlorosilanes and dichlorosilanes, on the other hand, give the corresponding aminosilanes in good yield. The presence of at least one tertiary alkoxy group in the molecule appears to be essential for the existence of a stable compound containing two amino groups attached to the same silicon atom.

REACTIONS

The aminosilanes can be considered as amides of substituted silicic acids. They undergo a number of the reactions which are analogous to those which take place with the amides of carboxylic acids. The reactions which are of immediate interest are those which take place between the *tert*-alkoxyaminosilanes and compounds containing an active hydrogen atom. Probably the most important reactions of this type are hydrolysis and alcoholysis. The properties of some *tert*-alkoxyaminosilanes are given in Table II.

Hydrolysis. When brought into contact with ice water the *tert*-alkoxyaminosilanes react rapidly with the evolution of ammonia to form the corresponding *tert*-alkoxysilanols.

$$(tert\text{-}RO)_2Si(NH_2)_2 + 2H_2O \longrightarrow (tert\text{-}RO)_2Si(OH)_2 + 2NH_3$$

The fact that, under the conditions of this reaction, there is very little loss by hydrolysis of the *tert*-alkoxy groups is of importance. This stability to hydrolysis, particularly in basic media, is characteristic of the *tert*-alkoxy silicon derivatives.

For example, 9.5 grams (0.046 mole) of di-*tert*-butoxydiaminosilane was shaken for about 5 minutes with 20 grams of crushed ice, during which time a mass of white needle crystals precipitated in the flask. The heat of the reaction was sufficient to melt most of the ice. The crystals were taken up in 100 cc. of low boiling petroleum ether. The petroleum ether layer was separated and evaporated under reduced pressure and gave 5.37 grams of white needlelike crystals, melting point 99–101° C. Analysis: Si calculated for $C_8H_{20}O_4Si$, 13.5; found, 13.7%. The water layer was separated and extracted twice with 50-cc. portions of ether. The combined ether extracts were dried over anhydrous potassium carbonate for 1 hour, filtered, and evaporated under reduced pressure. The residue (3.75 grams) consisted of crystals of di-*tert*-butoxysilanediol plus higher liquid condensation products.

The di-*tert*-alkoxysilanediols are apparently rather unstable except in the pure state. For this reason, when the pure compound is desired, it must be separated from the reaction mixture immediately upon completion of the reaction. If the diaminosilane is hydrolyzed in warm water or if the silanediol is allowed to stand in solution, the principal product is ordinarily a noncrystallizable liquid or resinous material.

The resinification reaction, which can be accelerated by the application of heat, is of importance. It takes place with ease and can be controlled to give products having a variety of properties. When the polysilicate resin is the desired end product, the isolation of the intermediate silanediol is unnecessary. The diaminosilane is merely hydrolyzed, and the entire semicrystalline hydrolysis product is separated and heated without further purification at, for example, 150° C. until a resin having the desired properties is obtained. Depending upon the degree of cure, the polysilicates so obtained may be highly viscous, tacky liquids, hard, brittle, soluble resins, or insoluble, infusible products which are extremely brittle.

During the resinification of the hydrolysis product of, for example, di-*tert*-butoxydiaminosilane, not only water but also *tert*-butyl alcohol and isobutylene are evolved. As the thermal resinification takes place the following changes are observed: (*a*) considerable weight loss occurs, accompanied by an increase in the silicon content; (*b*) the product becomes progressively more viscous until it reaches the stage where, although a liquid at elevated temperatures, it cools to a hard, rather brittle, almost colorless resin soluble in organic solvents; (*c*) if the heating is continued long enough, the product will eventually become insoluble and infusible, and finally will reach a state where its composition approaches that of silica.

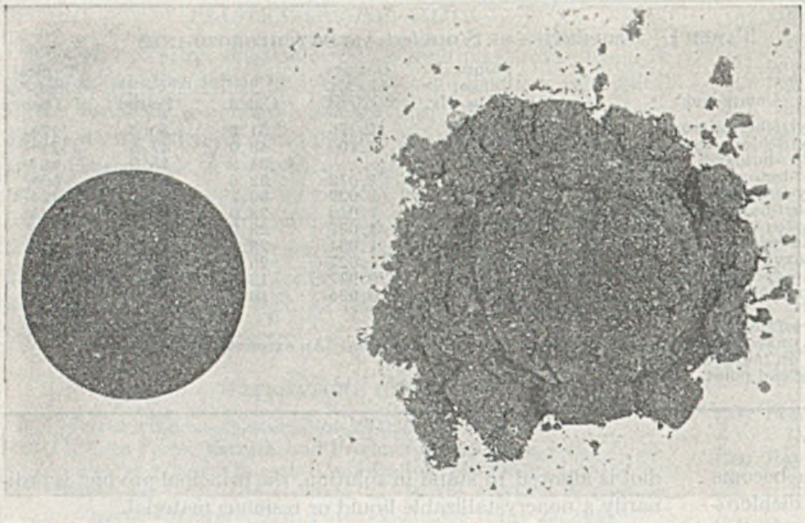
The stability to hydrolysis which is characteristic of the *tert*-alkoxy: silicon bond is again evident in the *tert*-alkyl polysilicates. They can be kept in contact with water (vapor or liquid) for long periods of time with no visible change. The fact that these resins are not only resistant to hydrolysis but are actually highly hydrophobic is the basis for most of the uses of the *tert*-alkoxyaminosilanes, which will be discussed in more detail.

Alcoholysis. The di-*tert*-alkoxydiaminosilanes react rapidly with most primary and secondary alcohols at ordinary temperatures to liberate one mole of ammonia.

$$(tert\text{-}RO)_2Si(NH_2)_2 + R'OH \longrightarrow (tert\text{-}RO)_2(R'O)SiNH_2 + NH_3$$

Table II. Properties of Some *tert*-Alkoxyaminosilanes

Compound	Boiling Range, ° C./Mm. Hg.	Density, G./Ml. at 20° C.	Refractive Index n_D^{20}	Nitrogen Analysis Calcd.	Nitrogen Analysis Found	Typical Yield, % of Theory
Methoxy-*tert*-butoxydiaminosilane	62–5/12	...	1.4130	17.1	15.1	20
Ethoxy-*tert*-butoxydiaminosilane	63–6/9	0.961	1.4185	15.7	14.3	65
Isopropoxy-*tert*-butoxydiaminosilane	64–6/8	0.934	1.4170	14.6	13.7	62
n-Butoxy-*tert*-butoxydiaminosilane	66–8/3	0.939	1.4260	13.6	12.9	48
sec-Butoxy-*tert*-butoxydiaminosilane	92–5/17	0.928	1.4210	13.6	12.6	70
Di-*tert*-butoxydiaminosilane	70–2/10	0.928	1.4192	13.6	13.2	81
Di-*tert*-amoxydiaminosilane	105–10/15	0.931	1.4300	12.0	11.4	71
Tri-*tert*-butoxyaminosilane	82–5/10	0.882	1.4060	5.3	5.3	85
Methoxydi-*tert*-butoxyaminosilane	72–3/15	0.924	1.4052	6.3	6.4	83
n-Butoxydi-*tert*-butoxyaminosilane	113–4/15	0.901	1.4149	5.3	5.0	55
Isopropoxydi-*tert*-butoxyaminosilane	83–4/17	0.899	1.4053	5.6	6.1	62
Diisopropoxy-*tert*-butoxyaminosilane	57–60/3	0.884	1.4015	5.9	5.3	78



Di-*tert*-butoxydiaminosilane (0.2%) added to asphalt

Untreated

Briquets of 90% Greystone Fines and 10% RC-3 Road Asphalt after 24 Hours in Water

With methanol both amino groups react readily, whereas with the higher alcohols the reaction with the second amino group takes place at a reasonable rate only on the application of heat.

$$(\textit{tert}\text{-RO})_2\text{Si(NH}_2)_2 + 2\text{R'OH} \longrightarrow (\textit{tert}\text{-RO})_2(\text{R'O})_2\text{Si} + 2\text{NH}_3$$

With primary alcohols at elevated temperatures the second amino group reacts fairly easily; with secondary alcohols it is significantly slower. In the case of tertiary alcohols the reaction with even the first amino group is extremely slow, and the second does not react.

It is interesting to note that the di-*tert*-alkoxydichlorosilanes show a much higher degree of reactivity with alcohols than do the corresponding aminosilanes. In the case of the chlorosilanes the reaction is carried out in the presence of a tertiary amine—for example, pyridine.

$$(\textit{tert}\text{-RO})_2\text{SiCl}_2 + 2\text{R'OH} + 2\text{C}_5\text{H}_5\text{N} \longrightarrow (\textit{tert}\text{-RO})_2(\text{R'O})_2\text{Si} + 2\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$$

The reaction with both chlorine atoms takes place readily in the case of primary alcohols and only slightly less readily with secondary alcohols; however, with tertiary alcohols only one chlorine reacts.

By reaction of the *tert*-alkoxyaminosilanes with polyhydric alcohols a variety of products may be obtained. Depending on the choice of reactants and the reaction conditions, these may vary in properties from liquids of medium to high viscosity to insoluble, infusible gels or powders.

An alkyd resin which has a substantial hydroxyl value may be considered a special type of polyhydric alcohol; the di-*tert*-alkoxydiaminosilanes react spontaneously with solutions of such alkyds. In small amounts they improve some of the characteristics of the alkyd film, whereas in larger amounts they may be used to effect the rapid total gelation of the alkyd solution.

Complete alcoholysis of the *tert*-alkoxyaminosilanes or *tert*-alkoxychlorosilanes results in mixed orthoesters. The outstanding property of these orthoesters is their resistance to hydrolysis. It was observed that the introduction of even one tertiary alkoxy group produces a striking increase in the stability under hydrolytic conditions. This is apparently due not only to the stability of the *tert*-alkoxy: silicon bond itself but also to a stabilizing influence which is exerted by the *tert*-alkoxy group even on primary alkoxy groups attached to the same silicon atom. This phenomenon is exemplified by the data in Table III. The data were obtained as follows:

HYDROLYTIC STABILITIES OF BUTYL ORTHOSILICATES. The apparatus consisted of a 150-ml. test tube fitted with a high speed multiple-blade stirrer and reflux condenser. The test tube was heated by an oil bath. Seventy-five milliliters of the hydrolysis medium were placed in the test tube and heated to 100° C., then 32 grams (0.10 mole) of the ester were added through the condenser. The reaction mixture was stirred rapidly for 8 hours while the bath temperature was maintained at 100 ± 2° C. and then cooled, and the organic layer was separated from the water layer in a separatory funnel. The water layer was then saturated with potassium carbonate and extracted several times with petroleum ether. The extracts were combined with the organic layer, dried over anhydrous potassium carbonate, filtered, and distilled. The components were identified by means of their physical constants. The percentage recovery of the original ester was taken as the criterion of resistance to hydrolysis. The experimental results are shown in Table III for the members of the series

$$(\textit{tert}\text{-C}_4\text{H}_9\text{O})_x(n\text{-C}_4\text{H}_9\text{O})_{4-x}\text{Si}$$

where $x = 0, 1, 2,$ and 3

A study of these data indicates that under the conditions used (*a*) the hydrolytic stability of a butyl orthosilicate is markedly improved when one or more of the butyl groups are tertiary, (*b*) the stability of the orthoester toward hydrolysis in alkali and acid increases greatly when the number of tertiary butyl groups is increased, and (*c*) the orthoesters containing one or more tertiary butyl groups are more stable in alkali than in acid when the respective concentrations of the hydrolysis media are the same.

REACTIONS WITH AMINES AND ORGANIC ACIDS. The *tert*-alkoxyaminosilanes will react with primary amines and with organic acids in a manner analogous to the reaction with alcohols.

$$(\textit{tert}\text{-RO})_2\text{Si(NH}_2)_2 + 2\text{R'NH}_2 \longrightarrow (\textit{tert}\text{-RO})_2\text{Si(NHR')}_2 + 2\text{NH}_3$$

$$(\textit{tert}\text{-RO})_2\text{Si(NH}_2)_2 + 4\text{R'COOH} \longrightarrow (\textit{tert}\text{-RO})_2\text{Si(OOCR')}_2 + 2\text{R'COONH}_4$$

INTERMOLECULAR CONDENSATION. It has already been mentioned that when a *tert*-alkoxytrichlorosilane is treated with ammonia the resulting product is not a triaminosilane but a polymeric material which continues to evolve ammonia slowly for a considerable period. In contrast the di-*tert*-alkoxydiaminosilanes are stable under ordinary conditions and, if kept from contact with moisture, can be stored indefinitely without decomposition.

An intermolecular condensation can be brought about, however, if the di-*tert*-alkoxydiaminosilane is heated to about 200° C. in the presence of a small amount of weakly acidic material. This condensation proceeds almost quantitatively with the elimination of ammonia, according to the following equation, to give a cyclic product:

$$x(\textit{tert}\text{-RO})_2\text{Si(NH}_2)_2 \xrightarrow[\text{heat}]{\text{catalyst}} [(\textit{tert}\text{-RO})_2\text{SiNH}]_x + x\text{NH}_3$$

To 10.3 grams of di-*tert*-butoxydiaminosilane was added 0.10 gram of ammonium sulfate, and the mixture was placed in a 50-

TABLE III. INFLUENCE OF THE TERTIARY GROUP ON THE HYDROLYTIC STABILITIES OF BUTYL ORTHOSILICATES

Hydrolysis Medium	Percentage of Ester Recovered			
	$(n\text{-BuO})_4$Si	$(n\text{-BuO})_3$-(*tert*-BuO)Si	$(n\text{-BuO})_2$-$(\textit{tert}\text{-BuO})_2$Si	$(n\text{-BuO})$-$(\textit{tert}\text{-BuO})_3$Si
Water	89.5	95.5	...	...
Hydrochloric acid				
1 *N*	0.0	78.2	91.6	...
3 *N*	...	...	72.9	84.7
5 *N*	...	...	...	16.2
Sodium hydroxide				
1 *N*	1.5	95.0	...	...
3 *N*	...	0.0	...	...
5 *N*	...	...	79.1	95.3
11 *N*	...	...	...	94.2

cc. Erlenmeyer flask and heated for 20 minutes; during this time the temperature was slowly increased from 125° to 230° C. Ammonia was evolved during the reaction, and, upon cooling, the product crystallized in long white needles, m.p. 181° C. Recrystallization from hot acetone gave 8.7 grams of purified product, m.p. 187° C. Analysis: N calculated for $C_8H_{19}NO_2Si$, 7.40; found, 7.11. The yield was 92% of the theoretical calculated for $[(C_4H_9O)_2SiNH]_x$.

The question as to whether this product is a dimer or a trimer is still undecided, since the evidence on the point is contradictory.

PRACTICAL APPLICATIONS

The first important uses developed for *tert*-alkoxyaminosilanes are those which depend primarily on the ability of these compounds to render water repellent almost any solid surface with which they come in contact. This effect is assumed to be due to a reaction between the aminosilane and the absorbed film of moisture on the solid surface to produce a surface film of *tert*-alkyl polysilicate. The initial water repellency so produced is ordinarily improved and made more permanent by a subsequent heat treatment of the treated article. The hydrophobic polysiloxane film may be assumed to have at least partially replaced the moisture film and hence to be tightly bound to the surface by molecular forces. This is borne out by the fact that the water repellency is relatively permanent and is ordinarily little affected by contact with organic solvents.

The same type of effect may be produced by use of the *tert*-alkoxychlorosilanes instead of the aminosilanes. In this case, however, the volatile by-product of the reaction is hydrogen chloride instead of ammonia, and the treatment is not readily applicable to acid-sensitive materials such as cellulose. The results obtained also appear to be much more susceptible to variations in the conditions of the treatment. It is, for example, difficult to obtain reproducible high contact angles between water and glass surfaces treated with *tert*-alkoxychlorosilanes, whereas the use of the corresponding aminosilanes gives uniformly acceptable results.

The *tert*-alkoxyaminosilanes may be applied in the vapor state, in the form of the undiluted liquid or as a solution in an inert solvent. The choice of methods depends mainly on two factors, the characteristics of the material to be treated and the equipment available. Since the *tert*-alkoxyaminosilanes are all relatively high boiling substances, their application in the vapor phase usually requires special equipment to maintain the vapor concentration at a level high enough to accomplish a satisfactory treatment in a reasonable length of time. For the majority of materials the aminosilane is best applied as a dilute solution in an inert solvent. The undiluted liquid has been found particularly applicable to certain types of finely divided solids.

A few examples of specific uses already developed will illustrate the technique involved and the results obtainable.

ANTISTRIPPING AGENT FOR ROAD AGGREGATE. The durability of road surfaces prepared from asphalt-bonded mineral aggregate is complicated by a phenomenon known as stripping. This term is applied to the separation of the asphalt from the rock due to the action of water. Under certain conditions of climate it is essential that one ingredient of the asphalt-rock mixture be an antistripping agent if stripping is not to be a significant factor in road failure.

It has been found that the di-*tert*-alkoxydiaminosilanes are excellent antistripping agents[3]. They can either be used to treat the rock aggregate prior to the addition of the asphalt or can be mixed into the asphalt prior to incorporation of the rock. In either case it is possible to obtain a superior antistripping effect with a very small quantity of the aminosilane. Di-*tert*-butoxydiaminosilane is particulary satisfactory in this application.

SURFACE TREATMENTS FOR WATER REPELLENCY. INORGANIC SURFACES. Treatment with *tert*-alkoxyaminosilanes to produce water repellency can be applied either to relatively large continuous surfaces or to granular or powdered materials in any state of division.

On surfaces such as those of glass or ceramic objects the aminosilanes are preferably applied either as the vapor or as a solution in an inert solvent. For example, treatment of a clean glass surface with a 1% solution of di-*tert*-butoxydiaminosilane in a dry hydrocarbon solvent, followed by heating to 100–150° C. for 1–2 hours, will make it highly water repellent.

With powdered materials it is necessary to use considerably larger proportions of the aminosilane because of the large total surface area to be covered. The quantity required may vary from around 1% by weight for larger size particles up to 7–10% for a fine grade of low density silica gel. The preferred method of application for powdered materials is to add (preferably as a fine spray) the undiluted liquid aminosilane—for example, di-*tert*-butoxydiaminosilane—thoroughly mix, as by tumbling, and cure at elevated temperatures. A wide variety of substances, such as simple salts, mineral fillers, and pigments, can be made water repellent by this technique.

ORGANIC SURFACES. The utility of the *tert*-alkoxyaminosilanes as water-repellent agents for textiles, paper, etc., has been the subject of an extensive investigation. Most of the aminosilanes produce some degree of water repellency, and a large number of compounds containing different numbers and types of alkoxy groups have been evaluated. The preferred class of compounds for most textile treatments comprises the diaminosilanes having one long-chain alkoxy group to accentuate the water-repellent characteristics and one lower molecular weight tertiary alkoxy group to give hydrolytic stability. Compounds of this type are under intensive study at the present time.

SUMMARY

1. By the reaction of a tertiary alcohol with silicon tetrachloride the mono-, di-, or trisubstituted chlorosilane can be produced in excellent yield.

2. The reaction of a di-*tert*-alkoxydichlorosilane or a tri-*tert*-alkoxychlorosilane with ammonia gives the corresponding monomeric aminosilane. The presence of at least one *tert*-alkoxy group per silicon atom appears to be necessary for the existence of a stable diaminosilane.

3. The di-*tert*-alkoxydiaminosilanes react spontaneously with water with the evolution of ammonia to give the corresponding silanediols or polysiloxane condensation products thereof.

4. The *tert*-alkoxyaminosilanes react with alcohols to give mixed orthoesters showing a high order of stability to hydrolysis.

5. On heating with acidic catalysts the di-*tert*-alkoxydiaminosilanes undergo an intermolecular loss of ammonia to give cyclic condensation products.

6. The *tert*-alkoxyaminosilanes are finding increasing industrial use, primarily because of their ability to make a wide variety of surfaces hydrophobic.

ACKNOWLEDGMENT

The authors are indebted to the Minnesota Mining and Manufacturing Company, on whose behalf this work was undertaken, for permission to publish these results, and to H. N. Stephens and to J. H. Kugler of the Minnesota Mining and Manufacturing Company for their helpful advice and assistance.

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RECEIVED May 1, 1947.

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[3] The authors acknowledge with thanks permission of the Minnesota Mining and Manufacturing Company to mention briefly in the present publication the results of certain of those phases of the application research which were conducted entirely in their laboratories.

POLYSILOXANE ELASTOMERS

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THE silicone rubbers are polymers made by the condensation and oxidation of especially prepared methylsiloxane. They are flexible at −65° and remain stable at 200° C. These characteristics make them useful at temperatures below and above those at which the ordinary rubbers can function. Because these rubbers adhere readily to glass, it is possible to devise material constructions with some of the desirable properties of both substances. Their chemical resistance makes them desirable for gasket applications. The ease with which they adhere to steel makes possible the fabrication of high temperature rubber belting for the process industries. Other types of coated fabrics may serve as diaphragms or hot gas ducts. Still others, because of their excellent ozone resistance and ability to withstand corona cutting, have become desirable electrical insulating tapes. The fact that the rubbers are unplasticized and do not contain solvent-extractable materials, promotes their use in systems where contaminants of the gasketing material should not exist. This report on the characteristics of these rubbers and a description of a few engineering applications will probably suggest solutions to other similar problems in the process industries.

THE chemical constitution of the polysiloxane elastomers, or silicone rubbers, is such that they have outstanding thermal stability and electrical insulating characteristics. The basic unit structure has many things in common with that of glass, and a chemical bond may be formed between the silicone polymer and glass itself. This unique property makes it possible to prepare materials which utilize the characteristics of both substances. The study of the mechanical, chemical, and electrical properties of this combination of materials forms the basis for this report on some engineering applications which have been made of the silicone rubbers.

The fundamental unit involved has been given the general formula RR′SiO, where R and R′ represent organic groups attached directly to silicon (*7*). The composition of R and R′, as well as the configuration given them in the polymer, determine to a large extent the characteristics of the final material.

The initial organosilicon composition may be made by several methods; three of them follow:

$$\text{Silicon halide} + \text{Grignard reagent} \longrightarrow \text{organosilicon halide} \qquad (1)$$

$$\text{Silicon metal (catalyzed)} + \text{organic halide} \xrightarrow[\text{heat}]{200\text{–}500^\circ\ \text{C.}} \text{organosilicon halide} \qquad (2)$$

$$\text{Silicon halide} + \text{hydrocarbon} \xrightarrow[\text{heat}]{500\text{–}1000^\circ\ \text{C.}} \text{organosilicon halide} \qquad (3)$$

Reaction 1 utilizes the classical Grignard method originally described by Kipping (*5*), and is the first to be reported in large scale production (*1*). Method 2 (*10*), now in commercial use, is one in which the organic halides are added directly to silicon metal to form the organosilicon compositions. Method 3 (*6*) is also direct; in this instance, however, the silicon halides and the hydrocarbons are caused to unite at high temperatures. Silicols are then prepared from the halides by hydrolysis. These, in turn, are condensed with the aid of oxygen and heat to give the silicone polymers. The polymers thus formed have been reported to be both chainlike (*9*) and cyclic (*4*) in nature. Probably the final structure is unique for each type of polymer involved, and is a combined modification of the two types, straight and cyclic. As the silicon-oxygen bond is apparently one of those upon which the structure of the silicone polymer is based, the fact that its bond energy (*11*) is about half again as much as that for carbon-carbon or carbon-sulfur linkage would indicate a thermally more stable type of structure. The bond energies, in kg.-cal. per mole, follow:

C—C	58.6	C—S	54.0	Si—C	57.6
C—O	20.0	C—Cl	66.5	Si—O	89.3
C—N	48.6	C—H	87.3		

The rubber (*8*) has been reported to be a specially prepared polymer of a purified dimethylsiloxane in which the condensation and aggregate formations have been so controlled that molecular elastomeric chains of several thousand units are formed without reduction to an insoluble polymer. This elastomeric network is unique among rubbers in that oxygen is the important condensing and rearrangement agent rather than sulfur, the common vulcanizing ingredient.

MECHANICAL PROPERTIES

The tensile strengths of various vulcanized elastomers in both gum and titanium dioxide–filled compositions (100 parts filler for 100 parts polymer) follow (in pounds per square inch):

Polymer	Natural	GR-S	GR-I	Buna N	GR-M	Silicone
Gum	3000	400	3000	600	3500	400
Filled	1500	700	1200	1000	1500	600

Natural, GR-I, and GR-M rubbers show high tensile strengths in the unfilled compositions. Buna N, GR-S, and silicone rubbers exhibit low values. The effect of the titanium dioxide filler was to reduce the tensile strength of natural rubber, GR-I, and GR-M, whereas it increased tensile strength for GR-S, Buna N, and silicone stocks. The tensile strength values for both the filled and unfilled silicone rubbers are similar to those obtained for the GR-S stocks. It has been possible to incorporate the necessary pigments into GR-S compositions and to make many usable rubbers from it.

Although titanium dioxide imparts relatively little reinforcing action, it was the chosen pigment because it is a material that will withstand the relatively high useful temperature of 200° C. displayed by the silicone rubbers. Carbon black, the outstanding reinforcing pigment used in most rubbers, gases badly at 200° C. and is not suitable at these temperatures. The problem with regard to the improvement of silicone rubbers is not only to better the characteristics of the polymer itself, but also to obtain effective compounding ingredients which are heat stable.

Figure 1 gives the variation with temperature of the common mechanical properties of silicone rubbers, and shows that this material maintains its characteristics over a wide temperature range. Although it has hardened and stiffened somewhat at −65° C., it is still quite rubbery and is in a very usable condition. Exposure of the material for 24 hours at the lowest temperatures made no appreciable change in the physical characteristics at these temperatures. This composition was unplasticized.

The same stock exhibits properties at 200° C. which are not very different from those at −65° C.; permanent set and resiliency characteristics are exceptions. At elevated temperatures this rubber "cold flows" considerably, almost proportionally to the temperature. The range of temperature above 250° C. through which the silicone rubber maintains constant characteristics is much greater than that for any of the carbon-base rubbers. Some carbon-base polymers, when sufficiently and properly plasticized, are temporarily usable at −65° C. In the majority of instances, however, those which have been prepared for low temperature use are unsatisfactory at the higher temperature portion of the range, and vice versa. More than one composition is then desirable to cover the entire range. Although this may be satisfactory from a chemical point of view, it may offer difficult mechanical problems where the temperature range of required operation is greater than that which the composition installed can serve.

ADHESION TO GLASS

Silicone rubbers will adhere to a properly prepared glass surface with a force which is greater than the breaking strength of the rubber itself (over 600 pounds per square inch). This adhesion exists upon a plain glass surface as well as on a glass fabric made of very fine filaments. Figure 2 gives the load-compression characteristics for a series of silicone rubber–glass fabric constructions. Three of the curves (*C, D, E*) are for sponge silicone rubber compositions with 50% voids.

Curve *A* shows that destruction of the glass reinforcing fabric occurs at a load of 3000 pounds per square inch. *B* demonstrates that the unreinforced silicone rubber is deflected as a logarithmic function of the compressive force applied. The construction represented by curve *C* has compression characteristics similar to that of *B*, except that at 60% deflection and above the glass fabric rupture is like that shown by curve *A*. The load-deflection characteristics of the sponge compositions given by curve *D* are comparable to those of the solid silicone rubber, *B*. The unreinforced sponge rubber (curve *E*) exhibits the usual high deflection–low compressive force ratio until collapse occurs in which region the deflection-load properties become similar to those of the solid rubber.

SWELLING CHARACTERISTICS

Vulcanized silicone rubbers are swelled to various degrees by different types of solvents. The actual swelling is dependent somewhat upon the amount of filler in the rubber. It is determined to a much greater extent by the nature of the solvent itself. Figure 3 gives rate-of-swelling curves for six solvents; each represents a different class of materials. These determinations, made at 20° C., show that water has the least effect. Acetone and mineral oil are more active; benzene, *n*-octane, and carbon tetrachloride are representative of the most effective groups. In the case of *n*-octane, swelling decomposition of the material occurred within the time of the experiment.

These swelling characteristics can be partially explained by examining the structure previously given for the silicone rubbers. The swelling by water is probably dependent on the silicon-oxygen configuration formed in the original polymeric condensation. At 165° C. and 100 pounds per square inch steam pressure, the effect of water vapor is much more rapid and considerably more extensive than at 20° C. An irreversible hydrolysis occurs which adversely affects the original properties of the rubber.

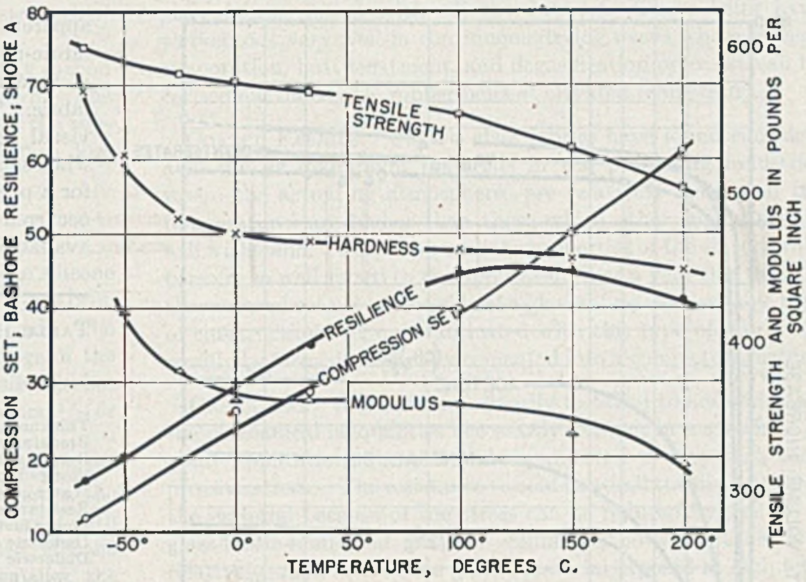

Figure 1. Effect of Temperature on Physical Properties of Silastic 125

A series of swelling tests comparable to those described in Figure 3 were performed in which the silicone rubbers were coated on, and adhered to, a glass fabric. The construction was such that parallel layers of fabric were situated each 0.03 cm. in a sheet 0.25 cm. thick. The rates of swelling as given in Figure 4 are comparable to those shown in Figure 3. The amounts of swelling have been considerably reduced, however, as follows: water 17%, benzene 55%, *n*-octane 53%, and carbon tetrachloride 50%.

The amount of glass fabric added to the construction was the same in each instance, 0.2 gram or 0.09 cc. per cc. volume. On a direct volumetric replacement basis the amount of swelling in each instance should have been reduced by 9%. The actual

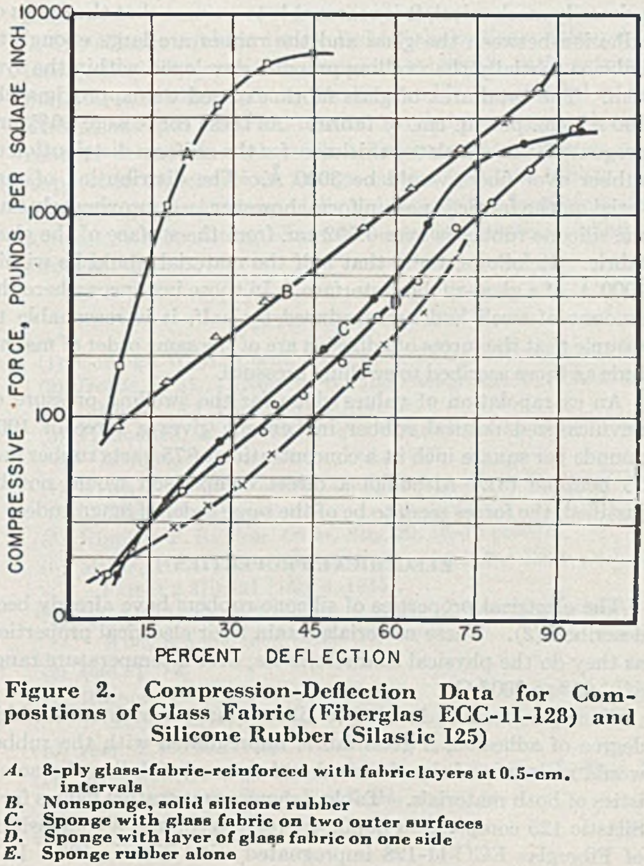

Figure 2. Compression-Deflection Data for Compositions of Glass Fabric (Fiberglas ECC-11-128) and Silicone Rubber (Silastic 125)

A. 8-ply glass-fabric-reinforced with fabric layers at 0.5-cm. intervals
B. Nonsponge, solid silicone rubber
C. Sponge with glass fabric on two outer surfaces
D. Sponge with layer of glass fabric on one side
E. Sponge rubber alone

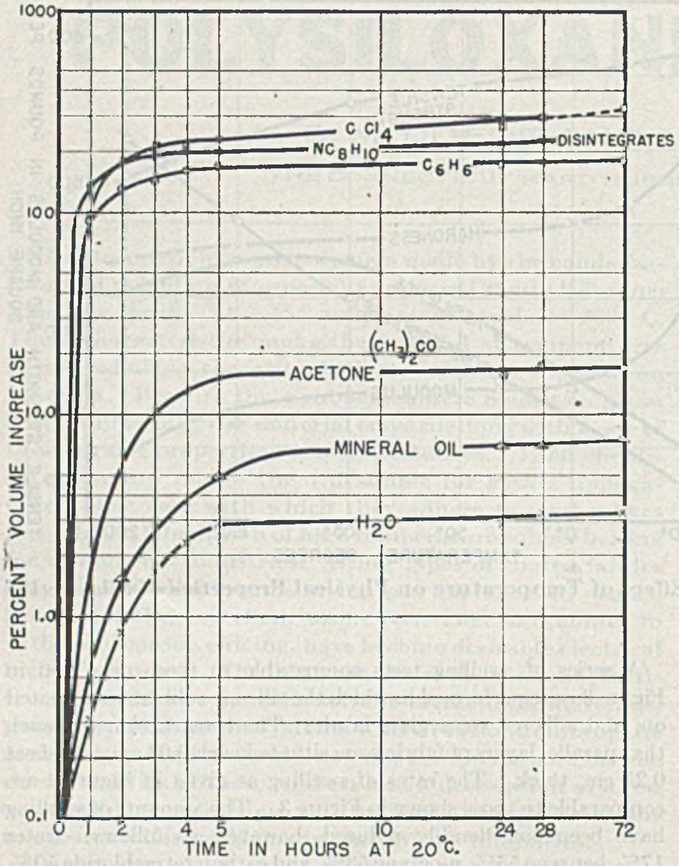

Figure 3. Volume-Time Data for Silastic 125 in Various Solvents

swell, however, was reduced as much as 55% in these experiments. The major decrease in swell then would be attributed to the interaction of the glass and silicone rubber. Since the structure was primarily mechanical, it is reasonable to assume that the forces of adhesion between the glass and the rubber are large enough to balance partially the swelling pressure developed within the system. The total area of glass fabric exposed was approximately 100 sq. cm. per sq. cm. of fabric. As these cords were 60% impregnated, the calculated thickness for the uniform distribution of rubber over fibers would be 3000 Å. The distribution of material on the fabric is not uniform, however. Approximately half the silicone rubber is over 0.002 cm. from the surface of the glass fabric. It follows, then, that half the material would lie within 1000 Å. of a glass-rubber interface. In those instances where the amount of swell had been reduced by half, it is reasonable to assume that the forces of adhesion are of the same order of magnitude as those ascribed to swelling pressure.

An extrapolation of values given for the swelling pressure of unvulcanized natural rubber in benzene gives a force of 1000 pounds per square inch at a concentration of 75 parts rubber and 25 benzene (*3*). Although a direct comparison would not be justified, the forces seem to be of the same order of magnitude.

ELECTRICAL PROPERTIES

The electrical properties of silicone rubbers have already been described (*2*). These materials retain their electrical properties, as they do the physical characteristics, over a temperature range of −65° to 200° C.

Since glass can be bonded to silicone rubber with such a high degree of adhesion, a glass fabric impregnated with the rubber would make use of the electrical and thermal stability characteristics of both materials. Table I shows comparative values for a Silastic 125 composition nonfabric-reinforced, and a composition of Fiberglas ECC-11-128 impregnated with Silastic 125. It is apparent that the elongation and breaking strengths of the glass-fabric-reinforced Silastic are those of the Fiberglas. The amount of water absorption is decreased one third by the addition of glass fabric. The resistance to ozone is excellent. There were no visual signs of cracking or evidences of physical deterioration when samples of the two materials were exposed to test conditions for a period one thousand times as long as that at which failure occurred for the most resistant carbon-base rubbers currently available.

TABLE I. PHYSICAL PROPERTIES OF SILICONE RUBBER, ALONE AND REINFORCED WITH GLASS FABRIC

	Silastic 125	Reinforced with Fiberglas
Thickness, inches	0.016	0.016
Breaking strength, lb./in.	9	225
Bursting strength, lb./sq. in.	15	276
Elongation, %	225	1.5
Water absorption after 100 hr., %	2.7	1.8
Resistance to ozone deterioration	Excellent	Excellent
Power factor at 1000 cycles sec.$^{-1}$, %	0.6	0.5
Dielectric constant at 1000 cycles sec.$^{-1}$	3.6	3.07
Dielectric strength at 60 cycles sec.$^{-1}$, volts/mil	1050	875

The power factor and dielectric constant are significantly better for the fabric-reinforced material than for the plain Silastic 125. The dielectric strength is, however, definitely reduced. Although the weight of glass used in the sample is 17% of the total weight, the gases trapped in the 40% voids in the unimpregnated portion of the fabric were effective in causing the dielectric strength failure to occur at a lower potential. The actual volume of the voids is 5% of the total volume of the sample. If the loss of dielectric strength is attributed to the existence of gas pockets (a reasonable assumption), it is understandable how relatively small

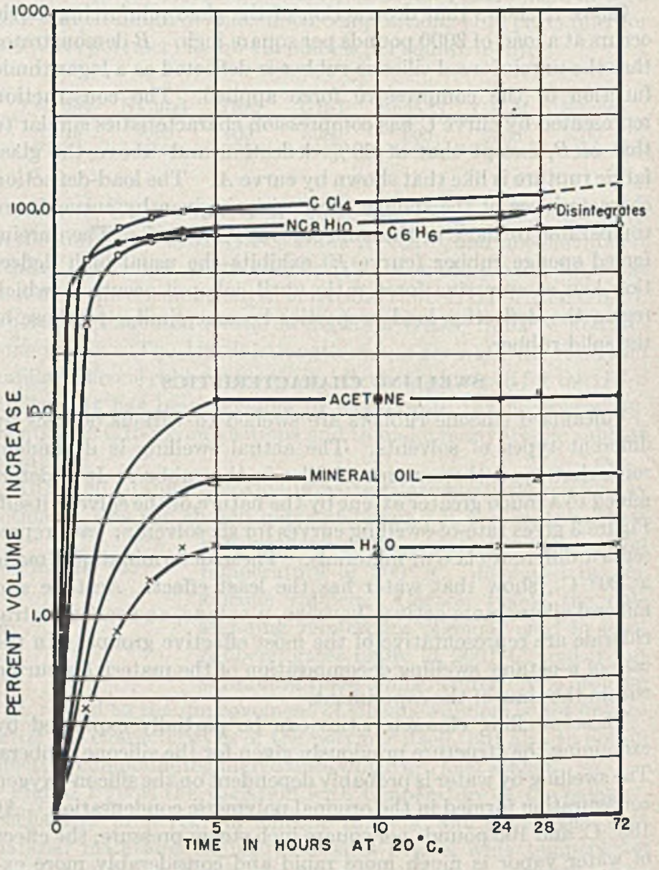

Figure 4. Volume-Time Data for Compositions of Silastic 125 and Fiberglas ECC-11-128 in Various Solvents

occluded voids can substantially reduce the dielectric strength of an electrical insulator.

The composition of both these materials is such that carbon tracking cannot occur after a dielectric strength breakdown. The potential necessary to continue an arc is determined by the conductivity of the path formed. The resultant silica surface does not form an electrically conducting one.

USES

There have been many interesting applications of the silicone rubbers. Many more are possible. In each instance it has been necessary to consider the particular problem involved. The applications have been so designed as to take advantage of the characteristics of the silicone rubbers. Whenever possible gasket thicknesses of $^1/_{64}$ or $^1/_{32}$ inch were used instead of the usual $^1/_{16}$ or $^1/_8$ inch.

When low temperature flexibility characteristics are necessary to a degree not provided by the ordinary synthetic rubbers, the silicone rubbers should be considered. Where an elastomer with thermal stability between 125° and 200° C. is needed, silicone rubber can serve. Unless special circumstances demand, the silicone rubbers should not be used where the temperature of application is between −25° and 125° C. They are not competitive materials in the ordinary sense of the word, but they do make possible economical designs for use in temperature ranges beyond which the ordinary rubbers serve.

From certain points of view the physical properties are not nearly so outstanding as might initially be desired. The designated properties given for rubber applications have frequently been stated for specification purposes and may bear little relationship to the actual requirements of the problem. Thus far it has not been advisable to make a direct substitution of an article of silicone rubber in a design where a contemporary synthetic had been attempted. In each satisfactory solution the final design has been based upon an application of the properties of this particular elastomer. Fortunately for the engineer there are many such problems. For illustration, several typical classes of problems are outlined which have been satisfactorily solved; the solutions should find further general application in the process industries.

Hydraulic Seals. One of the characteristics of silicone rubbers has been the fact that they cold flow at high temperatures. This property has been advantageously used in the design and construction of stationary seals for high temperature oil lines. The entire packing is well supported within a mechanical framework underneath a spring loading device so that the rubber is at all times under mechanical stress. Under this condition it flows into the physical irregularities of the metal surfaces present and seals all possible points of leakage. Packings such as this have served at temperatures of 175° C. on lubricating oil systems for operating periods of over a year.

In the glass processing industries it is often desirable to utilize steel tools with a rubber facing to support hot glass objects. The rubber protects the hot glass from both thermal and mechanical shock, as well as breakage. As silicone rubber adheres readily to steel and can momentarily withstand spot temperatures of 400° C., they have proved particularly useful in these applications.

Belting. Silicone rubbers are odorless, tasteless, and nontoxic. These properties have made it possible to build wire-cloth-reinforced belts for use in the food processing industries. Prepared foods can be placed directly upon the belt and dehydrated under such conditions that the belt temperature may reach 225° C. The rubber is unaffected by the water vapor or the food fluids themselves. Several of these belts have been in use for many months.

In those cases where the mechanical strength of wire cloth is not necessary, it has been possible to make processing belts from glass fabric coated with silicone rubbers. These belts have worked out very well in continuous drying ovens where solvent evaporation, heat treatment, and degasification processes can be carried out on flexible rubber belts at elevated temperatures.

Coated Fabrics. Coated glass fabrics have found considerable use as diaphragm materials in the processing industries where the actuating atmospheres are relatively inert, and the temperatures are higher than those which other coated fabrics will withstand. For many uses the properties of the silicone rubbers are so well suited to the application that a very thin layer of the material coated on one side of a glass fabric is a desirable type of construction. A unit fabricated with this type of fabric can readily be formed and finally cemented into a complete structure.

Gasketing. A gasket is ordinarily installed to accommodate the mechanical inequalities necessarily existent in a system. In many applications the material is subjected to very high compressive stress. The resistance to cold flow and the dislocation of the material because of the stress can be reduced by the use of glass-fabric-reinforced gaskets. Similarly, however, there is a relatively small area of the gasket material exposed at high temperatures to active solvents; the effect of the solvents is not nearly so great as the laboratory tests on completely immersed samples would indicate. It is possible to use these materials for gasket purposes on a high pressure steam line and in many systems where active materials are present.

Electrical Devices. The constructions coated with glass fabric–silicone rubber lend themselves excellently to the preparation of electrical insulating tapes which are required to function continuously at temperatures at least 100° C. higher than those which the present-day organic materials will withstand. This resistance to high temperature means not only that the equipment can be designed to function at higher temperatures, but also that electrical units can be located on processing equipment in positions where the mechanical advantage is improved. It also means that the units can be subjected to temporary overloads without fear of destruction of the rubber insulation within the unit.

The silicone rubbers are swelled by the ordinary mineral insulating oils. They contain, however, relatively little extractable material which can, in turn, be dissolved in the mineral oil itself. This means that electrical insulating oils in contact with silicone rubbers do not lose their electrical properties because of the acquisition of deleterious foreign matter from the rubber. This particular property is especially valuable where long life and high temperature operating characteristics are essential in oil-filled electrical devices.

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Received April 14, 1947.

SILICONE RESINS . . . .

Use in Protective and Decorative Finishes

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SILICONE resins are a recent addition to the list of vehicles and binders of interest to the protective and decorative coatings industry. They offer several properties which are not obtained with other resins and provide an unusual combination of resistance characteristics. Their use will permit the attainment of new levels in resistance to heat, chemicals, and weather. When their cost is lower, they will find general use in many types of finishes. Several modified silicone resins can be made, and those modified with alkyd resins are particularly promising. They possess most of the desirable characteristics and few of the disadvantages of the individual members.

SILICONE resins are organosilicon compounds which are believed to have a basic molecular structure of recurring —Si—O—Si— groupings similar to the arrangement in quartz. However, in silicones organic radicals such as methyls and phenyls are attached to the silicon atoms to provide solubility, toughness, and flexibility. The strength and stability of the silicon-to-oxygen and silicon-to-carbon linkages plus the presence of little or no chemical unsaturation is thought to be responsible in large part for the unusual resistance characteristics of silicones (Figure 1).

The mechanism of heat curing is believed to be mostly a cross linking through the condensation of residual hydroxyl groups. These hydroxyls remain from the hydrolysis of chlorosilanes in the formation of the resin.

PROPERTIES

Silicone resins range from hard, brittle, glasslike materials to viscous oils. Usually they are colorless or nearly so, and are easily soluble in aliphatic and aromatic hydrocarbon solvents. These solutions are low in viscosity at high resin concentrations. They wet pigments readily, and many of the common pigments can be used with them. No special care need be exercised in selecting pigment-dispersing equipment. Silicone paints have been made successfully with roller, pebble, and ball mills.

These paints may be made to have a very high clean-cut gloss, and to have an excellent purity of color and tint. The latter is possible because of the absence of color in the resin and the freedom from resin discoloration during baking or heat curing. Also, this permits the use of some of the lower cost white pigments which, because of their inferior opacity and inability to obscure vehicle discoloration, have not been extensively utilized in other types of baking enamels.

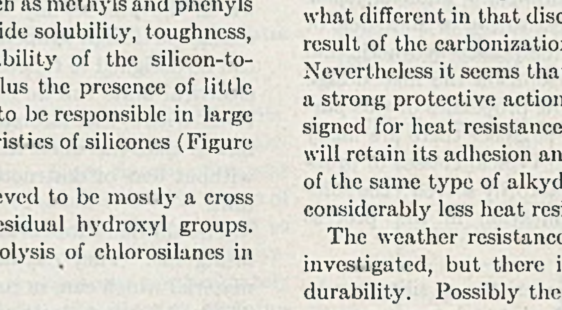


Figure 1. Probable Molecular Arrangement of a Cross-Linked Silicone Resin

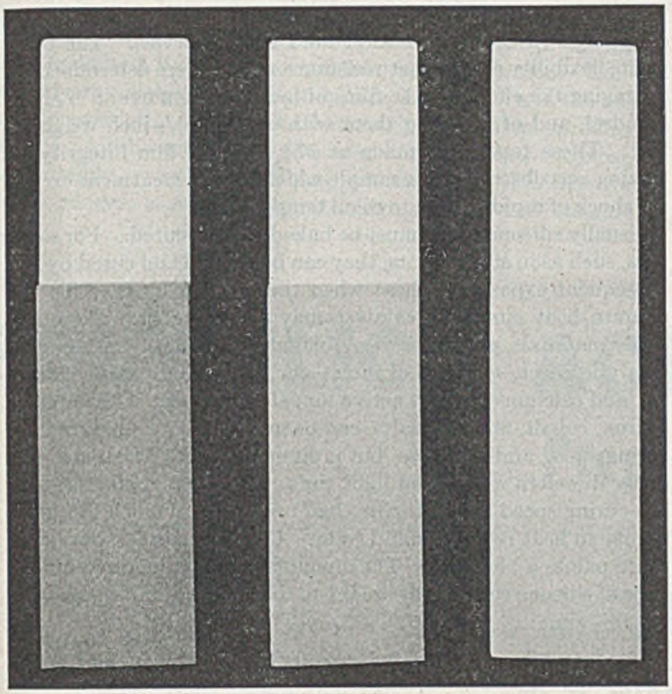
Possibly the outstanding properties of silicone finishes are their excellent resistance to heat, weather, and various chemicals When pigmented with heat-resisting pigments, these finishes withstand 1000° F. for a few hours and 500° F. for several hundred hours. With a more thorough selection of pigments, more knowledge of the most suitable proportions to be used, and a better understanding of silicone resin behavior, even greater heat resistance is anticipated.

Apparently the ultimate failure of a silicone resin at high temperatures is through oxidation of the organic radicals, leaving silica as a residue. Also there seems to be an intermediate stage caused by volatilization of low-molecular-weight polymers, and resulting in shrinkage and imbrittlement of the film. Discoloration, except that which may be attributed to the pigment, is not a part of this failure. Nor is any loss of gloss apparent until the final stages are reached. Usually the evidence of film failure is cracking or checking, and loss of adhesion to the substrate.

The effects of high temperatures on alkyd silicones are somewhat different in that discoloration does occur. Possibly this is a result of the carbonization of the fatty acid portion of the alkyd. Nevertheless it seems that the presence of the silicone resin exerts a strong protective action over the alkyd. An alkyd silicone designed for heat resistance will discolor somewhat at 480° F., but will retain its adhesion and toughness for several hours. A blend of the same type of alkyd with a melamine-formaldehyde resin is considerably less heat resisting (Figure 2).

The weather resistance of silicone finishes has not been fully investigated, but there is strong evidence pointing to unusual durability. Possibly the longest weather test is that of a white enamel which has been exposed four years on a Schenectady test fence facing south at 45° from the vertical. Dirt collection is the only evidence of failure; there has been no checking, cracking, chalking, or loss of gloss. This enamel is a straight silicone resin pigmented with rutile-titanium oxide. Another set of panels of a phthalocyanine blue-tinted chalking-type anatase-titanium oxide in a silicone resin has been exposed in Schenectady for nearly two years without showing any fading and chalking. The alkyd resin controls in this test have faded and chalked badly.

Evidence of this excellent weather resistance is being supported by tests in Florida. These have not been sufficiently prolonged to be convincing, but they are following the pattern of previous observations. These exposures may indicate the feasibility of using such pigments as the molybdate oranges more extensively for outdoor finishes. This particular test has not been long enough to prove utility, but after four months in Florida a molybdate orange in an alkyd resin has darkened considerably while the same pigment in a silicone resin has changed little.



Alkyd-melamine, 2 hours

Alkyd-silicone, 2 hours

Silicone, 24 hours

Figure 2. High Temperature (480° F.) Discoloration (*below*) of White Enamels in Comparison with Original Color (*above*)

There is no intention of claiming unusual weather resistance for any and all silicone paints. Some pigments which are poor in resisting ultraviolet light will fail as usual. Also, silicone resins which are too hard or which are not properly heat-cured will fail prematurely by checking and cracking.

When formulated with resistant pigments, silicone finishes are highly resistant to dilute alkalies and mineral acids. They have withstood 3% concentrations at 100° F. for over 100 hours without any apparent effect (Figures 3 and 4). Some organic acids, such as acetic, are more severe and have caused blistering in some tests. This may be a solvent effect more than an acid attack, since cured silicone resins are not resistant to hydrocarbon solvents. This deficiency has been somewhat lessened, and further improvement is expected. However, at present silicone finishes are inferior to alkyds and melamine resins in resisting such solvents as xylene. One means of overcoming this shortcoming will be by modification with alkyds. The silicones are resistant to alcohols.

Possibly iodine is the most potent stainer to be encountered by the usual run of protective coatings. It stains alkyds and alkyd-melamines badly, but has little effect on silicones (Figure 5). Also, silicones resist staining by mustard, grape juice, Mercurochrome, and tomato juice.

Silicone coatings adhere well to glass and such metals as steel and aluminum, but in this respect they are surpassed by alkyd finishes. Their adhesion is greatly improved by modification with alkyds. Since their adhesion to primers is much better than to metals, they are often applied over specially pigmented alkyd resins. Usually this is not desirable for high temperature resisting finishes, as the alkyd then becomes a weak link in the system. This is not necessarily true, however, in systems for withstanding alkaline conditions. Apparently the silicone top coat fully shields the much less alkali-resisting alkyd. Further evidence of this unusual protective action has been observed in the high resistance to acids of silicone paints containing zinc oxide as a portion of the pigment.

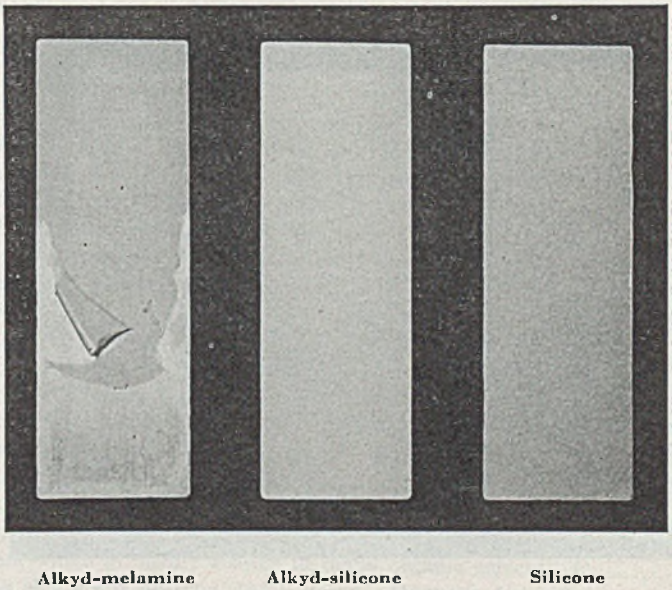
Another quality of silicone coatings, and possibly one which contributes to weather resistance, is low temperature flexibility. They have shown good results when given bending and mechanical shock tests at temperatures as low as −50° F. Resistance to burning is still another quality. This would be expected from a chemical structure based on silicon.

PIGMENTATION

The limited amount of work which has been done on the pigmentation of silicone resins indicates that many established concepts must be modified and new ones reckoned with. For instance, pigments which previously may have been considered unsuitable under certain conditions can be used in silicone resins with satisfactory results. Specifically the so-called chalking types of titanium oxides may be more generally employed in outdoor finishes, low-cost extended white pigments may be used in high temperature resisting enamels, some organic colors can be utilized at higher temperatures than were previously feasible, and new pigments may be developed or adopted from other industries to meet the new levels of performance attainable with these new resins.

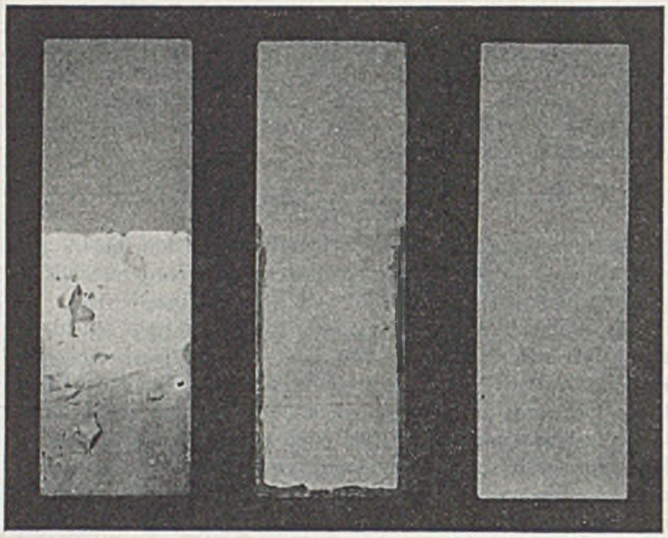
Since the first stages of film failure at elevated temperatures show as cracking or checking and loss of adhesion, it would be expected that micaceous and acicular pigments would be beneficial in heat-resisting finishes. This is true as shown when aluminum powder, mica dust, and asbestine are used. However, it might not be anticipated that, with titanium oxide, high temperature resistance varies inversely with the content of pigment; yet the heat resistance of a titanium oxide enamel is improved at increased pigment volume when other pigments and extenders, such as zinc oxide, lithopone, antimony oxide, calcium sulfate, and calcium carbonate, are added. Further study may modify these observations and may provide an explanation. Possibly this explanation will be associated with crystal structure and chemical treatment of the pigment, or with the effect of the pigments at elevated temperatures on the thermal stability and molecular rearrangement of the resin.

Based on present knowledge, the most heat-resistant silicone finishes are those pigmented with the conventional amount of aluminum powder. These finishes will withstand 1000° F. for a few hours and 750° F. for as much as 100 hours before there is considerable film failure and loss of adhesion. The best white enamels are those containing titanium oxide extended with cal-



Alkyd-melamine Alkyd-silicone Silicone

Figure 3. Resistance to Immersion in 3% Sulfuric Acid at 100° F. for 100 Hours



Alkyd-melamine, 24 hours

Alkyd-silicone, 48 hours

Silicone, 100 hours

Figure 4. Resistance to Immersion in 3% Caustic Soda at 100° F

cium sulfate. Such enamels have been held at 500° F. for 500 hours without cracking or checking. Also, there was little discoloration and loss of gloss. Adhesion and flexibility were impaired but not sufficiently to be regarded as failure. Other good white pigmentations are lithopone and antimony oxide with enough titanium oxide to provide the required opacity.

Among the other pigments which have been used successfully with silicone resins are carbon black, black iron oxide (but not for high temperature use), red iron oxide, cadmium red, lithol and toluidine reds (but not for use above 300° F.), phthalocyanine blue and gree, iron blue, ultramarine blue, chrome green, chrome yellow, and lead molybdate.

Table I gives the results of exposure to 500° F. for silicone enamels containing various pigments. The same lot of silicone resin was used in all enamels, and the curing catalyst was zinc octoate. Single coats (between 1.0 and 1.1 mils thick) of these enamels were applied to thin gage, sheet steel panels; they were placed in an electrically heated, ventilated oven, and their condition was observed after the stated time intervals. The composite flexibility and impact resistance ratings were determined by averaging the effects on the films of bending them over a $^1/_8$-inch mandrel, and of bumping them with a falling $^1/_2$-inch weighted ball. These tests were made at 77° F. The film integrity or crazing was observed on a sample which had no treatment except the shock of rapid cooling to room temperature.

Alkyd-melamine

Alkyd-silicone

Silicone

Figure 5. Resistance to One-Hour Iodine Staining

Usually silicone resins must be baked or heat-cured. For some uses, such as in stack paints, they can be applied and cured by the subsequent exposure to heat when the stack is in use. To accelerate heat curing, a catalyst may be desirable. There are many materials, particularly soluble salts of metals, which have a catalytic effect. Several of these—for instance, the salts of lead, tin, and calcium—are too active for safe handling. Others, such as iron, cobalt, and zinc salts, can be used. Iron is preferred for curing speed and hardness, but it diminishes heat resistance, and badly discolors whites and light tints. Cobalt and zinc provide less curing speed and hardness than iron, but are much less deleterious to heat resistance and color. Cobalt, however, does give white paints a blue tint. The amounts of metal required on the basis of silicone resin solids are 0.1 to 0.2% cobalt or iron, and 0.5 to 1.0% zinc.

Table I. Heat Resistance of Silicone Enamels at 500° F.

Pigmentation[a]	Composite Flexibility and Impact Resistance Rating after Heat Exposure 1 hr.	50 hr.	100 hr.	500 hr.	1000 hr.	Film Integrity Color after 1000 Hr. Craze	Color
Titanium oxide A (anatase), 20% PVC	5	4	3	4	4	3	0
Titanium oxide R (rutile), 30% PVC	1	3	4	5	5	5	0
Titanium oxide R, 25% PVC	1	3	3	4	5	5	0
Titanium oxide R, 20% PVC	1	3	3	3	4	4	0
Titanium oxide R, 15% PVC	1	3	3	3	4	3	0
Titanium oxide R, 10% PVC	1	2	3	3	4	2	0
Unpigmented silicone resin	1	2	2	3	3	1	0
Zinc oxide, 25% PVC	2	1	2	2	3	1	0
Zinc sulfide, 25% PVC	2	2	2	2	3	1	0
Lithopone, 25% PVC	2	2	3	3	4	1	0
Titanium-calcium R, 25% PVC	1	2	2	2	2	1	0
Antimony oxide, 25% PVC	1	1	2	2	3	1	0
90 titanium oxide R–10 zinc oxide, 20% PVC	2	2	2	4	4	2	0
50 titanium oxide R–50 zinc oxide, 25% PVC	2	2	3	4	4	2	0
50 titanium oxide R–50 zinc sulfide, 25% PVC	1	2	2	3	4	2	0
50 titanium oxide R–50 lithopone, 25% PVC	1	2	2	3	4	2	0
50 titanium oxide R–50 titanium = calcium R, 25% PVC	2	2	2	3	4	2	0
50 titanium oxide R–50 antimony oxide, 25% PVC	1	2	2	2	3	1	0
70 titanium oxide R–30 asbestine, 25% PVC	1	1	1	2	2	1	0
Carbon black	1	1	2	3	3	1	0
Iron blue	1	4	5	5	5	5	Brown after 100 hr.
Phthalocyanine blue	1	2	2	5	5	1	Faded after 100 hr.
Phthalocyanine green	1	3	4	5	5	1	0
Red iron oxide	1	2	2	3	4	1	0
Yellow iron oxide	1	3	5	5	5	1	Red after 100 hr.
Black iron oxide	1	2	3	4	4	1	Same
Cadmium red	1	2	2	3	3	1	0
Cadmium yellow	1	2	2	5	5	1	0
Lithol red	1	2	2	3	4	1	Darkened, then faded after 100 hr.
Toluidine red	1	2	2	4	4	1	Same
Chrome yellow (light)	1	3	5	5	5	1	0
Zinc yellow	1	4	5	5	5	5	Darkened after 50 hr.
Chrome orange	3	4	4	5	5	5	0
Molybdate orange	1	2	2	5	5	1	0
Chrome oxide	1	1	2	5	4	1	0

[a] PVC = pigment volume concentration.

[b] Ratings: 0 = no change; 1 = excellent (no cracking, checking, flaking, or crazing); 2 = good (slight cracking and crazing along edges of panels); 3 = fair; 4 = poor; 5 = very poor.

USES

Since silicone finishes are so new and facilities for producing them are limited, they have not yet been extensively used. Consequently any discussion of their applications must be in the nature of prediction. Until their cost is reduced by volume production, they will be confined to special uses where heat, chemical, and, possibly, weather resistance are essential. Finishes for kitchen ranges, stoves, furnaces, boilers, motors, hot exhaust stacks, and chemical plant equipment are examples. When costs become competitive through increased production or by modification with alkyd resins, there is a long list of possible uses, such as for finishing automobiles, refrigerators and other home appliances, hospital equipment, signs, metal furniture, gasoline pumps, farm machinery, and many other products.

RECEIVED April 5, 1947.

POLYSILICIC ACID ESTERS....

Preparation from Sodium Silicate

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BY TRANSFERRING low-molecular-weight silicic acid, prepared by acidification of sodium silicate, from aqueous solution to *n*-butyl alcohol, it has been found that partial esterification can be effected by dehydration through azeotropic distillation. The partially esterified polysilicic acid, containing from 0.5 to 0.6 butoxy group per silicon atom, is a resinous solid, soluble in organic solvents and stable over long periods of time in butyl alcohol solution at a concentration of 20% SiO_2. Compatibility with hydrocarbon solvents and stability toward gelling increase with the degree of esterification. A preliminary viscosity study indicates that the partially esterified polysilicic acid molecules may be spherical in shape.

THE possibility of preparing a highly reactive low-molecular weight silicic acid in aqueous solution by the acidification of sodium silicate has been known for many years. Mylius and Groschuff (*8*) found that, by carefully neutralizing a solution of sodium silicate in the cold with hydrochloric acid, a solution of silicic acid is obtained which passes freely through a dialyzing membrane. Tourky (*10*) visualized that freshly formed silicic acid in aqueous solutions is in an active condition capable of linking with other active molecules. Willstätter (*11*) has shown that silicic acid can exist in aqueous solution in the monomeric form for a short time, provided a small amount of hydrochloric acid is present as a stabilizing agent.

However, such silicic acid of low molecular weight is so unstable in aqueous solutions that any attempt to isolate it by evaporation of water, even at ordinary temperature, results in rapid polymerization to a gel. The direct esterification of silicic acid has therefore remained impractical until the recent discovery of a method for transferring silicic acid of low molecular weight from aqueous solution to solution in an alcohol. This transfer is accomplished by extraction of the acid with a suitable alcohol (*6*). Esterification is then effected by azeotropic distillation of water from the alcohol solution (*4*).

The success of this technique depends upon the careful choice of conditions to keep the degree of polymerization within suitable limits from the moment the silicic acid is generated from sodium silicate until the esterification is finally effected. For example, the acidification of the solution of sodium silicate must be carried out under conditions which give silicic acid of relatively low molecular weight—that is, at a low temperature with rapid mixing to obtain a relatively dilute solution having a final pH of 1.7. Transfer of silicic acid to the alcohol—for example, *tert*-butyl alcohol—must then be effected before polymerization has reached the gel stage.

So long as the alcohol solution contains an appreciable amount of water, esterification does not proceed to an extent sufficient to provide a product which is stable on long storage. In order to obtain a product of minimum molecular weight, water is promptly removed from the alcohol solution as rapidly and at as low a temperature as possible by azeotropic distillation under reduced pressure. As esterification proceeds and the silicic acid becomes more stable toward polymerization, the distillation temperature can be allowed to rise through (*a*) an increase in pressure, (*b*) substitution of a second higher boiling alcohol for that used in the extraction, or (*c*) both. In the last stages of the esterification the distillation is carried out under atmospheric pressure to effect removal of water continuously as it is formed. During all but the last stage of the esterification process the concentration of silicic acid, expressed in terms of SiO_2, is kept below 10% by occasional addition of alcohol, either that used for the extraction or a higher boiling alcohol of which the ester is desired. The concentration of the resulting substantially anhydrous solution of polysilicic acid ester is adjusted to about 20% SiO_2. In this form the ester, which contains up to about 0.6 alkoxy groups per silicon atom, is stable toward gelling at ordinary temperatures over a period of several years.

For practical purposes *tert*-butyl alcohol is the most satisfactory alcohol for use as the silicic acid extractant. During the esterification it is generally replaced by the higher boiling *n*-butyl alcohol, which makes possible more rapid removal of water from the system. Solvent-free butyl polysilicate containing 0.5–0.6 butoxy group per silicon atom is a somewhat tacky, resinous material which is readily soluble in many organic solvents, including choroform, acetone, and benzene. However, the esterification of the silicic acid is apparently incomplete, since the solvent-free product slowly becomes insoluble if permitted to stand for several days at ordinary temperatures. The presence of unesterified acid groups is also indicated by the chemical analysis of the product after it has been dried in a thin film under reduced pressure.

Less completely esterified intermediate products are soluble in alcohols, acetone, or other polar solvents, and are precipitated by the addition of benzene and other hydrocarbons. Upon evaporation of the solvent these products deposit a hard, brittle film which cannot be redissolved.

Polysilicic acid esters of higher boiling alcohols, such as octyl, dodecyl, cyclohexyl, stearyl, and methallyl alcohols, can be prepared conveniently from butyl polysilicate by an ester interchange reaction.

The preparation of organic solvent–soluble, partially esterified polysilicic acid from sodium silicate not only suggests a new method of approach for obtaining a better understanding of the chemistry of silicic acid but also opens up many practical possibilities involving the incorporation of silica, derived from sodium silicate, into organic products. For example, these products can be incorporated into alkyd resin finishes to improve hardness and rate of drying (*3*) or mixed with other types of resins to yield clear, hard, abrasion-resistant films useful as protective surface coatings on organic plastics (*1*).

LOW-MOLECULAR-WEIGHT SILICIC ACID

A study of the rate of polymerization of silicic acid in aqueous solution has shown that this material is least stable in aqueous solution in the pH range 5 to 7, and most stable at a pH of about 1.5 to 2.0. Therefore, in order to liberate silicic acid of lowest possible molecular weight, it is essential to carry out the neutralization in such a manner that the solution is converted practically instantaneously from the alkaline condition to a pH around 1 to 2.5. This is most simply effected by passing a dilute solution of sodium silicate in a thin stream into a violently agitated solution of dilute acid, the temperature preferably being maintained below 30° C., using such an excess of acid that the final pH does not rise above 2.0.

Preparation. The following example is illustrative. Separate dilute solutions of sodium silicate and sulfuric acid are prepared as follows: Sodium silicate, Grasselli No. 20 WW grade (a commercial water glass containing 28.40% SiO_2 and having a weight ratio of $SiO_2/Na_2O = 3.25$) is diluted in the proportion of 777 grams of sodium silicate (liquid) to 1138 grams of water, a total of 1915 grams or 1710 cc. Separately 1710 cc. of 7.35% sulfuric acid are prepared and cooled to 20° C. The diluted sodium silicate solution is then run into the equal volume of dilute acid, with violent agitation. The addition is made in a stream not over 0.1 inch in diameter added directly to the vortex created by the stirrer, and is complete in about 5 minutes. The pH of the resulting 3420 cc. of silicic acid solution is 1.7 ± 0.05. This solution is then ready for extraction of the polysilicic acid by an alcohol.

Extraction from Aqueous Solution with Polar Organic Solvents. J. S. Kirk (*5*) appears to be the first to have discovered that, by a combined salting-out and extraction process, soluble silicic acid can be transferred from an aqueous solution to organic solvents. Silicic acid alone cannot be salted out of aqueous solution; if, however, an organic solvent containing polar groups is present, saturation of the aqueous phase with a salt such as sodium chloride brings the silicic acid into a loose association with the organic solvent, so that a separate liquid phase is formed which can be mechanically separated from the brine layer. A possible explanation is that a hydrogen bond is formed between the hydrogen of the silanol group (—SiOH) and the electron donor atoms, such as oxygen or nitrogen, in the polar organic solvent. Solvents of this type have been classed as hydrogen-bonding agents.

Esters, amides, ketones, and alcohols can all function as extraction solvents in this way (*5, 6*). However, where the silicic acid is to be esterified, it is preferable to use an extracting solvent which has a relatively low boiling point and which can therefore be readily recovered from the final esterified product. For this purpose *tert*-butyl alcohol appears to be one of the most satisfactory.

Immediately after the preparation of the 3420 cc. of silicic acid solution already described, 1357 cc. (1070 grams) of *tert*-butyl alcohol are added. The mixture is stirred for 15 minutes and then permitted to stand for 16–18 hours at room temperature (below 30° C.) in order to ensure maximum yield. Up to this point the solution is completely homogeneous. However, upon adding 1017 grams of sodium chloride and stirring for 10 minutes, an alcohol-rich liquid phase appears containing silicic acid. The mixture is permitted to stand for 20 minutes in a separatory funnel; the lower, aqueous saline layer is drawn off; and the upper, alcohol layer is set aside for further processing.

As the separation of the two layers is sometimes incomplete because of emulsification, it is advisable to add 24 cc. of a 2% gelatin solution prior to the addition of salt. The gelatin apparently brings about coagulation of a small amount of unidentified material which is responsible for the formation of an emulsion.

In a typical experiment performed in this manner the separated alcohol layer (1540 cc.) contained 14.0% silica, 0.96% sodium chloride, and 10–15% water, as determined by titration with the Fischer reagent (*9*). The yield of silica is about 80–85% of that originally present in the sodium silicate.

RELATION BETWEEN MOLECULAR WEIGHT AND YIELD

If the separation of the alcohol phase is complete, the yield is primarily dependent upon the molecular weight of the silicic acid in the aqueous solution at the time of extraction. Although there is little or no change in the appearance of the aqueous silicic acid solution, there is a progressive increase in the molecular weight of the silicic acid as the solution is aged, the rate being a function of the concentration of silicic acid, the pH, and the temperature.

An empirical titration method has been developed to follow this polymerization (*2*). This method depends upon the discovery that the precipitation of soluble silicic acid by gelatin is inhibited by water-miscible organic solvents containing electron-donor groups—for example, the diethyl ether of diethylene glycol (diethyl Carbitol). However, the concentration of the latter organic solvent required to inhibit precipitation depends upon the concentration of electrolyte in the mixture and upon the molecular weight of silicic acid. The precipitation point is relatively independent of the concentrations of gelatin and of silicic acid. The test is carried out as follows:

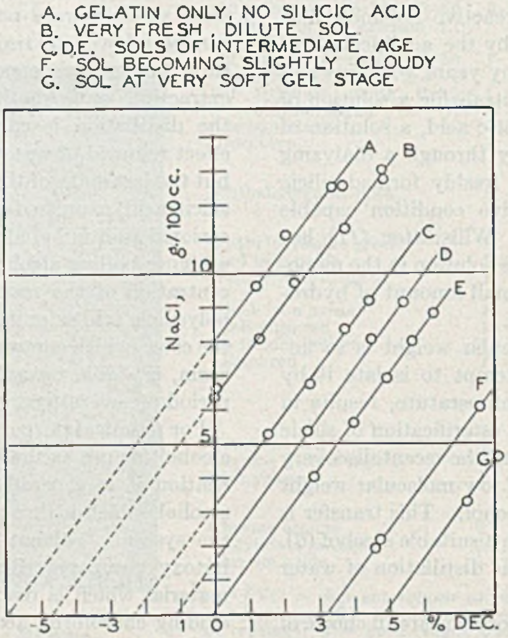

Figure 1. Titration Curves of Silicic Acid Solutions of Different Molecular Weights

Ten cubic centimeters of a solution of silicic acid, free from organic solvents and containing from 4–6% SiO_2 at a pH of 1.5 to 2.5, are pipetted into a 1×8 inch test tube. To this are added 2 or 3 cc. of an aqueous solution of diethyl ether of diethylene glycol (diethyl Carbitol) containing 500 grams per liter, the pH being adjusted to 2.5 with hydrochloric acid. To this are added 5 cc. of a 2% solution of high grade edible gelatin (Knox Super XXX). Sufficient diethyl Carbitol solution is used to prevent the formation of a precipitate when the gelatin solution is added. This mixture is then titrated with a standard solution of sodium chloride containing 300 grams per liter (previously adjusted to pH 2.5 with hydrochloric acid) until the solution becomes turbid. This is observed by holding the tube against an aperture $^1/_4$ inch in diameter illuminated from behind by a 60-watt lamp. The end point is arbitrarily taken when the clear outline of the aperture can no longer be discerned. This relatively crude method is satisfactory, since the end point is quite sharp; the mixture usually changes from perfect transparency to extreme turbidity within 0.2 to 0.3 cc. The mixture is shaken vigorously for about 10 seconds after each addition of salt solution before the turbidity is observed. The turbid solution is then cleared up by adding another 1 or 2 cc. of the diethyl Carbitol solution and again titrated to the end point with sodium chloride solution. At each end point the total concentrations, in terms of grams per 100 cc., of sodium chloride and of diethyl Carbitol are calculated with the total volume at each end point taken into account. These values are plotted on rectangular graph paper with the sodium chloride concentration as ordinate and the concentration of diethyl Carbitol as abscissa. The end points will be found to lie on a straight line, which can be extrapolated to the diethyl Carbitol axis. Such plots are shown in Figure 1.

If distilled water, adjusted to pH 2.5 with hydrochloric acid, is used instead of the silicic acid solution, a similar precipitation of gelatin alone is observed. This precipitate is solubilized by diethyl Carbitol, and the end points obtained on titration with salt solution similarly fall on a straight line. As shown in Figure 1, the position of the lines obtained with sols of increasing molecular weight move progressively to the right—that is, higher concentrations of diethyl Carbitol are required to prevent precipitation. The intercept on the diethyl Carbitol axis therefore serves to indicate the relative molecular weight of the silicic acid.

In order to have an arbitrary scale with positive values, a function X was adopted such that

$$X = 6 + C$$

where C = intercept on diethyl Carbitol axis

This X value then ranges from 0 for gelatin solutions alone (or for silicic acid sols of extremely low molecular weight) to about 11 or 12 for silicic acid solutions which have polymerized to the gel stage and which, therefore, contain material of very high molecular weight.

The values in Table I show the increase in the X value which occurs as an aqueous silicic acid solution, prepared as described, is permitted to age at pH 1.7 and at 12°, 25°, and 48° C., respectively.

If the aqueous silicic acid solution is permitted to age for different periods of time before the *tert*-butyl alcohol is added and the alcohol solution is then salted out within about 15 minutes, the yield of silicic acid increases with the X value as follows:

X Value of Sol	Yield as SiO_2, %
3.0	37
5.0	53
8.5	82

The ratio of the volumes of *tert*-butyl alcohol to silicic acid solution used has only a minor effect on the over-all recovery of polysilicic acid. For example, in the case of the silicic acid solutions aged at pH 1.7 at 12° C. to various X values prior to the addition of alcohol and salt, the following results were obtained:

tert-BuOH Used/L. Silicic Acid Soln.	Silicic Acid Yield as % SiO_2 $X = 3.5$	$X = 6.5$	$X = 8.0$
200	37	60	73
400	40	73	80

In general, a somewhat higher recovery of silicic acid of lower molecular weight is obtained when the *tert*-butyl alcohol is added to the silicic acid sol immediately after its preparation and the mixture then permitted to stand in order to allow the silicic acid to polymerize in the presence of the alcohol. However, in this case it is not possible to follow the polymerization by the titration procedure described because of the presence of the alcohol.

ESTERIFICATION OF SILICIC ACID

The freshly prepared alcoholic solution is a clear liquid having a viscosity little higher than *tert*-butyl alcohol. It contains a small amount of mineral acid, corresponding to a pH of 2, which appears to have a stabilizing effect, since attempts to lower the acidity by adding small amounts of neutralizing agent caused more rapid gelling. If held at ordinary temperatures (20–30° C.) the extract sets to a hard, clear gel in 2 to 4 days. Stability can be improved by diluting the solution with additional *tert*-butyl alcohol or cooling it to -20 °C. However, a much greater degree of stability is obtained by removing residual water, either with desiccants or preferably by vacuum distillation at low temperature, separating the water as the alcohol-water azeotrope.

To 1540 cc. of a solution of silicic acid in *tert*-butyl alcohol, prepared as described, an equal volume of *n*-butyl alcohol is added together with 6 grams of barium chloride. The purpose of the latter is to replace the small amount of sulfuric acid present in the extract with an equivalent amount of hydrochloric acid by the precipitation of barium sulfate.

The mixture is placed in a 3-liter flask fitted with a 1- or 2-inch-diameter fractionating column about 2 feet long having sufficient condenser capacity to permit as much as a 4:1 reflux ratio.

Distillation is carried out at 30 mm. mercury pressure with a reflux ratio of less than 1:1 and at a rate sufficient to remove 1131 cc. over a 2-hour period. During this time the original volume is maintained in the distilling flask by the further addition of *n*-butyl alcohol. The temperature in the distilling flask during this step rises from 28° to 39° C. Distillation is then continued at 60 mm. mercury over a period of 5 hours, during which time 1696

Table I. X Value of Silicic Acid Solution (6% SiO_2) Aged at pH 1.70

Hours	At 12° C.	At 25° C.	At 48° C.
0	3.0	3.0	3.0
2	3.4	4.3	7.8
5	4.0	5.6	...
10	4.8	7.0	...
20	6.3	9.1	...
35	8.0	...	...

Table II. Properties of Typical Batches of Polysilicic Acid Ester

	Extraction		Distn. Time, Hr.			Analysis, %				Gel
Code	Age of aqueous soln., hr.	Yield of SiO_2, %	30 mm.	55–65 mm.	760 mm.	H_2O	SiO_2	BuO/Si	Benzene Compatibility	Time at 99° C., Hr.
733-40	0.25	45	2.5	4.8	...	0.14	19.5	0.31	68	350
-41				13.3	...	0.12	19.8	0.38	100	380
-42				20.8	...	0.064	20.8	0.43	>200	450
-43				37.3	...	0.023	20.2	0.48	>200	750
420-53	0.0	30	2.0	2.0	...	0.20	20.0	0.33	30	152
-64					6	0.20	19.6	0.59	>100	>1500
420-70	2.5	58	1.8	2.3	...	0.12	23.36	0.34	31	63
414-61					2	0.13	20.0	0.48	>100	1250
420-66	16.5	83	1.2	1.8	...	0.15	19.7	0.35	20.6	53
420-68	37.5	87	1.5	2.2	...	0.15	23.5	0.29	17.3	16
698-119	0.5	45	2.5	1.3	...	0.26	...	...	32	72
-122				2.2	...	0.06	20.2	0.44	80	168

cc. of *n*-butyl alcohol are added and 3260 cc. of distillate removed. During this operation the temperature in the flask rises from 39° to 60° C.

At this point the solution in the distilling flask has a volume of about 1510 cc. and contains approximately 15% SiO_2. About 12 grams of Dicalite filter aid are added, and the liquid is filtered to remove precipitated salts and traces of silica gel.

Distillation is then continued at atmospheric pressure with a reflux ratio of at least 4:1 after addition of 485 cc. of *n*-butyl alcohol, the distilling rate having been adjusted so as to remove 752 cc. of distillate over a period of 5 hours. The temperature in the distilling flask finally reaches about 121° C.

The 1210 cc. of product at this point are then mixed with 10 grams of Dicalite and 20 grams of Darco decolorizing carbon and again filtered.

A typical product has the following analysis, after having been adjusted to about 20% SiO_2 by the addition of anhydrous *n*-butyl alcohol:

SiO_2, %	20.11	Total solids, %	33.98
Water, g./100 cc. soln.	0.11	Analysis of solids, %	
Chlorine, %	0.03	SiO_2	59.0
pH	3.8	C	28.98
		Degree of esterification, BuO/Si	0.613

METHODS OF ANALYSIS

Silica. A 2- to 3-gram sample of the solution of esterified polysilicic acid is weighed into a tared, covered platinum crucible, evaporated slowly to dryness on a steam plate, moistened with a few drops of 1:1 sulfuric acid, and ignited slowly in a muffle for 1 hour. The crucible is weighed, 4 to 5 drops of 1:1 sulfuric acid and 10 cc. of hydrofluoric acid are added, and the mixture is heated gently on the steam plate, evaporated to dryness, ignited, cooled in a desiccator, and weighed. The loss in weight after treatment with hydrofluoric acid is equivalent to the weight of silica in the sample.

Chlorine. This is determined by evaporating a weighed sample to dryness, decomposing the residue with sodium peroxide in a Parr bomb, and determining chloride in the residue gravimetrically as silver chloride.

Water. Five cc. of the polysilicic acid ester solution is measured into a 125-cc. Erlenmeyer flask and diluted with 10 cc. of anhydrous methanol. Water is titrated by the Fischer method (*9*).

Total Solids. Because of the resinous nature of the dried product, the solvent can best be removed by evaporation from a thin film under reduced pressure. A measured volume (3–5 cc.) of solution of butyl polysilicate is placed on a tared 3 × 5 inch glass plate in a desiccator through which perfectly dry air is drawn for 24 hours at 0.5 mm. pressure, and the weight of the residue is determined.

pH. The pH of the mixture is determined by mixing a sample with an equal volume of distilled water, shaking until a thorough dispersion is obtained, and measuring the pH with a glass electrode.

Stability. The stability of the solution of polysilicic acid ester is determined by sealing 5-gram samples in thoroughly cleaned 6 × $^5/_8$ inch Pyrex test tubes and immersing the samples in a steam bath at 98–99° C. until the gel point is reached, at which the liquid will no longer flow. This is taken as the gel time. It is important that the test tubes be cleaned in a chromium oxide–sulfuric acid cleaning solution, rinsed at least six times with distilled water and three times with acetone, and then dried at 110° C.

Compatibility with Benzene. One cc. of a polysilicic acid ester solution containing 20% SiO_2 is measured into a 10 × 1 inch test tube. Benzene is added from a buret until a slight turbidity appears, and the result is expressed as the volume of benzene in cc. required to reach this end point. However, this test is applicable only to samples which have been esterified to a low degree. Highly esterified products are completely miscible with benzene.

Degree of Esterification. A weighed sample of the solution is evaporated in a thin film on the inner walls of a 1-liter flask subjected to vacuum (2 mm. pressure) and heated externally by live steam. The dried residue usually tends to flake from the sides of the flask and is easily removed. Heating at 2 mm. pressure is continued for $2^1/_2$ hours in order to ensure complete removal of butanol. The residue obtained in this manner, or that obtained in the determination of total solids, is analyzed for carbon by combustion and for silica as described. The degree of esterification, calculated from these data, is expressed as the ratio of ester groups to silicon atoms. If silica and per cent carbon are determined on the same residual solids, it is not necessary to use a weighed sample of the solution or to transfer the residue quantitatively from the container in which the evaporation is carried out.

EFFECTS OF INCREASING DEGREE OF ESTERIFICATION

As indicated in Table II, continued distillation at 65 mm. pressure over a period of 37 hours reduces the water content of the solution of polysilicic acid ester in *n*-butyl alcohol from 0.14 to 0.023%. At the same time the degree of esterification increases from 0.31 to 0.48 butoxy groups per silicon atom. This increase in the degree of esterification results in improved compatibility with a hydrocarbon solvent such as benzene and also increases the stability of the sample toward gelling in the accelerated aging test at 99° C.

The stability of the resulting product toward gelling when heated at 99° C. is reduced, for a definite degree of esterification, as the aqueous silicic acid solution is aged prior to the extraction step. This can be noted by comparing the samples having a degree of esterification between 0.30 and 0.35.

VISCOSITY OF BUTYL POLYSILICATE SOLUTION

The approximate viscosity of a typical *n*-butyl alcohol solution of polysilicic acid ester was determined over a range of concentrations to learn whether the molecular weight could be determined by this method. However, as shown below, the results indicate that the molecules may be roughly spherical rather than linear, and therefore molecular weight cannot be determined by the Staudinger equation.

A sample of butyl polysilicate (20.2% SiO_2) in *n*-butyl alcohol (No. 733-43, Table II) was diluted to several lower concentrations with the same solvent, the viscosity at 25° C. determined by means of Ostwald pipets, and the specific viscosity calculated from the equation

$$\eta_{sp} = \frac{\eta_s}{\eta_0} - 1$$

where η_{sp} = specific viscosity
η_s = viscosity of solution as measured by Ostwald pipet
η_0 = viscosity of *n*-butyl alcohol

The results are shown in Table III.

Table III. Viscosity and Density Data

SiO_2, % by Wt.	Ostwald Pipet Sec. at 29.5° C.	Density at 29.5° C.	η_s/η_0
0	28.8	0.802	1.00 ± 0.005
1.43	30.4	0.811	1.067
2.65	31.8	0.820	1.129
5.16	35.1	0.835	1.270
9.66	43.2	0.864	1.613
20.2	88.0	0.931	3.540

As will be shown, these data appear to conform with the equation suggested by Guth, Gold, and Simha (*7*) for a dispersion of spheres:

$$\eta_{sp} = 2.5c + 14.1c^2$$

where c = volume fraction of suspended spheres or dispersed phase, cc./100 cc.

It is therefore tentatively concluded that the polysilicic acid units may be roughly spherical in shape, since linear or elongated molecules would not show this viscosity behavior.

Although the value of c cannot be measured directly, it is possible to estimate its value indirectly if one assumes that the total volume occupied by the solute is directly proportional to the silica content of the solution and that the volumes occupied by the solvent and solute are additive.

Thus from the assumption that (volume of solute) + (volume of solvent) = (total volume), for 100 grams of solution one can write:

$$\frac{aS}{d} + \frac{100 - aS}{0.802} = \frac{100}{D} \tag{1}$$

where S = % by weight of SiO_2 in solution
aS = % by weight of solute, a being the conversion factor
d = unknown density of pure solute
0.802 = density of n-butyl alcohol solvent
D = density of solution

Rearranging Equation 1,

$$\frac{a(d - 0.802)}{d} S = \frac{100(D - 0.802)}{D}$$

or

$$bS = \frac{100(D - 0.802)}{D} \tag{2}$$

or

$$D = \frac{80.2}{100 - bS}$$

where $b = \frac{a}{d}(d - 0.802)$

From density data $b = 0.685$; then, rearranging Equation 2,

$$D = \frac{0.802}{1 - 0.00685\,S} \tag{3}$$

From Equation 1, the volume of the solute

$$V_s = \frac{aS}{d} = \frac{100}{D} - \frac{(100 - aS)}{0.802}$$

Substituting for D,

$$V_s = \frac{S(a - 0.685)}{0.802} \tag{4}$$

Then c = fractional volume of solute, or

$$c = \frac{V_s}{V_s + \frac{100 - aS}{0.802}} \tag{5}$$

Substituting for V_s and simplifying:

$$c = \frac{S(a - 0.685)}{100 - 0.685(S)} \text{ or } a = \frac{100c}{S} + 0.685\,(1 - c) \tag{6}$$

From the viscosity data and the equation $\eta_{sp} = 2.5c + 14.1c^2$ or $c = -2.5 + (6.25 + 56.4\eta_{sp})^{1/2}/28.2$ the values of c and hence a (from Equation 6) have been calculated as shown in Table IV.

Table IV. Calculated Values of c and a

SiO_2, %	η_{sp}	c	a
1.43	0.067	0.022	2.2(1)
2.65	0.129	0.041(5)	2.3(0)
5.16	0.270	0.075	2.1(5)
9.66	0.613	0.138	2.0(7)
20.20	2.540	0.335	2.1(2)
			Average a = 2.2

From the relation $b = 0.685 = \frac{a}{d}(d - 0.802)$, taking $a = 2.2$,

$$d = 1.17 \pm 0.08$$

The relative constancy of a indicates that the experimentally determined viscosity-concentration relation approximately follows the theoretical equation for spherical particles in suspension.

BUTYL POLYSILICATE IN SOLUTION

The value $a = 2.2$ suggests that, in the original concentrated solution containing 20.2% SiO_2, the concentration of actual solute may be about 2.2 × 20.2 = 44(.5)% by weight, although the total solids, after being dried under vacuum, amounted to only 32 to 35%. It is therefore probable that in the solution the polysilicic ester is associated with a certain fraction of the n-butyl alcohol solvent. One possible explanation is that the roughly spherical molecules of polysilicic ester have a highly branched and open structure within which solvent is held mechanically.

The butyl polysilicate solution also contains chemically bound water (probably in the form of unesterified silanol, —SiOH, groups) which is partially liberated upon evaporation of the solvent. For example, in the sample 733-43 used for viscosity measurements, the free water, by titration with the Fischer reagent, amounted to only 0.023%; yet in the butanol recovered from a dried sample 2.39% water was found, based on the weight of the original solution. Carbon and hydrogen analyses of the residue show that another 1.35% water is present (also based on the weight of original solution) which is probably still present as uncondensed silanol groups. Thus the empirical composition of the solute may be:

SiO_2, % by wt.	20.2
$(C_4H_9)_2O$ present as C_4H_9OSi groups	11.1
H_2O	3.7
C_4H_9OH by difference	9(.5)
Total	44(.5)

Assuming volumes are additive, the volume of 44.5 grams of this solute would be about (20.2/2.2) + 11.1/0.767 + 3.7 + (9.5/0.802) = 39.2 cc.; this corresponds to a density of 1.13 grams per cc., which is within the range of the value 1.17 ± 0.08 calculated from density and viscosity data.

Procedure. A 9.112-gram sample of solution 733-43 was placed in a tared, well dried, round 250-cc. Pyrex flask connected through a dry ice trap to a vacuum pump. The flask was partially immersed in water at 35–40° C. and rotated as the solvent was evaporated in order to deposit the residue as a thin film on the walls. After 3½ and 4 hours, respectively, dry air was led into the flask, which was stoppered and weighed. Only 22 mg. were lost in the last half hour. Residue weight = 3.150 grams, or 34.6% of the original weight. The condensate in the trap contained 0.218 gram water by titration, or 2.39% on the original sample weight. Analysis of the residue gave silica, 63.30; carbon, 25.61; and hydrogen, 5.28%. From the carbon and silica analysis the ratio of $(C_4H_9O)/Si$ = 0.505, which is in good agreement with 0.48 found by previous analysis. However, the hydrogen corresponding to C_4H_9 would amount to only

$$\frac{(25.61)(9)(1.008)}{(4)(12)} = 4.84\%$$

The difference of 0.44% is greater than experimental error and is believed due to —SiOH groups in the dried sample. On the original sample weight this would amount to

$$\frac{0.44(18)(34.6)}{(2)(1.008)(100)} = 1.35\%$$

Thus the original solute must have contained 2.39 + 1.35 = 3.74% water; this corresponds to (3.74/9) × (60/20.2) = 1.23 unesterified hydroxyl groups, together with about 0.5 butoxy group per silicon atom.

It is recognized that the analysis for hydrogen is not sufficiently accurate to justify such detailed calculation, but this and similar analyses lead to the general conclusion that in polysilicic acid there is about one hydroxyl group per silicon atom which is less readily esterifiable than the remainder.

CHANGES IN WATER CONTENT DURING STABILITY TESTS

The presence of unesterified hydroxyl groups is also indicated by the observation that, when solutions of butyl polysilicate are heated in sealed tubes at 100° C., the water content at first rises, then diminishes to a new minimum, and thereafter again increases. During the second rise in the water content the viscosity of the solution also begins to increase and thereafter continues to rise until the gel point is reached. This behavior is indicated in Table V.

Table V. CHANGE IN CONCENTRATION OF WATER IN TYPICAL SAMPLES

	Degree of Esterification, BuO/Si = 0.48		Degree of Esterification, BuO/Si = 0.31	
Hr. Heated	Viscosity, cp.	H_2O, %	Viscosity, cp.	H_2O, %
0	1.21	0.07	1.23	0.14
10	...	0.16	...	0.25
20	...	0.25	1.23	0.33
30	1.21	0.24	1.235	0.20
40	...	0.18	...	0.23
50	1.21	0.14	1.25	0.30
65	...	0.22	...	0.31
76	1.23	0.26	1.28	0.34

It is postulated that the unesterified hydroxyl groups within the polysilicic acid molecule slowly undergo intramolecular condensation; thus they liberated water and account for the initial rise in the water content of the solution. This water may then be consumed in the hydrolysis of butoxy groups, liberating *n*-butyl alcohol and forming new hydroxyl groups, although this second increase in hydroxyl groups has not been checked by actual analysis. This process would lead to a decrease in the water content of the system. Finally, the newly formed hydroxyl groups may then permit intermolecular condensation and the growth of larger molecular units, water again being liberated in the process, and the viscosity increasing. This increase in viscosity may be due to the further mechanical entanglement of *n*-butyl alcohol solvent within the growing polysilicic ester molecular units.

ACKNOWLEDGMENT

The authors thank those who have contributed to this research, with special acknowledgment to J. S. Kirk, H. B. Fernald, K. W. Greenan, C. L. Rollinson, and J. W. Robinson.

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RECEIVED February 17, 1947. Contribution from the Cleveland Experimental Laboratory, Grasselli Chemicals Department, and the Chemical Department, Experimental Station (Contribution 219) of E. I. du Pont de Nemours & Company, Inc.

BUTOXYCHLOROSILANES....

Hydrolysis and Condensation

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BUTOXYSILOXANES are formed by controlled hydrolysis and condensation of *n*-butoxychlorosilanes in the presence of a tertiary amine as an acid acceptor. Hexa-*n*-butoxydisiloxane (*n*-butyl disilicate) is obtained from *n*-tributoxychlorosilane. High boiling liquid cyclic siloxanes $[(n\text{-BuO})_2SiO]_n$, where *n* ranges from 3 to 8 are obtained from the difunctional compound *n*-dibutoxychlorosilane. Although *n*-monobutoxychlorosilane gives only insoluble gels, soluble resinous products containing slightly over one butoxy group per silicon are obtained by interpolymerizing a mixture of the mono- and di-*n*-butoxychlorosilanes. The liquid cyclic butoxysiloxanes possess a high degree of thermal stability and low temperature coefficient of viscosity.

PRESENT knowledge of alkyl polysilicates, or, more properly, the alkoxysiloxanes[1], rests largely upon the work of Schumb and Holloway (*7*), who prepared ethoxysiloxanes from the corresponding chlorosiloxanes; Konrad, Bächle, and Signer (*3*), who studied the intermediate hydrolysis products of methyl orthosilicate; and Signer and Grosse (*9*), who investigated the cyclohexoxysiloxanes obtained by the reaction of cyclohexoxychlorosilanes with silver carbonate. More recently Peppard, Brown, and Johnson (*5*) have further demonstrated the possibility of preparing alkoxysiloxanes by hydroysis and condensation of alkoxychlorosilanes.

In view of the earlier background developed on the hydrolysis and condensation of alkyl and aryl chlorosilanes to yield liquid and resinous silicones, recently summarized by Rochow (*6*), it seemed worth while to investigate the preparation of similar polymeric products which might be obtained from typical alkoxychlorosilanes by hydrolysis under carefully controlled conditions. The *n*-butoxychlorosilanes $n\text{-}C_4H_9OSiCl_3$, $(n\text{-}C_4H_9O)_2SiCl_2$, and $(n\text{-}C_4H_9O)_3SiCl$ were chosen for this purpose.

In order to prepare polysiloxane structures analogous to the silicones, it was necessary to use a method of hydrolyzing the chloro groups and effecting subsequent condensation without hydrolyzing or causing rearrangement of the butoxy groups. It had been shown by Signer and Grosse (*9*) that this can be accomplished in the case of the cyclohexoxychlorosilanes by treatment with silver carbonate in ether. However, the same result can be more readily accomplished by treating alkoxychlorosilanes with a theoretical quantity of water (0.5 mole water per chlorine) in the presence of a slight excess of pyridine to act as an acceptor of hydrogen chloride. A similar technique, except that excess water was used, has recently been described by Peppard, Brown, and Johnson (*5*), who also found that, unless an acid acceptor is used, hydrolysis of alkoxychlorosilanes proceeds with simultaneous disproportionation to orthosilicate and silica.

TYPES OF PRODUCTS OBTAINED

The polymeric products synthesized by this technique appeared, in general, similar in structure to the methylpolysiloxanes as

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[1] The nomenclature, as summarized in *Chemical and Engineering News*, 24, 1233–4 (1946), is preferred over the older terminology.

reported by Patnode and Wilcock (*4*). These range from liquids through resins to gels, depending upon the ratio of butoxy groups to silicon. Oily polymers were produced where the ratio of BuO/Si was greater than about 1.4, whereas viscous sirups or resins were found with ratios of 1.0 to 1.4, and insoluble gels below 1.0. (Throughout this paper Bu refers to the *n*-butyl group.) However, the analogy with methylsiloxanes is by no means complete, the course of the polymerization apparently having been modified by the presence of butoxy groups.

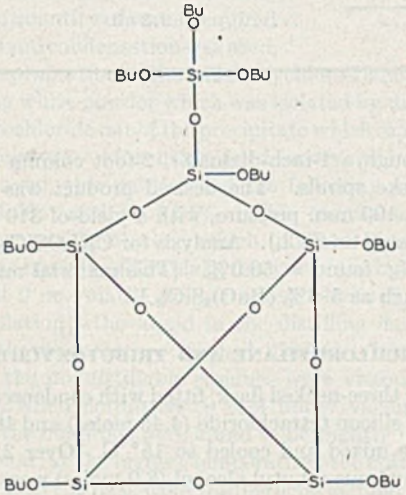

Figure 1. Possible Structure of Higher Boiling Fraction

From tributoxychlorosilane, $(BuO)_3SiCl$, a high yield of hexabutoxydisiloxane was obtained, a result completely analogous to the preparation of hexaethoxydisiloxane reported by Peppard, Brown, and Johnson (experiment 1). From dibutoxydichlorosilane, $(BuO)_2SiCl_2$, there resulted a clear, viscous, oily product having the general formula $[(BuO)_2SiO]_n$. Upon careful distillation this was found to consist almost entirely of high boiling, cyclic siloxanes containing from three to eight siloxane units (SiO) per ring. In contrast with the higher-molecular-weight hydrolysis products of dimethyldichlorosilane, reported by Patnode and Wilcock (*4*) and Hunter, Hyde, Warrick, and Fletcher (*1*), practically no higher-molecular-weight ring or straight-chain products were found (experiments 2 to 7, inclusive). From monobutoxytrichlorosilane, $BuOSiCl_3$, there was obtained a viscous, nonvolatile sirup which formed a weak, brittle gel when heated under vacuum to 300° C.; this is not surprising in view of the fact that the monomer is trifunctional (experiment 9).

Mixtures of mono- and dibutoxychlorosilanes gave products ranging from resinous masses containing slightly over one butoxy group per silicon atom to high boiling oils; this indicated considerable interpolymerization (experiment 10a). However, in the case of an equimolar mixture of monobutoxytrichlorosilane and tributoxychlorosilane there was less evidence of interpolymerization, since the principal products were hexabutoxydisiloxane and a soft resin containing 1.17 butoxy groups per silicon atom (experiment 10b). Nevertheless, some interpolymerization had actually occurred, since some intermediate high boiling oils were also found, and the residue was soluble in chloroform, in contrast with the brittle, insoluble polymer which would otherwise have been produced from the monobutoxytrichlorosilane.

In experiment 10b, small quantities of two high boiling oils were recovered having rather unusual compositions. In spite of the low molecular weight, which corresponded to only five or six silicon atoms per molecule, the BuO/Si ratios found in these oils were surprisingly low—1.89 and 1.48, respectively. The structure of these obviously highly cyclized compounds offers interesting speculation. For example, the higher boiling fraction (350–410° C. at 3 mm.) appears to contain about six silicon atoms and eight to nine butoxy groups per molecule, based on analysis and molecular weight data. Knowing the tendency of the siloxanes to form cyclic bodies, and assuming that only monobutoxy and tributoxy silyl groups are present, one possible structure is indicated in Figure 1. A similar methylpolysiloxane is described by Scott (*8*).

In an attempt to obtain nongelled products containing less than one butoxy group per silicon, the interpolymerization of mixtures of dibutoxydichlorosilane and silicon tetrachloride was tried (experiments 11 and 12). Most of the silicon tetrachloride was apparently converted to an insoluble polymer during the course of the hydrolysis, but there was definite evidence of some interpolymerization with the dibutoxydichlorosilane, since there was only a low yield of cyclic dibutoxysiloxanes which would otherwise have been formed from the latter intermediate. Instead there was a low yield of high boiling oils having BuO/Si ratios ranging from about 2.0 down to 1.48, along with a considerable portion of a nonvolatile, viscous, oily residue having the analysis and molecular weight corresponding to $[(BuO)_{1.05}SiO_{1.5}]_{10}$. Apparently all polymeric products containing less than about one butoxy group per silicon atom were insoluble in the reaction mixture and were removed by filtration along with the pyridine hydrochloride.

PROPERTIES OF CYCLIC BUTOXYSILOXANES

Under ordinary conditions the cyclic butoxysiloxane oils appear to be completely stable, in contrast with the lower esters, such as ethyl orthosilicate, which are readily hydrolyzed by atmospheric moisture. These mixed oils having the formula $[(BuO)_2SiO]_n = 3$ to 8 were quite resistant to hydrolysis when shaken with water at ordinary temperature, but tended to precipitate silica when the dispersion was heated. Semiquantitative tests indicate that there is appreciable hydrolysis when these cyclic siloxanes are heated in distilled water for 48 to 72 hours at 95° C., the cyclic trimer being less stable than the tetramer and higher cyclic products (experiment 13). However, none of the cyclic products was quite as resistant to hydrolysis as the hexabutoxydisiloxane and *n*-butyl orthosilicate. (The lower stability of the trimer toward hydrolysis may be the result of strain in the siloxane ring. Hunter, Hyde, Warrick, and Fletcher (*1*) report that the hexamethyltrisiloxane is thermally less stable than the tetra- or pentasiloxane.)

The unusual thermal stability of the butoxysiloxanes was indicated by the fact that no decomposition was observed during distillation under vacuum at temperatures up to 380° C. Even a small amount of decomposition would have been noted, since the evolved gases would have caused an immediate drop in pressure. However, when air was blown through the oil at 220–300° C., there was a 38% loss in weight, at which point the material became very viscous and started to gel (experiment 14). Sodium alcoholate brought about a disproportionation of the mixed cyclic butoxysiloxanes; this resulted in the formation of a fraction consisting largely of butyl orthosilicate and a highly viscous residue (experiment 15). Concentrated nitric acid, hydrofluoric acid, or ammonium hydroxide, when warmed with the cyclic oils, caused rapid decomposition.

The following properties were observed (determined on a composite of products obtained from $(BuO)_2SiCl_2$ in experiments 2 to 7, distilling in the range from 200–360° C. at 3 mm.):

Specific gravity, d_{20}^{20}	1.0028	Viscosity, cp.	
Flash point (C.O.C.), ° F.	405	+100° F.	10.15
Fire point (C.O.C.), ° F.	475	−40° F.	119.0
Pour and cloud point, ° F.	Under −75		

Particular attention should be called to the low change in viscosity with temperature, which approaches that of the alkyl silicone oils.

Table I. Hydrolysis and Condensation

Expt. No.	Butoxychlorosilanes, Mole	H_2O, Mole	Pyridine, Mole	Distillate					Residue		
				Wt., g.	Range, ° C.	Mm.	BuO/Si	Mol. wt.	Wt., g.	BuO/Si	Mol. wt.
1	$(BuO)_3SiCl$, 0.2	0.2	0.22	26.6	175–180	3	3.0	......	1.0 oil	...	....
9	$BuOSiCl_3$, 0.2	0.3	0.6	None	To 320	3	...	......	Insol. gel	...	....
10a	$BuOSiCl_3$, 0.101 + $(BuO)_2SiCl_2$, 0.044	0.198	0.395	1.5	To 420	0.5	1.6	......	14.0 resin	1.13	2030
10b	$BuOSiCl_3$, 0.1 + $(BuO)_3SiCl$, 0.1	0.2	0.4	14.0	175–180	3	3.0	577	9.7 resin	1.17	....
				2.8	285–325	3	1.89	1100			
				3.5	350–410	3	1.48	972			
11	$(BuO)_2SiCl_2$, 0.1 + $SiCl_4$, 0.1	0.3	0.6	6.6	175–380	3	2.2 to 1.5	588 to 1200	6.0 viscous oil	1.06	....
12	$(BuO)_2SiCl_2$, 0.05 + $SiCl_4$, 0.10	0.25	0.05	1.8	210–300	3	.....	......	2.3 oil	1.05	1200

RESINOUS BUTOXYSILOXANE POLYMERS

From a mixture of monobutoxytrichlorosilane containing a minor proportion of dibutoxydichlorosilane (experiment 10a), the principal product was a viscous sirup having the empirical formula $[(BuO)_{1.13}SiO_{1.44}]_{13.4}$ calculated from the analysis for carbon, hydrogen and silicon, and molecular weight. Since it was evident that harder resins might be obtained if the ratio BuO/Si were slightly lower, an attempt was made to produce a polymer using a still smaller proportion of dibutoxydichlorosilane. However, from a mixture of 0.04 mole of dibutoxydichlorosilane with 0.36 mole of monobutoxytrichlorosilane, only a gel was obtained upon evaporation of the solvent from the filtered reaction mixture.

Attention was therefore turned to the possibility of obtaining the desired resin by the partial hydrolysis of butoxy groups, starting with pure dibutoxydichlorosilane. As indicated in experiment 16, this was accomplished by emulsifying a solution of dibutoxydichlorosilane in benzene in a mixture of pyridine and ice water. Isolation of the polymeric product from the solvent yielded a resin containing slightly over one butoxy group per silicon, from which no volatile material could be detected when heated to 360° C. at 3 mm. (experiment 16). However, when ammonium hydroxide and sodium bicarbonate were used in place of pyridine, no resinous material could be isolated from the solvent layer, which contained only a small amount of oil boiling at 160–200° C. at 3 mm. (experiment 17).

The resinous material produced in experiment 16 had unusual thermal stability. Polymers of this type have been heated in vacuum (2 mm.) to 475° C. without evolving sufficient gas to cause a noticeable drop in pressure in the system. However, thermal decomposition occurs at an appreciable rate at 525° C. The resin is soluble in chloroform, benzene, and acetone. Firm, highly adherent films were obtained on glass by evaporation of these solutions. Although these films remained unchanged in contact with the atmosphere over a period of several weeks, they became loose and brittle when exposed to steam for several hours or permitted to stand in the laboratory atmosphere for several months. Analyses indicated that organic matter was lost during exposure to moist air; this suggested that partial hydrolysis had occurred.

MONOBUTOXYTRICHLOROSILANE

In a 3-liter flask, fitted with stirrer, 1410 grams of silicon tetrachloride (8.3 moles) were cooled to 15° C., and a mixture of 610 grams of *n*-butyl alcohol with 450 grams of benzene was added, with good agitation and cooling, over a period of 3 hours. The mixture was permitted to stand 18 hours and then fractionally distilled through a 1-inch-diameter, 2-foot column packed with $^1/_8$-inch Fenske spirals. The desired product was collected at 82–85° C. at 100 mm. pressure, with a yield of 810 grams (47% theoretical based on $SiCl_4$). Analysis for $C_4H_9OSiCl_3$: calculated Cl = 51.25%; found = 50.0%. [This material may have contained as much as 5–6% $(BuO)_2SiCl_2$.]

DIBUTOXYDICHLOROSILANE AND TRIBUTOXYCHLOROSILANE

In a 3-liter three-necked flask, fitted with condenser and stirrer, 757 grams of silicon tetrachloride (4.45 moles) and 1000 grams of benzene were mixed and cooled to 15° C. Over 2.5 hours 658 grams of anhydrous *n*-butyl alcohol (8.9 moles) were added, with good agitation and cooling. After standing for 24 hours at room temperature, the mixture was fractionally distilled into three rough cuts, from which the following fractions were isolated by separate distillations:

Crude Butoxytrichlorosilane. Boiling point 31–45° C. at 11 mm.; 100 grams (10.8% of theoretical) were obtained.

Dibutoxydichlorosilane. Boiling point 82–84.5° C. at 7.5 mm.; 320 grams, or 28.2% yield based on $SiCl_4$, were obtained. Analysis: calculated Cl = 28.98%; found = 28.2%. For hydrolysis experiments this material was redistilled, and a middle cut boiling at 103° C. at 20 mm. was isolated; found, 28.9% Cl.

Tributoxychlorosilane. Boiling point 126–128° C. at 10 mm.; 236 grams (19.0% of theoretical) were obtained. Analysis: calculated Cl = 12.54%; found = 12.65%. Approximate specific gravities of these products at room temperature were as follows: $(BuO)_3SiCl$, 0.97; $(BuO)_2SiCl_2$, 1.05; and $BuOSiCl_3$, 1.17.

HYDROLYSIS AND CONDENSATION

The results obtained upon hydrolysis and condensation of tributoxymonochlorosilane, monobutoxytrichlorosilane, and various butoxychlorosilane mixtures are summarized in Table I. In these experiments the indicated quantities of pyridine and water in 200–300 cc. of anhydrous ether were added to the butoxychlorosilanes in 200–300 cc. of anhydrous ether, with vigorous agitation. The mixture was then refluxed for 18 hours under continuous agitation, care being taken to exclude atmospheric moisture. At the end of this period the precipitate of pyridine hydro-

Table II. Hydrolysis and Condensation of $(BuO)_2SiCl_2$

Expt. No.	$(BuO)_2$-$SiCl_2$, Mole	H_2O, Mole	Pyridine, Mole	Reaction Medium, Cc.	Addn. of H_2O	% Product Distilling below 260° C., 3 mm.	Residue
2	0.2	0.2	0.4	Ether 600	With pyridine	51	<3%
3	0.2	0.2	0.4	Benzene 300 + dioxane 50	In dioxane after pyridine	65	<3%
4	0.2	0.2	Excess	Pyridine 300	With pyridine	55	<3%
5	0.2	0.2	0.4	None	With pyridine	38	<5%
6	0.2	0.2	0.4	Dioxane 200 + ether 450	In dioxane before pyridine	0.025 mole $(BuO)_4Si$	Gelled
7	0.1	0.1	None	Dioxane 150	In dioxane	0.020 mole $(BuO)_4Si$	Viscous, BuO/Si = 1.0

Table III. Analytical Data on Cyclic Butoxysiloxanes

B.P. Range at 3 Mm.°C.	Wt., Grams[a]	Analysis, % C	H	SiO_2	Refractive Index (20°C.)	$[(BuO)_2SiO]_n$	Mol. Wt. Calcd.	Found
185–190	10.0(4.6)	50.94	9.73	31.16	1.4196	$n = 3$	571	602
220–225	19.7(3.3)	51.00	9.79	31.00	1.4220	$n = 4$	761	776
245–250	7.9(3.4)	50.96	9.69	31.03	1.4228	$n = 5$	951	983
275–280	13.4(3.4)	50.16	9.51	32.24	1.4230	$n = 6$	1142	1205
300–320	11.8(2.8)	48.90	9.34	34.07	1.4240	$n = 8$	1522	1585
Calcd. for $(C_4H_9O)_2SiO$		50.5	9.55	31.5				

[a] Figures in parentheses are weights of intermediate fractions.

chloride which had formed was separated from the reaction mixture by filtration, and the ether was then removed from the filtrate by distillation at atmospheric pressure. The residue was then subjected to fractional distillation at 3 mm. pressure until either the residue in the distilling flask had gelled or the temperature within the flask had reached 400–500° C.

In experiment 1, in which twice the stoichiometric quantity of water required for hydrolysis and condensation was used, a considerable proportion of the tributoxychlorosilane was decomposed to a fine white powder which was isolated by dissolving the pyridine hydrochloride out of the precipitate which separated from the reaction mixture. After being dried for several hours at 110° C. in an air oven, this powder had the following analysis: Si, 30.33; C, 21.60; and H, 4.01%. This corresponds to 0.416 butoxy group per silicon atom, which indicates that the excess water brought about considerable hydrolysis of the butoxy groups. In experiment 9 no volatile products were observed in the final vacuum distillation; the liquid in the distilling flask suddenly gelled when the temperature reached 320° C. In experiments 10a and 10b the nondistillable residues were viscous liquids at 475° C., but, when permitted to cool under vacuum to room temperature, the materials were found to be slightly tacky resins. It was noted that, at the highest temperature, the entry of a slight amount of air into the flask caused superficial gelling, probably as a result of oxidation. In experiments 11 and 12 it was obvious that a considerable proportion of starting materials was converted to insoluble products which were discarded, along with the pyridine hydrochloride precipitate. The isolated products therefore represent only the soluble portions of the polymeric materials produced.

The hydrolysis and condensation of dibutoxydichlorosilane was carried out under a variety of conditions (Table II) in an attempt to vary the proportions of the cyclic siloxanes produced. In each case the dibutoxydichlorosilane was mixed in the reaction vessel with at least half of the indicated reaction medium (except in experiment 5 where no medium was used), and the water then added in the indicated manner with vigorous agitation, in most cases over a period of 30 minutes. In all cases the water content of the pyridine and solvent was determined, and this water was taken into account in calculating the total amount of water used. The mixture was then refluxed at least 1 hour; the pyridine hydrochloride and ether were then removed by the method already described, and the oily residue was fractionally distilled.

This procedure was varied in experiment 5 where no solvent was used; in this case the heat of reaction raised the temperature of the mixture to 120° C. The mixture was then further warmed to melt the pyridine hydrochloride, and stirring and heating were continued for 30 minutes. Agitation was then stopped to permit the pyridine hydrochloride layer to separate, and the mixture was permitted to cool. The upper oily layer was poured off the lower solidified layer of pyridine hydrochloride and fractionally distilled. In this case when the pyridine hydrochloride was dissolved in cold water it yielded a white precipitate, which, after being washed with water and methanol and dried in 110° C., weighed 3.0 grams. This indicated that the fused pyridine hydrochloride caused some side reactions, although no disproportionation to butylorthosilicate occurred, since no fraction boiling around 119° C. at 3 mm. was observed.

In experiments 6 and 7 butylorthosilicate, boiling at 115–121° C. at 3 mm., was identified by analysis for carbon and hydrogen:

	Calcd., %	Found, %
C	60.0	60.01
H	11.32	11.41
Si	8.8	8.4

In experiment 6 the residue was a brittle mass containing 23.67% silicon and 34.25% carbon; this suggested that the residue may have been silica gel saturated with high boiling butoxysiloxane oil. The residue obtained in experiment 7 was a viscous fluid at 475° C. which cooled to a soft resin soluble in acetone and benzene. The resin, which weighed 7.0 grams, contained 22.3% silicon, 7.19% hydrogen, and 38.2% carbon; this corresponded to about one butoxy group per silicon atom.

In experiment 8 the distillates from experiments 2 to 5, inclusive, were carefully fractionated through a $^1/_2$-inch-diameter 13-inch column packed with $^1/_8$-inch Fenske spirals. In this fractionation the various cuts from the previous experiments were added to the distilling flask when the temperature in the flask had reached the lower boiling point of the particular fraction. The distillation curve at 3.0 mm. is shown in Figure 2. The weights of the different fractions are indicated in Table III, the values in parentheses being the weights of the intermediate fractions. Analyses and molecular weights indicate that the various cyclic siloxanes were isolated in relatively pure condition, except perhaps for the highest boiling compound.

HYDROLYSIS OF BUTOXY SILOXANE OILS

In order to obtain a roughly quantitative idea of the relative resistance of the siloxane oils toward hydrolysis, weighed samples were sealed with 10.0 grams of water in clean $^1/_2$-inch Pyrex test tubes and heated to 98° C. (in boiling water) for 48 to 72 hours. The tubes were then cooled and opened, and a portion of the aqueous layer was clarified by filtering rapidly into a second tube through dry filter paper in a small covered funnel, to minimize evaporation. The concentration of n-butyl alcohol in the filtrate was then determined by refractive index (Table IV). Additional tests on the trimer and tetramer, together with the disiloxane and orthosilicate, are also included.

Since the percentage hydrolysis in the cases of the orthosilicate

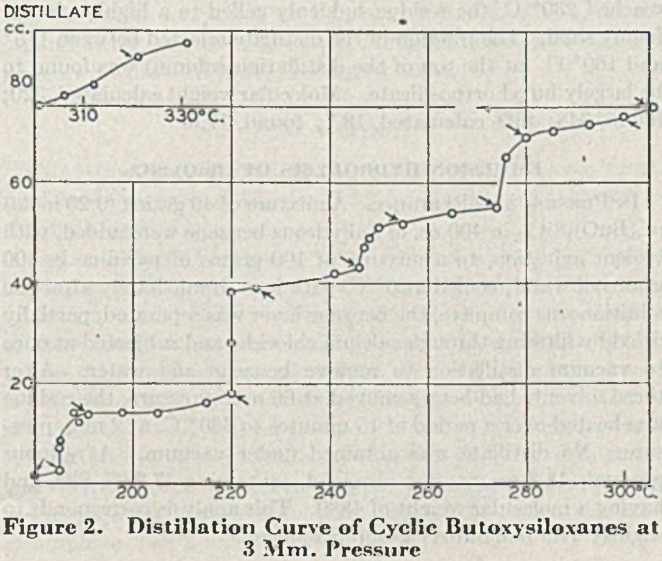

Figure 2. Distillation Curve of Cyclic Butoxysiloxanes at 3 Mm. Pressure

Table IV. Hydrolysis of Butoxysiloxane Oils

Sample	Vol. Sample, Cc.	Vol. H_2O, Cc.	Hrs. at 98° C.	Filtrate Refractive Index at 25.7° C.	n-BuOH in Filtrate Cc./100 Cc.	n-BuOH for Complete Hydrolysis, Cc./100 Cc.	Approx. Hydrolysis, %
n-BuOH	0.1	10.0	...	1.3342	1.0	...	..
	0.2	10.0	...	1.3350	2.0	...	..
	0.5	10.0	...	1.3372	5.0	...	..
	1.0	10.0	...	1.3410	10.0	...	..
Distd. H_2O	...	...	...	1.3333	...	...	..
$[(BuO)_2SiO]_3$	1.0	10.0	48	1.3369	4.6	9.7	47
$[(BuO)_2SiO]_3$	0.9	10.0	72	1.3395	8.0	8.7	92
$[(BuO)_2SiO]_4$	1.0	10.0	48	1.3333	0	9.7	0
$[(BuO)_2SiO]_4$	2.0	10.0	72	1.3391	7.5	19.4	39
$[(BuO)_2SiO]_5$	1.0	10.0	48	1.3336	0.5	9.7	5
$[(BuO)_2SiO]_6$	1.0	10.0	48	1.3335	0.3	9.7	3
$[(BuO)_3Si]_2O$	2.0	10.0	72	1.3342	1.0	21.5	5
$(BuO)_4Si$	2.0	10.0	72	1.3342	1.0	22.8	5
$[(BuO)_3Si]_2O$	...	...	...	1.4152	...	...	..
Partially hydrolyzed sample of $[(BuO)_3Si]_2O$	...	...	...	1.4150	...	...	..
$(BuO)_4Si$	...	...	...	1.4115	...	...	..
Partially hydrolyzed sample of $(BuO)_4O$	...	...	...	1.4113	...	...	..
n-BuOH	...	...	...	1.4015	...	...	..

and disiloxane appeared to be so slight, it was suspected that n-butyl alcohol might have been held in the unhydrolyzed oily layer. However, this did not seem to be the case, since the upper layers after the hydrolysis experiments had refractive indices very close to the original values, as shown at the end of Table IV

OXIDATION OF HEXABUTOXYDISILOXANE AND CYCLIC TETRAMER

About 25 grams of hexabutoxydisiloxane were heated to 240° C., and air was bubbled slowly through the oil while the temperature was raised, over a period of 30 minutes, to 312° C. The viscosity increased rapidly, and the residue was extremely viscous at ordinary temperature and gelled on standing 1 week.

A similar experiment, starting with 5.7 grams of octabutoxytetrasiloxane (cyclic tetramer), yielded a highly viscous product weighing 3.5 grams which was on the point of gelling.

In a third experiment, under identical conditions, 6.0 grams of the cyclic hexamer became extremely thick at the same point, the residue weighing 3.7 grams. Carbon analysis indicated that the very viscous, partially gelled product contained about 1.2 to 1.3 butoxy groups per silicon.

DISPROPORTIONATION OF CYCLIC BUTOXYSILOXANES CATALYZED BY SODIUM BUTYLATE

To 16.8 grams of the mixed cyclic butoxysiloxanes used in experiment 8 were added 50 cc. of anhydrous n-butyl alcohol, in which 0.2 gram of sodium had been dissolved. The mixture was refluxed at 100° C. under anhydrous conditions and then distilled at 3 mm. pressure. When the temperature in the still reached 230° C. the residue suddenly gelled to a highly viscous foamy solid. The fraction of the distillate selected between 115° and 160° C. (at the top of the distillation column) was found to be largely butyl orthosilicate. Molecular weight calculated, 320; found, 348; SiO_2 calculated, 18.7; found, 17.6.

EMULSION HYDROLYSIS OF $(BuO)_2SiCl_2$

In Presence of Pyridine. A mixture of 49 grams (0.20 mole) of $(BuO)_2SiCl_2$ in 400 cc. of anhydrous benzene were added, with violent agitation, to a mixture of 100 grams of pyridine in 400 grams of water, cooled at 0° C. with ice. Immediately after the addition was complete, the benzene layer was separated, partially dried by filtering through calcium chloride, and subjected at once to vacuum distillation to remove benzene and water. After these solvents had been removed at 66 mm. pressure, the residue was heated over a period of 15 minutes to 360° C. at 2 mm. pressure. No distillate was obtained under vacuum. A resinous product (18.3 grams) was obtained, containing 47.23% SiO_2 and having a molecular weight of 4889. This analysis corresponds to slightly over one butoxy group per silicon.

In Absence of Pyridine. A mixture of 24.5 grams of $(BuO)_2SiCl_2$ (0.1 mole) and 100 cc. of benzene was poured rapidly into 300 grams of a mixture of ice and water to which 42 grams of sodium bicarbonate had been added. The mixture was stirred vigorously for 3 minutes and the organic layer separated. Since it smelled strongly of hydrochloric acid, it was again slurried and mixed with the cold sodium bicarbonate solution to which 25 cc. of 1:1 ammonium hydroxide had been added. There was considerable emulsification. A portion (about 25 cc.) of the benzene layer was separated, filtered through anhydrous calcium chloride, and the benzene removed as in the previous experiment. The resulting 3.4 grams of liquid residue were distilled at 20 mm. pressure. All of the material had distilled when the temperature of the flask reached 200° C. No resinous polymer was produced.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

In all experiments involving the preparation and hydrolysis of butoxychlorosilanes, precautions were taken to exclude atmospheric moisture from the reagents and reaction vessels by the use of Drierite tubes on all vents. Water determinations on all solvents were by means of the Karl Fischer reagent.

Analyses for carbon and hydrogen were made by the ordinary combustion method; care was taken to raise the temperature of the sample gradually and to complete the combustion in pure oxygen at bright red heat, since some of the silica residues tended to retain carbon in a form that was not readily oxidized. Silica was determined by decomposition of the samples in concentrated nitric acid, followed by gravimetric determination of silica in the residue by fuming with hydrofluoric and sulfuric acids.

Molecular weight determination was carried out by the freezing point method, using anhydrous benzene. In all cases the molecular weights were found to be lower than theoretical when the conventional freezing point constant for benzene was employed. However, as described by Hyde, Frevel, Nutting, Petrie, and Purcell (*2*), a freezing point constant for benzene of 58.4 is found in work with siloxanes. In the case of the butoxysiloxanes the molecular weights calculated with this constant were slightly higher than theoretical.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of members of the Du Pont Experimental Laboratory at Cleveland, particularly K. W. Greenan, R. E. Lawrence, and C. P. Weise, who performed the chemical analyses and molecular weight determinations reported in this paper, and Michael Sveda, who gave helpful comments and suggestions.

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Received February 17, 1947.

Properties of Polyorganosiloxane Surfaces on Glass

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A VARIETY of organosilicon films have been applied to glass surfaces. Contact angle with water, surface resistivity, and dry lubricity of the treated surfaces were invariably found to be considerably increased over the values for untreated glass. Contact angles of 90–110° were readily obtained from a wide selection of organosilicon structures with no marked systematic variations between species. The coefficient of friction for glass surfaces treated with a series of alkyltrichlorosilanes decreased progressively as the length of the alkyl chain increased. All types of organosilicon films studied were capable of raising the surface resistivity of glass from 10^{-8} or 10^{-9} up to 10^{-12} to 10^{-13}. These high resistivities were maintained until the contact angle to water dropped below 60°. The thermal stability of methylsiloxanes was higher than that of other aliphatic groups investigated. Phenyl groups appear to have thermal stability in the same range as methyl. A study was made of the film spreading of several organosilicon derivatives on water. Monolayers of organosiloxanes transferred from water to glass surfaces by the Langmuir technique behave similarly to films prepared by dipping in solvent solutions. Development of these surface properties are attributable to the formation of a chemical bond between surface film and glass.

IN EARLY laboratory research on organosilicon synthesis it was observed that the surface of glass apparatus used in this work quickly changed from the normal behavior of the water-wetting type to one of extreme water-repellent character. At the same time the feel of the glass became much smoother; this indicated that the coefficient of friction also had been considerably affected. The tenacity with which these films adhered to the glass surfaces suggested the possibliity of important applications in glass and ceramic industries. Furthermore, it was found (*6, 10*) that the large loss in surface resistivity common to glass and ceramic bodies under high humidity conditions could be completely eliminated by treatment with a variety of organosilicon compounds.

The present paper deals with the results of a further study of the effects of a variety of organosilicon compounds on cleaned glass surfaces. The treating method was varied in accordance with the requirements of specific experiments and the type of organosilicon compound involved. Measurements of the contact angle with water, coefficient of friction, and electrical resistivity were used as means of evaluation.. In this manner the effect of structure or character of the organosilicon compound, alkyl chain length, and the effect of temperature on such treated surfaces could be ascertained.

PREPARATORY PROCEDURES

Cleaning Glass. Cenco microscope slides of soda-lime glass, used where indicated, were cleaned with chromic acid-sulfuric acid cleaning solution, repeatedly washed with distilled water, and dried first with a blast of warm air and then over an open gas flame. Slides cleaned in this manner showed a 0° contact angle with water.

In the experiments where Pyrex borosilicate glass was used, the plate and the rider were mechanically cleaned by polishing with rouge and water, rinsed, and dried as were the slides.

Preparing Specimens for Resistivity Studies. The slides used for measurement of surface resistivity were banded with silver by painting with Du Pont Company silver paint No. 4503 and baking 5 minutes at 450° C. Two bands 0.5 cm. wide, 2.0 cm. long, and 1.5 cm. apart were applied to each slide.

Surface Treatments. For the tests performed on soda-lime glass, the microscope slides were immersed for 30 minutes in solutions containing 0.02% of various organosilicon compounds in redistilled benzene. The slides were then removed and air-dried.

In some instances monolayers cast on water by the Langmuir technique were transferred to glass surfaces for comparison with films obtained by the solution treatments just described. In order to determine the effect of heat on the surface films so obtained, slides were placed in a small muffle furnace for 15 minutes each at 100° intervals up to 600° C., using individual slides for each evaluation.

In the study of treatments on borosilicate glass the test surfaces consisted of 2-inch plane-square plates. After rouge-polishing, they were immersed for 1 minute in 0.1 *M* solution of the organosilicon derivative in toluene, drained, dried in warm air, rinsed with distilled water, and again dried.

TEST METHODS

Contact Angle. The angle of wetting with water was measured in the manner of Adam and Jessop (*1*) commonly known as the plate method.

Coefficient of Friction. Static friction measurements were conducted on treated microscope slides by the tilting plate method of Langmuir (*8*). The coefficient was evaluated as the tangent of the angle that the plate was tipped away from the horizontal before movement of the glass rider occurred. The rider used in the measurements on the slides of soda-lime glass was a borosilicate tripod weighing 1.4 grams, the feet of which were three spherical beads of about $^1/_8$-inch radius set about 0.5 inch apart. The rider in these tests was untreated; it was polished with clean crocus cloth before each evaluation. These tests were made in an atmosphere of 50% relative humidity.

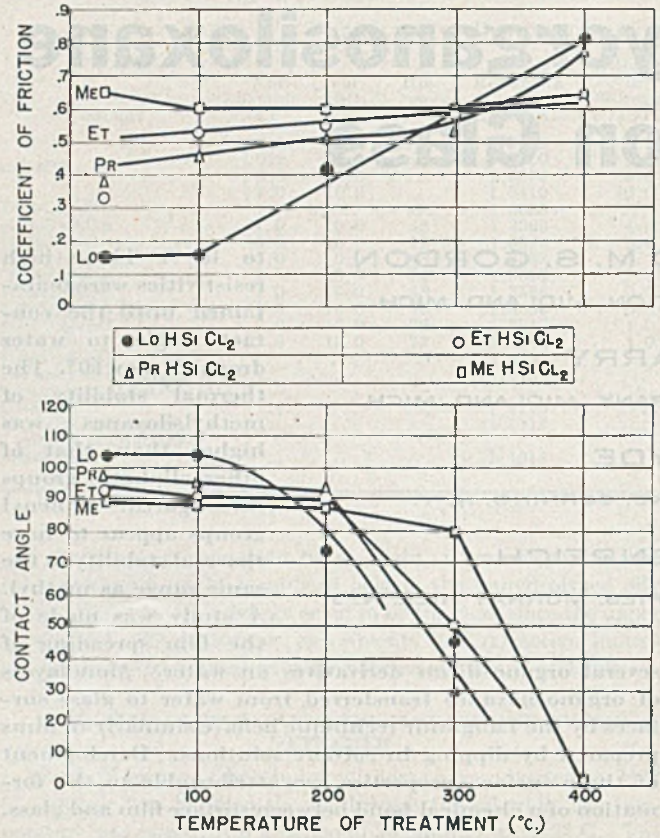

Figure 1. Coefficient of Friction and Contact Angle Measured on Soft Glass Treated by Dipping in 0.02% Benzene Solutions of Alkyldichlorosilanes

In evaluating the treatments on borosilicate glass plates, the rider consisted of a hollow spherical segment of borosilicate glass of $^3/_4$-inch radius weighing 8.6 grams; it was cleaned and treated in each test in a manner identical with the treatment of the plates. These tests were carried out under a bell jar in an atmosphere of dry nitrogen.

Surface Resistivity. The surface resistances of the treated slides were measured at 50% relative humidity between two silvered bands 1.5 cm. apart at a potential of 500 volts.

DISCUSSION OF RESULTS

Experimental work reported here covers data obtained from a wide selection of organosilicon structures. These data are compiled in Table I. The observations on related compounds are discussed together under the appropriate group headings as follows.

Monoalkyldichlorosilanes. The data, relating to contact angle and coefficient of friction measured on surfaces of soda-lime glass treated with this class of compounds, are plotted in Figure 1, correlated with the temperature of the heat treatment of the slide after application of the layer. The contact angle initially observed with no heating, or on the slide heated to 100° C., shows an increase with the length of the alkyl group in the dichlorosilane used. Similarly, the coefficient of friction is reduced in an orderly manner with increasing size of the alkyl group, just as found by Hardy and Bircumshaw (*3*) for homologous series of alkanols and fatty acids. These properties do not persist at elevated temperature, apparently because of oxidative attack of the alkyl group. In this regard the long lauryl group is quite vulnerable, and serious loss of hydrophobicity and dry lubricity are already apparent at 200° C. The contact angle for the ethyl and propyl compounds is quite low at 300° C., whereas the relatively stable methyl derivative shows its sharpest drop beyond 300° C. For the surfaces treated with the lower alkyldichlorosilanes the change in coefficient of friction is not so striking, and, even after 15 minutes at 400° C., the surface treated with the methyl derivative is still at its original level. The coefficient of friction for the glass used in these experiments was found to be 1.46.

The absence of strict parallelism between the contact angle and friction coefficient where the burning off of the methyl group is concerned can probably be explained by the fact that only a random or patchwork defect in the surface layer is created. Contact angle measurements are a function of adsorption, a molecular phenomenon which is not critical where the adsorption areas are in the order of the size of water molecules or aggregates of water molecules, whereas friction measurement probably concerns a macro effect distributed over the whole area of contact between the surfaces involved.

The fixation of the surface layers responsible for the properties just given is believed to be attributable to a reaction, with the elimination of hydrogen chloride between the organosilicon halide and the surface hydroxyls (both Si—OH of the glass surface and the water adsorbed thereon).

Alkylhydropolysiloxanes, (RHSiO)$_x$. These compositions are derived from the above alkylhalosilanes by hydrolysis in ether solution at 0–10° C. Benzene solutions thereof, applied to soda-lime glass, show coefficients of friction and contact angles which correspond quite closely to the values for the monoalkyldichlorosilanes. These data are plotted in Figure 2. Again the contact angle is highest for the Lorol derivative (derived from Du Pont Lorol chloride, a technical grade of lauryl chloride); the values for methyl and ethyl derivatives are somewhat lower. The results without heat treatment were slightly erratic. The lubricating character resulting from these treatments is directly dependent on the size of the R group in the compound employed. The Lorol derivative shows the lowest coefficient of friction but suffers the most serious destruction on heating around 200° C. or above.

Alkyltrichlorosilanes, RSiCl$_3$. The Lorol and stearyl members of this class of compounds were applied to soda-lime glass in the same manner as the alkyldichlorosilanes, and the

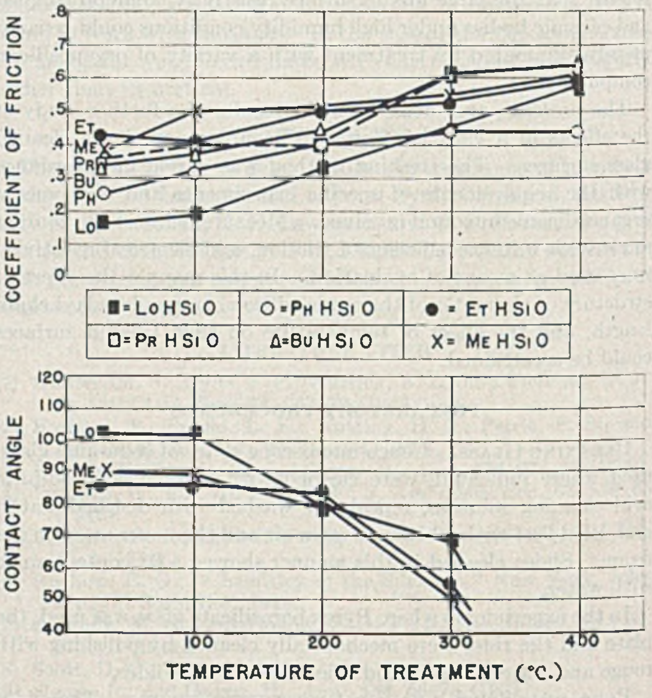

Figure 2. Soft Glass Treated in 0.02% Benzene Solutions of Monoalkylsiloxanes

Table I. Surface Properties of Soda-Lime Glass[a] Treated with Various Organosilicon Derivatives

Compound	Contact Angle after 15 Min. at the Following Temp. (° C.)							Coefficient of Friction after 15 Min. at the Following Temp. (° C.)							Electrical Resistance at 50% Relative Humidity, Ohms
	25	100	150	200	250	300	400	25	100	150	200	250	300	400	
$MeHSiCl_2$	89	88	...	87	..	80	0	0.65	0.60	..	0.60	..	0.60	0.65	....
$EtHSiCl_2$	94	91	...	91	..	50	...	0.34	0.53	..	0.55	..	0.60	0.62	....
$PrHSiCl_2$	97	95	...	93	..	30	...	0.38	0.47	..	0.51	..	0.53	0.78	....
$LoHSiCl_2$	104	104	...	74	..	45	...	0.15	0.16	..	0.42	..	0.59	0.81	....
$[MeHSiO]_x$	89	89	...	78	..	50	...	0.38	0.50	..	0.51	..	0.55	0.59	9.3 × 10^{12}
$[EtHSiO]_x$	86	86	...	82	..	55	...	0.43	0.41	..	0.50	..	0.54	0.59	....
$[PrHSiO]_x$	...	...	...	...	..	...	...	0.36	0.40	..	0.40	..	0.62	..	....
$[BuHSiO]_x$	...	...	...	...	..	...	...	0.34	0.38	..	0.44	..	0.62	0.65	....
$[LoHSiO]_x$	102	101	...	80	..	69	...	0.16	0.19	..	0.33	..	0.45	0.58	....
$[PhHSiO]_x$	...	...	...	...	..	...	...	0.25	0.32	..	0.40	..	0.44	0.44	....
$LoSiCl_3$	110	114	112	90	0	...	...	0.24	0.25	..	0.36	0.49	0.47	0.60	9.0 × 10^{12}
$StSiCl_3$	90	96	102	70	25	0	...	0.27	0.28	..	0.36	..	0.55	0.70	1.0 × 10^{13}
$[StSiO_{1.5}]_n$	70	90	100	102	54	0	...	..	..	..	..	..	..	..	7.0 × 10^{11}
$StSi(OEt)_3$	64	100	97	95	50	0	...	..	..	..	..	..	..	..	3.5 × 10^{12}
$[StMeSiO]_n$	93	94	96	97	74	70	30	..	..	..	..	..	..	..	....
$StMeSiCl_2$[b]	91	92	96	97	70	60	... (0 at 350°)	..	..	..	..	..	..	..	6.0 × 10^{12}
$LoMeSi(OEt)_2$	74	75	...	65	..	55	20	..	..	..	..	..	..	..	....
$LoMeSi(OEt)_2$[b]	75	79	...	70	55	47	... (0 at 350°)	..	..	..	..	..	..	..	....
$LoMeSi(OEt)_2$[c]	81	93	...	93	81	76	73 (0 at 450°)	..	..	..	..	..	..	..	....
500-cs. dimethylsiloxane	54	70	...	102	..	110	103 (85 at 500°, 0 at 525°)	..	..	..	..	..	..	..	8.0 × 10^{12}
245-cs. diethylsiloxane	98	104	...	106	..	96	93 (44 at 475°, 0 at 500°)	..	..	..	..	..	..	..	1.0 × 10^{13}
610-cs. methylphenylsiloxane	0	77	...	81	..	83	81 (60 at 450°, 0 at 475°)	..	..	..	..	..	..	..	....
100-cs. methylsiloxane	86	86	89	90	91	93	34 (93 at 350°, 0 at 425°)	..	..	..	..	..	..	..	....
$EtO[Me_2SiO]_{10}Et$	34	51	...	74	75	75	... (39 at 350°, 0 at 375°)	..	..	..	..	..	..	..	....
$EtO[Me_2SiO]_{10}Et$[c]	80	83	...	91	..	92	83 (78 at 475°, 0 at 500°)	..	..	..	..	..	..	..	....
Stearic acid	40	40	...	40	..	40	... (0 at 350°)	..	..	..	..	..	..	..	....
Stearic acid[b]	36	39	40	40	40	40	... (0 at 325°)	..	..	..	..	..	..	..	....

[a] Cenco microscope slides: contact angle = 0°; coefficient of friction = 1.43; resistance = 10^8–10^9 ohms.
[b] B-layers transferred from water
[c] B-layers transferred from 0.01 *N* HCl.

data, which are plotted in Figure 3, show the same general behavior. Up to 150° C. the layers show persistent or even improved properties (presumably because of fixation of the film by siloxane condensation between the reactive groups of the derivative and the hydroxyl groups in the surface of the glass). Fifteen-minute treatments beyond 150° C., however, cause a progressive drop in contact angles with water and increase in friction coefficients. The Lorol and stearyl derivatives are seen here to be very similar in their general surface properties.

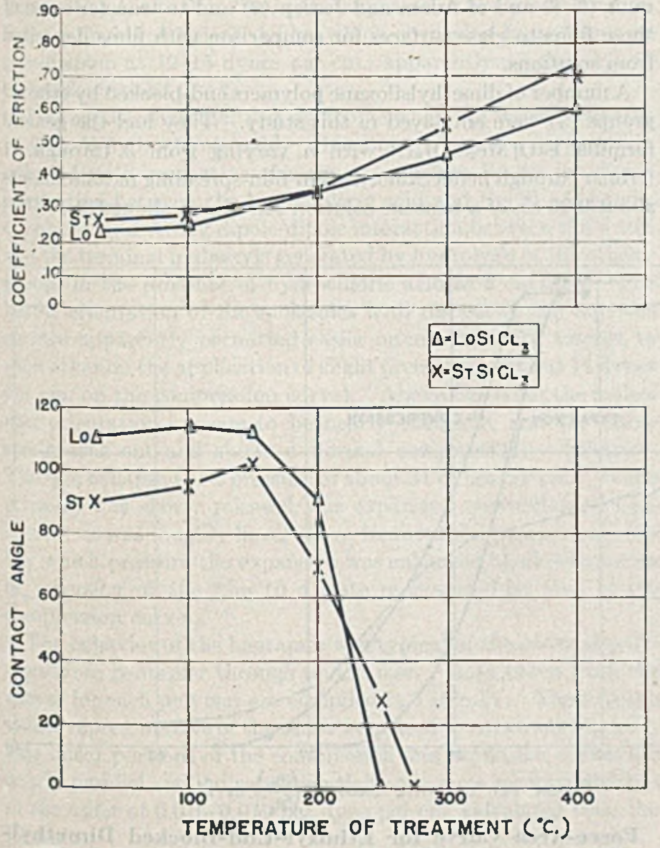

Figure 3. Soft Glass Treated in 0.02% Benzene Solutions of Lorol Silicon Trichloride and Stearyl Silicon Trichloride

The contact angle behavior for $StSiCl_3$ was nearly reproduced when either its hydrolysis product or $StSi(OEt)_3$ was similarly applied to glass from 0.02% benzene solution.

The use of methylchlorosilanes for glass and ceramic treatments applied in vapor form has been described by Norton (*10*). In general, similar results are obtained either by solvent application or vapor treatment. While the methylchlorosilanes are more advantageous for vapor applications because of higher vapor pressure characteristics, the long-chain alkyltrichlorosilanes appear to be somewhat more desirable for solvent application because their vapor pressures are much lower. If both water repellency and high thermal stability are required, however, it is essential that methylchlorosilanes or methylsiloxanes be employed.

A study of the effect of alkyl group chain length on coefficient of friction was conducted using a more extended series of alkyltrichlorosilanes applied to borosilicate glass. The data are summarized in Table II and plotted in Figure 4. Methyl and ethyl compounds effected little or no change from the 0.45 blank on the

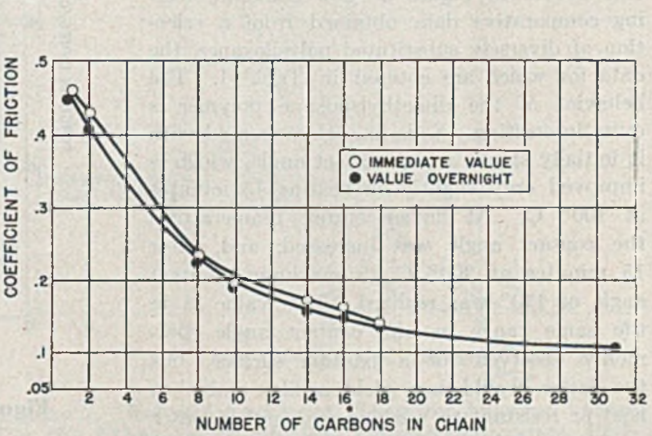

Figure 4. Coefficient of Friction of Pyrex Treated with 0.1 *M* Solutions of Alkyltrichlorosilanes

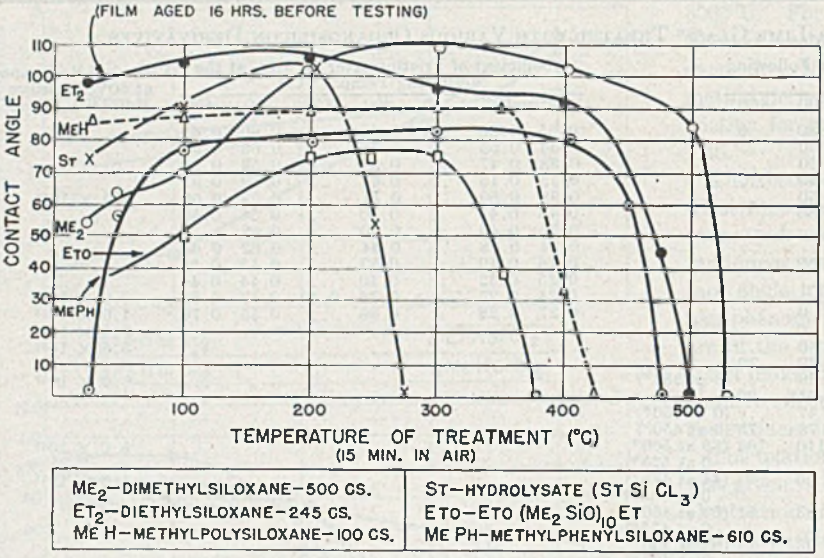

Figure 5. Contact Angles of Soda-Lime Glass Surfaces Treated with 0.02% Benzene Solutions of Organosiloxanes

polished but untreated surfaces. The same regular decrease in coefficient with increasing chain length is apparent as in the case of Hardy's work, although in the present study the coefficients seem to approach a limiting value asymptotically as the chain length increases.

TABLE II. SURFACE PROPERTIES OF TREATED BOROSILICATE GLASS

Treating Compound	Coefficient of Friction	
	Immediately after treating	After aging overnight
CH_3SiCl_3	0.460	0.458
$C_2H_5SiCl_3$	0.431	0.409
$C_8H_{17}SiCl_3$	0.234	0.228
$C_{10}H_{21}SiCl_3$	0.198	0.193
$C_{14}H_{29}SiCl_3$	0.171	0.159
$C_{16}H_{33}SiCl_3$	0.162	0.151
$C_{18}H_{37}SiCl_3$	0.141	0.139
$C_{31}H_{63}SiCl_3$	...	0.107
Blank	0.451	...

ORGANOSILOXANE POLYMERS. Although interesting surface effects are readily obtained with the chloride intermediates discussed, it is generally more convenient in industrial applications to use chloride-free hydrolysis products. The curves in Figure 5 show some interesting comparative data obtained from a selection of diversely substituted polysiloxanes, the data for which are entered in Table I. The behavior of the dimethylsiloxane polymer is quite interesting. Soda-lime glass treated with it initially shows a low contact angle, which is improved only slightly on heating 15 minutes at 100° C. At higher curing temperatures the contact angle was increased, and, after 15 minutes at 300° C., a maximum contact angle of 110° was realized. This value is in the same range as the contact angle commonly observed for a paraffin surface, but the latter would not yield a film stable to heat or resistant to washing with either water or solvents. In contrast to wax films, the dimethyl siloxane film is fixed when cured at high temperatures, probably by surface reaction; after that it is resistant to solvents and only slightly injured by elevated temperatures short of 500° C., where the film is lost through oxidative attack. The high contact angle combined with high thermal stability of films from dimethylsiloxane polymers is further manifestation of the unique chemical properties previously pointed out (*5*) for these structures. Because of the small amount of dimethylsiloxane fluid necessary to produce a very high degree of water repellency, the efficiency of this product is well within an economical range for practical applications to glass and ceramic materials in all forms.

Surfaces prepared using polydiethylsiloxane and polymethylphenylsiloxane were quite similar to those employing the dimethyl siloxanes but appeared to have somewhat less thermal stability.

Siloxane films containing only one octadecyl or dodecyl radical per silicon produced maximum contact angles nearly as high as the dimethylsiloxanes, but these films were completely destroyed at temperatures between 200–300° C. The polymethylsiloxane $[MeHSiO]_x$, which has previously been reported by Norton (*11*) and Sauer *et al.* (*12*) appeared to be different from other organosiloxane films in that its initial contact angle at room temperature was only slightly lower than the maximum angle obtained after heating the film.

STUDY OF H-LAYERS. It was anticipated that the surface treatments described resulted in monolayers of the organosilicon derivatives attached to the glass surface. Hence, it was desirable to characterize films cast on water by the techniques of Langmuir (*7, 8*) and of Adam and Jessop (*2*) and to transfer some of these films to glass surfaces for comparison with films deposited from solutions.

A number of dimethylsiloxane polymers end-blocked by ethoxyl groups (*4*) were employed in this study. They had the general formula $EtO[Me_2SiO]_nEt$ with *n* varying from 3 through 11 (trimer through hendecamer). For film-spreading measurements about 0.06 cc. of a benzene solution containing about 1.2×10^{-5}

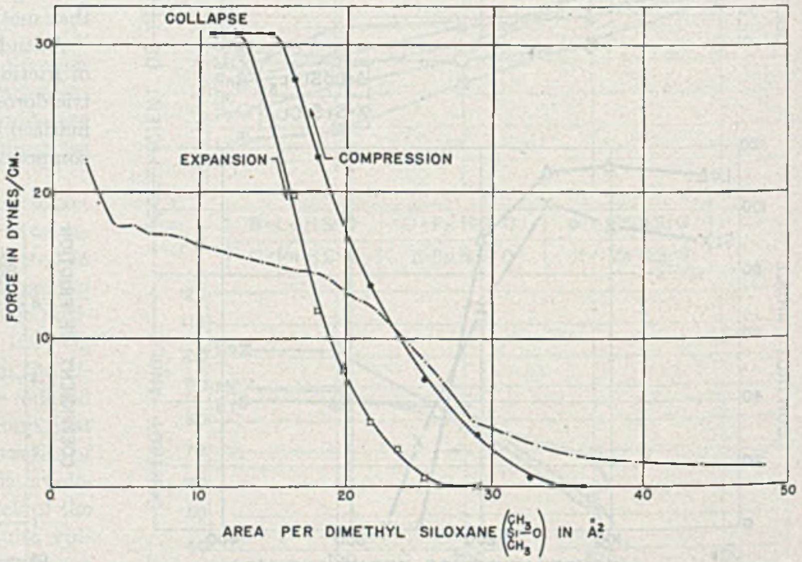

Figure 6. Force-Area Curve for Ethoxyl-End-Blocked Dimethylsiloxane Heptamer (1,13-Diethoxytetradecaheptasiloxane)

——, on 0.01 *N* hydrochloric acid
—.—, on distilled water

Table III. Force-Area Relations for Dimethylsiloxane Heptamer Film on 0.01 *N* Hydrochloric Acid

(Weight of polymer spread, 2.28×10^{-9} grams; number of molecules in film, 1.095×10^{13}; number of Me_2SiO units represented, 7.665×10^{16})

Observations		Calculations	
Barrier position on a 14-cm. trough, cm.	Torsion angle θ, degrees	Film area, sq. Å./Si unit	Pressure on film = 0.29θ, dynes/cm.
During Compression			
20	0	36.0	0.00
18	2	32.4	0.58
16	12	28.8	3.48
14	25	25.2	7.25
12	47	21.6	13.6
11	63	19.6	18.3
10	77	18.0	22.3
9	95	16.4	27.6
8	106	14.8	30.7
7	106	12.6	30.7
6	106	10.8	30.7
During Expansion			
8	106	14.8	30.7
9	68	16.4	19.7
10	41	18.0	11.9
11	27	19.6	7.83
12	15	21.6	4.35
13	8	23.4	2.32
14	2	25.2	0.58
16	0	28.8	0.00

gram of the derivative was placed on the freshly swept water surface of a Cenco hydrophil balance. After evaporation of the solvent, the area of the remaining H-layer was compressed and expanded by means of a movable barrier while the surface pressure was simultaneously determined by means of a float connected to a torsion head. The data relating to the heptamer appear in Table III. The area, computed in square Ångströms for one (Me_2SiO) unit, was plotted against the observed pressure of dynes per cm.; the force-area curve so obtained is illustrated in Figure 6.

On pure distilled water the film behavior was as sketched in Figure 6 by the broken line. Its large area at low pressures indicated a highly unoriented film which showed a high degree of compression at 12-15 dynes per cm., apparently attributable to poor orientation.

This erratic character was overcome when the layers were cast on 0.01 *N* hydrochloric acid. Here the molecules were probably oriented with respect to the aqueous surface by an ion-dipole interaction between the hydrochloric acid and the Si—O bonds, enhanced by a strong dipole-dipole interaction between the water and the terminal hydroxyls generated by hydrolysis of the ethoxy groups in the presence of hydrochloric acid as a catalyst. The better orientation of the molecules with respect to the aqueous surface apparently permitted easier orientation with respect to each other on the application of slight pressure (to about 14 dynes per cm. on the compression curve). Above this point the molecular orientation appears to be nearly complete, and the curve straightens out and shows a normal compressibility behavior. The film collapsed at a pressure of about 31 dynes per cm. When pressure was slowly released, the expansion curve showed hysteresis; it was roughly linear down to about 6 dynes per cm., below which pressure the expansion was enhanced by disorientation or reversion of the film to a state represented by that of the compression curve.

The behavior of the heptamer was typical of the series of polymers from pentamer through undecamer. Data taken from the curves for each polymer are compiled in Table IV. The average values representative of the series were used to construct Figure 7. The linear portions of the compression and expansion curves are nearly parallel and indicate essentially the same compressibilities in the order of 0.016–0.019 per dyne per cm. calculated from the formula:

$$\frac{1}{a_0} \cdot \frac{\Delta a}{\Delta F}$$

where a_0 is taken as the extrapolate area at zero pressure, Δa is the change in area with ΔF, the change in force.

The limiting area a_0 for the expansion curve in Figure 7 is about 22, and for the compression curve about 25 square Ångström units. From the limiting density of 0.975 for dimethylsiloxane polymers the volume of one (Me_2SiO) unit may be computed to be 125 cubic Ångströms. Dividing the limiting areas into this volume gives a film thickness in the range of 5.0–5.7 Å. This is compatible with measurements made on Fisher-Hirschfelder models of the polymers in their most extended form. It is concluded from these observations that the films were monomolecular layers.

The trimer and tetramer depart from the other members in the above series (Table IV). The thickness of the layer generated on expansion of the compressed film, particularly in the case of the trimer, suggests that the molecules have been up-ended and lifted from the surface, and that a random network of strong dipole interactions (hydroxyl end groups) maintains the film in a disoriented state.

The behavior of the high polymer commercial (DC 200) fluids was inconsistent with observations on the group typified by Figure 7. The force-area curves for a 74-centistoke and a 200-centistoke commercial fluid are sketched in the figure by dotted lines; these show collapse of the films at rather low pressures (about 10 dynes per cm.). Nonpolar end groups (Me_3SiO—) and possibly a small amount of chain branching in these compounds may be responsible for easier lifting of the films. That solution treatment of glass with these fluids gave better contact angles than the more easily orientable ethoxy-end-blocked decamer (Figure 5) is attributable to loss of the latter, since this low polymer is more easily volatilized. This was overcome, and the decamer showed much improved contact angles when it was transferred as a B-layer from 0.01 *N* hydrochloric acid, where hydrolysis of the ethoxy groups generated strongly polar hydroxyl groups, which fixed the chains to the glass surface (Table I).

Comparison of B-Layers and S-Layers. When monolayers of a number of organosilicon compounds were prepared on an aqueous surface and transferred to glass slides by the technique of Langmuir, a number of interesting observations were made. First, the slide did not pick up a layer when passed down through the surface film on water; when withdrawn, a monolayer was picked up. This signifies that polar centers were absent on the top face of the layer but were concentrated on the film-water

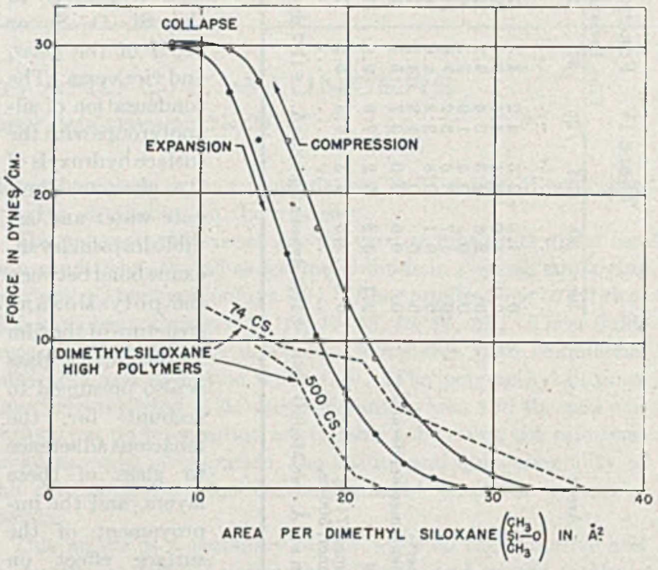

Figure 7. Force-Area Curves Showing Average Values for the Ethoxyl-End-Blocked Dimethylsiloxanes, EtO-(Me_2SiO)$_x$Et, from the Pentamer through Hendecamer on 0.1 *N* Hydrochloric Acid

Table IV. Force-Area Relations for Ethoxy-End-Blocked Dimethylsiloxane Polymers

Area[a]	Film Pressure during Compression, Dynes/Cm. 35	30	28	26	24	22	20	18	16	14	12	10	8	Film Pressure during Expansion, Dynes/Cm. 10	12	14	16	18	20	22	24	26	28	30
Trimer[b]	...	...	...	...	...	..	..	..	0.7	2.5	3.6	4.9	9.6	..	..	..	..	..	..	...	...	...	...	...
Tetramer[c]	...	...	...	...	...	..	..	..	0.5	3.1	6.3	9.6	12.0	..	..	..	..	..	..	...	...	...	...	...
Pentamer	0	1.0	2.5	4.2	4.5	7.1	11.2	17.3	22.8	27.2	29.6	30.7	..	29.1	22.0	13.8	9.2	5.9	3.8	2.4	1.5	0.5	0	0
Hexamer	0.1	1.0	2.4	4.5	6.6	9.9	14.3	20.9	25.8	31.4	..	..	..	..	..	31.4	16.8	11.6	6.7	3.7	1.8	0.9	0	0
Heptamer	0	2.3	4.3	6.4	9.2	12.7	17.6	22.3	28.6	30.7	30.7	..	..	..	30.7	27.2	21.0	11.9	7.4	4.0	2.0	0.3	0	0
Octamer	0	0	0.5	1.9	3.8	6.6	10.9	15.5	26.1	27.5	30.7	..	..	..	30.7	23.0	12.1	6.2	2.9	.7	0.1	0.0	0	0
Nonamer	0	1.7	3.6	5.2	7.6	11.3	15.2	20.0	25.3	30.4	30.4	..	..	..	30.4	30.4	23.6	17.3	12.4	8.1	4.6	2.4	0.6	0.1
Decamer	0	0.1	0.8	2.2	4.0	6.9	10.4	14.4	19.0	23.8	28.4	29.4	29.4	29.4	22.0	21.3	15.4	10.0	6.0	4.1	1.2	0.3	0	0
Hendecamer	0	0	0	1.8	4.5	7.0	10.0	13.0	17.0	21.6	28.1	30.1	30.1	30.1	24.9	17.9	13.2	8.9	5.6	2.6	0.7	0.3	0	0
Average, pentamer-hendecamer	0	0.9	2.0	3.7	5.7	8.8	12.8	17.6	23.5	27.5	29.7	30.1	29.8	29.5	26.8	23.6	15.9	10.3	6.4	3.7	1.7	0.7	0.1	0
Heptamer[d]	2.1	3.8	5.2	7.9	9.9	11.7	13.1	14.5	14.6	15.3	15.8	16.2	17.0	..	..	..	..	..	..	...	...	...	...	...
High polymer, 74-cs.	0.8	2.5	3.3	4.3	5.2	7.1	9.0	9.3	9.6	10.1	10.5	..	..	..	10.5	9.4	8.6	8.0	7.5	5.9	3.6	2.7	1.7	0.7
High polymer, 500-cs.	...	...	...	...	...	..	1.7	5.2	8.3	9.4	..	..	..	..	..	9.4	8.3	5.0	1.0	0	...	...	...	...

[a] Area in sq. Å. per Me$_2$SiO unit. [b] 19.7 dynes at 5.0 sq. Å. [c] 17.7 dynes at 3.6 sq. Å. [d] On distilled water.

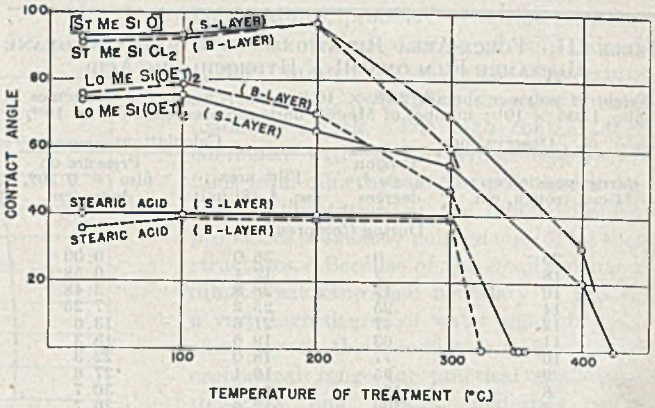

Figure 8. Comparison of Solvent-Applied Films with Films of Compressed Monolayers Transferred to Glass from Aqueous Surface

interface. The amount of material transferred to the glass slide in each case could be read directly from the hydrophil balance, and it checked the apparent area of the slide within a few per cent. Further, the slide was wet when withdrawn from the water; this indicated that the siloxane derivative was separated from the glass surface by a film of water. At this point the layer could easily be washed from the glass surface; attempts to measure contact angle on the fresh film often showed nearly 0° values. On standing at room temperature until the water film was dried off, the contact angles were found to increase to the values recorded in the table; they improved only slightly on aging 12 hours. The layers were firmly adherent to the glass, probably by dipole association or hydrogen bonding of the silanol hydroxyls to the Si—O—Si or SiOH of the glass, and vice versa. The condensation of silanol groups with the surface hydroxyls of the glass to eliminate water and establish a primary siloxane bond between the polysiloxane structure of the film and that of the glass is also presumed to account for the tenacious adherence to glass of these layers, and the improvement of the surface effect on aging or, especially, on heating for short periods at elevated temperatures. The high contact angles thus are attributable both to a layer of hydrophobic alkyl groups oriented outward in an unreversible film and to a paucity of polar centers (the Si—O—Si and SiOH groups of the original glass surface) where the water might establish hydrogen bridges as a prerequisite to wetting.

That the solvent layers were nearly identical in character to the transferred monolayers (B-layers) was demonstrated by contact angle measurements on microscope slides for several compounds laid down in both manners. A few examples are plotted in Figure 8, where the contact angles were determined on the heat-treated slides; the S-layers (those from solvents) are indicated by the solid lines and the B-layers by the broken lines. In the lower set of curves, stearic acid showed practical identity of behavior for the two methods of application. The same may be said for LoMeSi(OEt)$_2$ as justified by the middle set of curves. The upper set of curves compares the application of (StMeSiO)$_x$ or StMeSi(OH)$_2$ from solution with the B-layer from StMeSiCl$_2$, which was hydrolyzed at the aqueous surface from which the layer was subsequently transferred. The close agreement of B- and S-layers suggests that the latter represent essentially monolayer depositions in common with the former.

The contact angles for the stearic acid films are observed to be relatively low compared with the organosilicon films which are high by virtue of fixation, to some extent at least, by chemical reaction (silanol condensation) as already described. Further vindication of this viewpoint is manifest in the tenacity of the stearyl methyl silicone film on washing the slide with solvents under conditions whereby stearic acid films were removed. The case for the LoMeSi(OEt)$_2$ is probably intermediate by reason of incomplete hydrolysis of the ethoxyl groups, which is quite slow compared to hydrolysis of silicon halides. When the Lorol

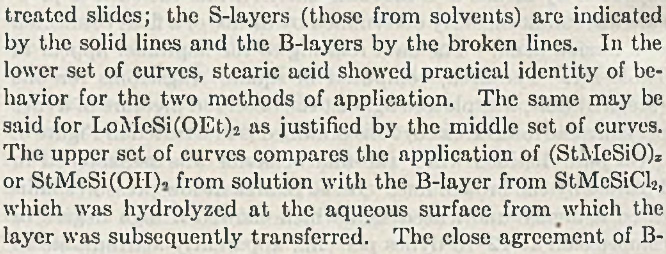

Figure 9. Surface Resistance of Soft Glass Treated with Various Organosilicon Compounds

methyl compound was transferred from 0.01 N hydrochloric acid, it exhibited much higher contact angles (Table I). Hydrolysis, catalyzed by the acid, probably generated a great number of hydroxyls which, by condensation with those in the glass surface, more firmly fixed the film.

Of all the compounds discussed, those of the type $(R_2SiO)_x$ appear to be the least reactive however applied to the glass surface (Figure 9). A marked degree of orientation is not manifest initially as observed from contact angle measurements. Subsequent heating in the case of the dimethylsiloxane film, for example (Figure 5), soon results in a maximum value characteristic of the compound. Presumably, the heating has facilitated displacement of the adsorbed water molecules on the glass surface to allow highly intimate contact and probably chemical reaction with the siloxane in an oriented position. Films applied to glass using either halides or their hydrolysis products, after proper thermal treatment, are not removed by solvents which ordinarily dissolve such hydrolysis products. It is therefore not unreasonable to consider that chemical attachment plays an important part in either case. In the case of the organosilicon halides, orientation may be considered as prerequisite to the occurrence of a reaction. As a result, plates so treated immediately show the characteristics of oriented films.

ELECTRICAL PROPERTIES. The surface resistances of the treated microscope slides were determined at 50% relative humidity by measurements between 2-cm. silver bands 1.5 cm. apart at a potential of 500 volts. A number of treatments including $StSiCl_3$, $StMeSiCl_2$, methylhydrogenpolysiloxane, dimethylsiloxane, diethylsiloxane, and methylphenylsiloxane polymers showed surface resistances in the order of 10^{12} to 10^{13} ohms against a value of 10^8 to 10^9 for the untreated glass slide. On testing the treated slides after 15 minutes of heating at various temperatures, the high surface resistivities persisted up to 375–400° C., but the films burned off above this temperature range. Although stearic acid films showed resistivities of the same order of magnitude, the effect was lost sharply above 300° C.

In general the data show that, when the contact angle of a treated surface drops below 50–60°, the electrical resistivity drops by a factor of the order of 10^4. There does not seem to be any direct correlation between resistivity and contact angle for angles above 60°. The resistivities are pretty much the same whether the contact angle is 70° or 110°. From Livingston (*9*) a contact angle of 50–60° would correspond to about 75% of a complete layer adsorbed. On this basis three fourths of a complete layer is sufficient coverage such that the film conductivity becomes quite small. A possible conclusion, then, is that for contact angles greater than 60°, the conductivity is due chiefly to the subsurface moisture which passes from the atmosphere through the layer of organic molecules and into the surface layers of the glass. Thus, while the contact angle, determined by the characteristics of the top of the organic layer, is high, the resistivity reaches a limiting value, since the conductivity is determined by the moisture content just below the organic layer.

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RECEIVED May 28, 1947.

POLYMETHYLSILOXANES....

Thermal and Oxidation Stabilities

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EARLY in the war the polyorganosiloxanes (*19*), or silicone fluids, were brought to the attention of the Navy although they were still in the development stage. Because of their small rates of decrease of viscosity with temperature, their low vapor pressures and low freezing points, and the wide range of viscosity grades available, these fluids were investigated as possible lubricants and power transmission fluids for unusual applications. As the polymethylsiloxanes have very low temperature coefficients of viscosity and adequately low freezing points and vapor pressures, this type of silicone polymer has been the most carefully studied to date. The synthesis and many of the physical and chemical properties of the methyl-substituted polyorganosiloxanes have already been described (*3, 4, 6, 7, 11, 12, 17, 18, 19, 21, 23*). Silicone polymers may be prepared having linear, cyclic, branched, and cross-linked structures (*4, 11, 17, 18*), depending on the methylchlorosilanes hydrolyzed. The commercial polymethylsiloxanes (*4, 17, 18, 19, 21*) are mixtures of essentially linear homologs with a more or less wide range of molecular weights, depending on the viscosity.

The polymethylsiloxanes may be used as lubricants under certain conditions (*5*) and as hydraulic fluids in systems employing gear and piston type pumps (*9*). Other applications to lubrication have been discussed (*6, 14, 15, 18, 19, 21, 22*). These fluids were also found to be much less flammable than commercial lubricants and hydraulic fluids (*20*). The polymethylsiloxanes have been reported to be very resistant to heat and thermal oxidation, but no information is available concerning the safe temperature range of operation, the nature and objectionability of the decomposition products, and possible catalytic effects of metals.

This article is a summary of our work on the oxidative and thermal breakdown of polymethylsiloxanes and related catalytic effects. Table I lists the polymethylsiloxanes discussed and some of their viscometric properties. The viscosity-temperature coefficient (*24, 25*) is defined by the relation,

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THE polymethylsiloxanes (or silicone fluids) are unusually stable to oxidation. No significant changes attributable to oxidation have been observed at 175° C. At 200° C. oxidation occurs as revealed by viscosity changes and the evolution of formaldehyde and formic acid. The increase in viscosity of the fluids after oxidation is attributed to the condensation of two or more siloxane radicals from which methyl groups have been ruptured. The oxidation stability of the fluids decreases rapidly above 200° C., the maximum temperature at which they may advantageously be used in an oxidizing atmosphere. Copper, lead, and selenium inhibit the oxidation of the silicone fluids at 200° C. as reflected by decreases in evolution of formaldehyde and formic acid. Copper and selenium also inhibit the viscosity changes, and tellurium accelerates oxidation at this temperature. None of the other metals investigated significantly affects the stability of the fluids at 200° C. At 225° C. tellurium inhibits in the dynamic method, as do copper, lead, and selenium; evaporation losses with these metals are abnormally high. Hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane are identified among the products evolved. A reaction of lead oxide with the siloxane is postulated to explain the high evaporation losses observed with lead. The results of the static tests, although less accelerated, are in substantial agreement with those by the dynamic method. Viscometric evidence of the thermal instability of the polymethylsiloxanes at 250° C. has been obtained. Thus, at this and higher temperatures in an oxidizing atmosphere both cracking and oxidation take place.

$$VTC = \frac{\eta_{100^\circ\text{ F.}} - \eta_{210^\circ\text{ F.}}}{\eta_{100^\circ\text{ F.}}}$$

where η = kinematic viscosity

The fluids were made available by the Corning Glass Company Fellowship at Mellon Institute, the Dow Corning Corporation, and the Research Laboratories of General Electric Company. Fluids A, B, and W were prepared at Mellon Institute early in the war and are not typical of present commercial production. These fluids are believed to contain some unreacted hydroxyl groups, and increased in viscosity with time when stored in the dark at room temperature. The other fluids showed insignificant viscosity changes after one year under these conditions. Fluid E-3 was specially prepared to have low temperature characteristics and and contains branched structures. The other silicones are essentially open-chain polymers of polymethylsiloxane with trimethyl terminal groups, and probably differ only in the methods of synthesis. The infrared adsorption spectra of many of the silicones were examined, and no branched or cyclic structures could be detected.

STABILITY TESTS

Several different procedures were used in the investigation of the thermal and oxidation stabilities of the silicones. The dynamic type of aeration apparatus (*2*) was used extensively. A 25-gram sample was used with a gas flow of 20 ml. per minute. Runs were made at 175°, 200°, and 225° C. (±1.5°), and lasted 168 hours. The effluent gases from the oxidation cell were bubbled through 10 ml. of 0.1 *N* potassium hydroxide solution, which was back-titrated at intervals with 0.1 *N* hydrochloric acid to determine the amount of volatile acidic products (calculated as moles of formic acid per gram of sample). The neutral solutions from the determination of volatile acids were tested for aldehydes, by means of the hydroxylamine hydrochloride method (*13*) with bromophenol blue as indicator. It was difficult to obtain reproducible results with this method and, as formic acid also reacts with hydroxylamine hydrochloride, the bisulfite method (*1*) was adopted. The viscosities of the fluids before and after each test, and in some instances at intervals during the 168-hour run, were determined in Cannon-Fenske modified Ostwald viscometers according to A.S.T.M. Method D445-42T. The effect of metals on the thermal and oxidation stabilities of a typical commercial silicone (C-4) was studied by aerating it at the test temperatures in the presence of clean, polished metal strips having dimensions of $1^1/_4 \times {}^1/_4 \times {}^1/_{32}$ inch.

The metals investigated include antimony, cadmium, copper, lead, nickel, platinum, selenium, silver, tellurium, tin, and zinc; each was at least 99.8% pure. The alloys were duralumin 24 ST, SAE 1020 cold-rolled steel, and SAE 30915 stainless steel. Experiments were made with silicone C-4 in the absence and presence of metals using air, oxygen, nitrogen, and helium. The air was purified as described (*2*). The oxygen and nitrogen had a minimum purity of 99.5%; nitrogen comprised the bulk of the impurities in the oxygen, and oxygen was the principal impurity in the nitrogen. The helium was Navy balloon grade, 98.2% pure; nitrogen was the principal impurity, and the oxygen content was less than 0.1%. Traces of the lower hydrocarbons and carbon dioxide may also have been present. All gases were dried by passing through anhydrous calcium chloride.

Static-type oxidation experiments were also made on the same silicone fluid at 225° and 250° C. This consisted in heating 25 grams of fluid in a 100-ml. beaker in a forced-draft oven from 24 to 168 hours. The oven temperature was controlled to ±1.5° C. Metal specimens of the same size were used in this procedure as in the dynamic method. The change in viscosity and the evaporation loss were found to be valuable criteria of stability. The stability of this silicone in a closed system was also investigated. A 25-gram sample in the absence and presence of various metals was sealed in a 50-ml. Pyrex vial under atmospheres of air, nitrogen, and helium gases, and maintained at 250° C. for 24-, 72-, and 168-hour intervals. The dissolved air was replaced by bubbling the desired gas through the sample for 30 minutes before the glass vial was sealed. The change in viscosity was used as a criterion of thermal stability.

DYNAMIC OXIDATION

The silicones listed in Table I were oxidized with air at 200° C. in an all-glass system, as just described. The viscosity of the oxidized sample was determined at 24-hour intervals, as were the moles of formaldehyde and formic acid produced. The presence of formaldehyde in the volatile oxidation products was shown by the reaction with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) (*8*). This was confirmed by the melting point of the dimedone (5,5-dimethylcyclohexane-1,3-dione) derivative (*10*). In some runs the odor of formaldehyde was readily detectable. A white deposit was also observed after some tests in the condensers above the oxidation cells. Upon

TABLE I. VISCOMETRIC PROPERTIES

Source	Identification	Viscosity at 100° F., Centistokes	A.S.T.M. Slope	Kinematic Viscosity Index	Viscosity-Temp. Coefficient
Mellon Inst.	W-2	138	0.238	144	0.584
	W-3	232	0.219	..	0.585
	A-1	22.9	0.410	191	0.641
	A-2	65.6	0.323	161	0.649
	B-1	210	0.249	139	0.651
	B-2	247	0.240	..	0.642
	B-3	276	0.242	..	0.641
	B-4	359	0.216	..	0.653
Dow Corning	C-1	19.7	0.341	197	0.581
	C-2	45.4	0.288	169	0.591
	C-3	44.9	0.288	169	0.591
	C-4	72.4	0.219	156	0.594
	D-1	82.5	0.253	153	0.594
	D-2	162	0.221	140	0.595
	D-3	271	0.203	..	0.595
	D-4	640	0.183	..	0.601
General Electric	E-1	24.7	0.328	188	0.585
	E-2	104	0.244	148	0.594
	E-3	312	0.212	..	0.622
	E-4	466	0.188	..	0.597

heating this deposit, formaldehyde was identified as a decomposition product. It also reduced Fehling solution; therefore, it was concluded to be paraformaldehyde, a polyoxymethylene. Even where no deposit of paraformaldehyde was observed, it is possible that polymers of lower molecular weight were formed. As formaldehyde is readily oxidized, it is likely that formic acid was present. Its presence was confirmed by the increase in aldehyde content after reduction of the solution containing the volatile products.

Silicones A, B, and W increased in viscosity rapidly with time. All of them gelled within 72 hours of oxidation with the exception of A-1, which required 125 hours for gelation. Silicone B-3 required only 25 hours for gelation. These silicones are believed to contain some unreacted hydroxyl groups, since they reacted with lead oxide (PbO) at room temperature to form a semisolid mass. Patnode and Schmidt (*16*) discussed this reaction and showed that trimethylsilanol reacts with lead oxide to form an insoluble product. No definite evidence of a reaction with lead oxide was found with any of the other silicones listed in Table I. The viscosity changes observed for these silicones on oxidation are, in part, due to the condensation of the silanols to form larger molecules and thus increase the viscosity.

Figure 1*A* shows viscosity changes with time for the completely methyl-substituted siloxanes. None of the C or E series silicones oxidized to a gel within the 168-hour period. Fluid E-3 showed the greatest viscosity increase for this group. Only the least viscous of the D series remained liquid during the oxidation test; the gelation time of the others in this series varied inversely with initial viscosity. The number of moles of formaldehyde and formic acid produced is plotted against time in Figure 1*B*. This quantity is only approximately equivalent to the number of moles of methyl groups cracked off or oxidized from the siloxane chain, since paraformaldehyde is known to be formed in some runs; it is also likely that some formaldehyde is oxidized to carbon dioxide.

Figure 1 indicates that the lower the viscosity of the silicone, the smaller the changes in viscosity with times of oxidation. The viscosity changes in the methyl-substituted siloxanes may be accounted for by the condensation of two or more of the siloxane residues from which the methyl groups were ruptured. The apparent stability of the less viscous silicones as revealed by viscosity changes is misleading, for as much formaldehyde plus formic acid was evolved by them as by the more viscous silicones. No correlation between viscosity increases and the amounts of methyl oxidation products formed by the various silicones was obtained, except the generalization that the viscosity increases for a given evolution of formaldehyde and formic acid were greater for the more viscous silicones. It seems unlikely that any simple general relation can be found to hold for a mixture of linear polymers, as the viscosity increase caused by the addition of a polymer to a solvent is a function of the molecular weight, molecular weight distribution, configuration, solubility of the polymer, and the viscosity and nature of the solvent.

No Si—Si linkages could be detected from the infrared absorption spectra of these oxidized silicones, and it seems probable that the condensation products are linked through oxygen. Neither was there any definite indication of branched or cyclic structures in their spectra. As the sensitivity of this method to such structure decreases with increasing molecular weights, their complete absence is not established. However, there was no marked increase in their concentration. This suggests that the methyl groups ruptured or oxidized from the siloxane chain are principally from the terminal silicon atoms. The only silicone (E-3) known to contain branched structures showed abnormal viscosity increases for the amounts of formaldehyde and formic acid produced, as compared to other fluids of comparable initial viscosity. This may be attributed to the greater thickening action of the branched-chain condensation products of oxidation. The early gelation of some of the D series fluids would contradict the hypothesis just suggested, since no branched structures were detected in those examined. However, it is possible that the concentration of the branched-chain siloxanes was too small for detection by infrared spectroscopy.

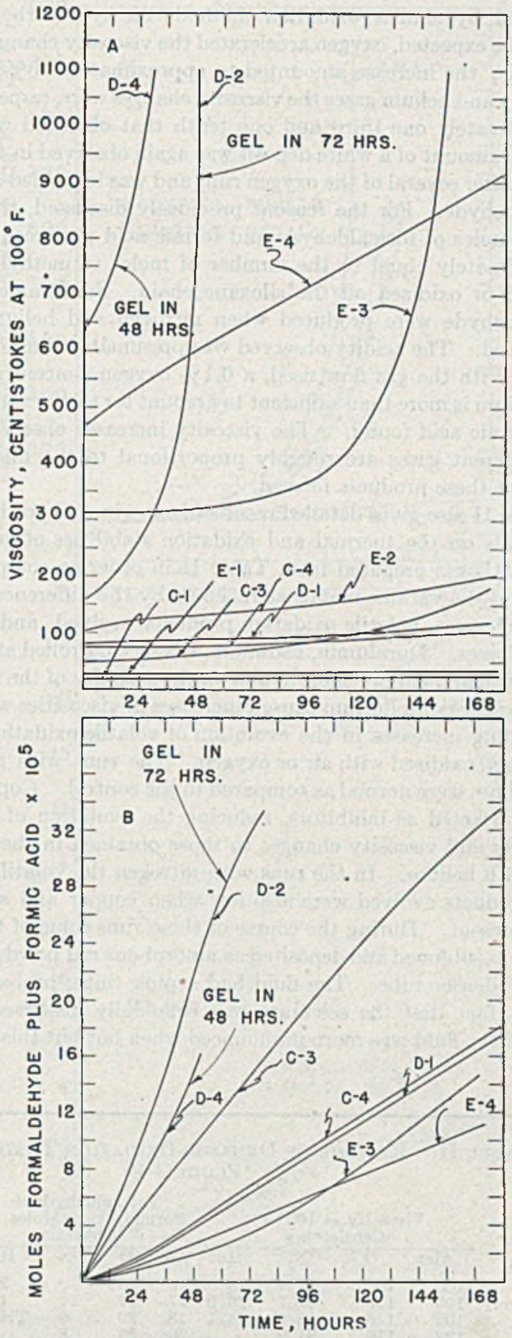


Figure 1. Comparison of Dynamic Oxidation Stabilities of Silicones at 200° C.

The oxidation with air of commercial silicone C-4 at 175° C. for 168 hours revealed that the only significant viscosity changes took place within the first 24 hours. This is attributed to the evaporation of the low-molecular-weight polymers present in the original fluid. There was no appreciable evolution of acids or formaldehyde.

Table II gives results of the dynamic tests at 200° C. on silicone C-4 with air, oxygen, nitrogen, and helium gases. The effect of temperature variations due to the control of the thermostat are reflected in the results shown, since the check runs were not made simultaneously. Repeat runs showed that the viscosities of the silicone fluid, after the 168-hour test with a given gas, agree reasonably well and compare favorably with the reproducibility obtained by similar oxidation methods on hydrocarbons. As would be expected, oxygen accelerated the viscosity changes more than air; the increase amounted to approximately 50%. With nitrogen and helium gases the viscosity changes were, respectively, approximately one third and one tenth that obtained with air. A small amount of a white deposit was again observed in the condenser after several of the oxygen runs and was identified as paraformaldehyde. For the reasons previously discussed, the number of moles of formaldehyde and formic acid produced is only approximately equal to the number of moles of methyl groups cracked or oxidized off the siloxane chain. Small amounts of formaldehyde were produced when nitrogen and helium gases were used. The acidity observed was presumably due to formic acid. With the gas flow used, a 0.1% oxygen concentration in the helium is more than sufficient to account for the formaldehyde and formic acid found. The viscosity increases observed with the different gases are roughly proportional to the number of moles of these products formed.

Table II also gives detailed results of experiments on the effect of metals on the thermal and oxidation stabilities of fluid C-4. Table III was prepared from Table II in order to compare the effects of the various metals as reflected by the difference in viscosity changes, volatile oxidation products evolved, and evaporation losses. Duralumin, cadmium, silver, cold-rolled steel, tin, and zinc had no appreciable action on the stability of the silicone. The presence of tellurium caused increases in viscosities with corresponding increases in the evolution of volatile oxidation products when oxidized with air or oxygen. The runs with nitrogen and helium were normal as compared to the control. Copper and selenium acted as inhibitors, reducing the evolution of volatile products and viscosity changes to those obtained in the control runs with helium. In the runs with nitrogen the volatile oxidation products evolved were also low when copper and selenium were present. During the course of these runs some of the selenium was sublimed and deposited as amorphous red powder in the cool condenser tube. The fluid had a pink tinge, probably due to the fact that the selenium was colloidally dispersed. The color of the fluid was more pronounced when hot but this may be partially explained by the settling of the larger particles after the bubbling had ceased.

Table II. Results of Dynamic Oxidation Tests at 200° C. on Fluid C-4[a]

Metals Present	Viscosity at 100° F., Centistokes				Formaldehyde + Formic Acid, Moles × 10⁵/Gram				Weight Loss, %			
	Air	O	N	He	Air	O	N	He	Air	O	N	He
None (control)	100	108	81.4	78.6	15	25	..	2	3	2	1	1
	105	137	92.7	76.0	17	21	..	1	2	..	1	1
	102	116	86.2	74.1	18	26	9	Trace	2	2	2	1
	122	119	81.2		20	26	8	..	2	2	2	
	94.1	130	79.2		16	30	8	..	1	3	2	
	118	112	80.5			28	12	..	2	1	1	
Average	107	120	83.6	76.2	17	26	9	1	2	2	1.5	1
Duralumin 24 ST	114	119	85.2	78.8	25	23	9	2	2	2	..	1
		140										
Cadmium	101	113	80.6	78.9	16	22	7	3	2	2	..	1
Copper	82.6	79.6	88.3	78.0	6	4	2	3	..	1	2	1
	79.6	81.1			2	3			1	3		
Lead	146	149	91.5	153	2	2	Trace	1	4	6	4	2
	115	119	104		2	2	1	..	..	9	6	
	90.2	108			2	2			3	4		
	112				6				6			
Selenium	78.1	76.4	78.2	78.4	2	2	1	2	2	2	2	1
	77.5	76.9	78.1	74.4	2	Trace	1	Trace	2	1	1	2
Silver	114	125	76.1	79.2	21	21	10	..	3	2	2	1
	86	128			16	28			..	1		
Steel, cold-rolled	112	127	105	78.6	15	28	..	1	3	2	2	2
Tellurium	114	145	78.2	77.6	16	32	..	Trace	1	1	..	1
	133	146		79.0	34	26		1	2	1		1
Tin	112	127	80.4	76.8	14	21	11	2	2	2	1	1
Zinc	107	116	77.5	76.8	19	22	9	1	2	2	2	1
		148				20				2		

[a] Initial viscosity, 72.4 centistokes at 100° F.

The presence of lead in the silicone fluid caused larger viscosity increases than in the control runs. The total amount of formaldehyde and formic acid was low when air, oxygen, and nitrogen were used, but the evaporation losses were high in all these cases. The silicone fluid was turbid after all the runs except where helium was used. The turbidity was observed to increase with time of oxidation.

Dynamic type tests at 225° C. were also made on the same silicone fluid. In the absence of metal the fluid gelled within 24 hours when air or oxygen was used. The amount of formaldehyde plus formic acid formed in 24 hours was twice as great as the amount formed in 168 hours at 200° C. In all these runs there was a heavy deposit of paraformaldehyde in the condenser tube after both air and oxygen runs. The evaporation losses at gelation were approximately 2%. In the 168-hour runs with nitrogen and helium gases the viscosities and the evaporation losses were approximately twice as great as after the tests at 200° C. Runs with air in the presence of various metals were also made, and (as in the control) the silicone fluid turned to a gel within 24 hours except when copper, lead, selenium, or tellurium were present. The fluids gelled between 72 and 96 and between 96 and 120 hours, respectively, in the presence of copper and lead. The fluid remaining after 168 hours in runs when selenium and tellurium were present was less viscous than the original fluid, having a viscosity of 60 centistokes at 100° F. The weight loss amounted to approximately 70%, and only small amounts of formaldehyde and formic acid were produced. A considerable volume of a volatile water-insoluble liquid was collected in the aqueous solution through which the effluent gases were bubbled. A crystalline deposit also collected in the condenser tube after each run with air in the presence of lead, selenium, and tellurium. The liquid was identified spectroscopically as being predominantly octamethylcyclotetrasiloxane, and the crystalline deposit as hexamethylcyclotrisiloxane.

From these experiments it is apparent that the polymethylsiloxane fluid is much less stable to oxidation at 225° than at 200° C. No accelerative action of metals on the viscosity changes could be detected at 225° because of the rapid gelation encountered in the control runs. The presence of copper, lead, selenium, and tellurium at 225° inhibited the rate of change of viscosity and the evolution of formaldehyde and formic acid. At 200° C. lead did not materially affect the changes in viscosity, although it reduced the evolution of formaldehyde and formic acid. Tellurium at the lower temperature accelerated the oxidation rate as reflected by these criteria. All of these metals accelerated the evaporation of the silicone, as compared to the control runs with helium. This suggests that they react in some manner to break the siloxane chain with the formation of lower molecular weight and more volatile products.

In the runs with lead the silicone became turbid within the first 24 hours of oxidation, and the turbidity increased with time. At the end of the run a white deposit had settled in the bottom of the oxidation cell. Patnode and Schmidt (*16*) showed that a reaction takes place between trimethylsilanol and lead oxide which they consider to be as follows:

$$2(CH_3)_3SiOH + PbO \longrightarrow [(CH_3)_3SiO]_2 + H_2O$$

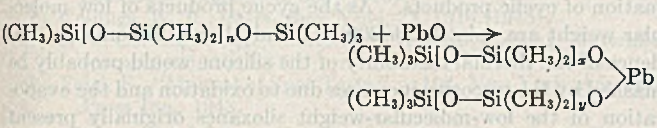
It is possible that under the influence of heat, lead oxide reacts with a siloxane to break the

Table III. Analysis[a] of Effect of Metals on Thermal and Oxidation Stability of Fluid C-4 at 200° C. for 168 Hours

Metal	Viscosity Increase				Moles of Formaldehyde + Formic Acid				Weight Loss			
	Air	O	N	He	Air	O	N	He	Air	O	N	He
Duralumin 24 ST	N	N	N	N	N	N	N	N	N	N	N	N
Cadmium	N	N	N	N	+?	N	N	N	N	N	N	N
Copper	−	−	N	N	−	−	N	N	N	N	N	N
Lead	+	+?	+	+	..	..	−	N	+	+	+	N
Selenium	−	..	N	N	..	..	−	N	N	N	N	N
Silver	N	N	N	N	N	N	N	N	N	N	N	N
Steel, cold-rolled	N	N	N	N	N	N	N	N	N	N	N	N
Tellurium	+	+	N	N	+	+	..	N	N	N	N	N
Tin	N	N	N	N	N	N	N	N	N	N	N	N
Zinc	N	N	N	N	N	N	N	N	N	N	N	N

[a] N = normal as compared to control, + = increase as compared to control, − = decrease as compared to control.

chain and thus form a compound with lead similar to the preceding. The reaction may be represented as follows:



$$(CH_3)_3Si[O—Si(CH_3)_2]_nO—Si(CH_3)_3 + PbO \longrightarrow \left.\begin{array}{l}(CH_3)_3Si[O—Si(CH_3)_2]_xO \\ (CH_3)_3Si[O—Si(CH_3)_2]_yO\end{array}\right\rangle Pb$$

The turbidity may be due to the presence of such a compound. If this product is thermally unstable, the lower-molecular-weight silicones formed would evaporate; this would account for the losses in weight observed. The increase in evaporation losses with increasing temperature could be accounted for by the greater speed of the reaction or the thermal instability of the intermediate. Although no insoluble products were observed with the other metals causing large evaporation rates, it is possible that they or their oxides may react as postulated.

Dynamic-type oxidation experiments at 250° C. were started, but no further work was done after several explosions which were attributed to the spontaneous ignition of some of the silicone decomposition products.

STATIC OXIDATION

Static tests were used at the higher temperatures since they are simpler and less accelerative than the dynamic tests. The same silicone fluid, C-4, was used. It was heated at 225° C. in the absence and presence of antimony, copper, lead, nickel, platinum, selenium, silver, tellurium, tin, and zinc; each was at least 99.8% pure. Alloys used were duralumin 24 ST, SAE 1020 cold-rolled steel, and SAE 30915 stainless steel. The viscosity at 100° F. and the evaporation loss were determined after exposures of 24, 48, 72, 96, 120, and 168 hours. The fluid gelled in all cases between the 120–168 hour interval except in the runs made in the presence of antimony, lead, and selenium. Antimony caused the gelation of the fluid between the 96–120 hour interval; when lead or selenium was present, the fluid did not gel after 168 hours of exposure.

Figure 2A shows the variations in viscosity of the fluid with time. The presence of most of the metals caused no abnormal viscosity changes as compared to the control runs, as indicated by the narrow cross-hatched band in which these curves all lie. The samples containing lead and particularly those containing selenium caused much smaller viscosity changes than those found in the control runs. Tellurium and antimony increased the viscosity somewhat more than did the control. The shape of the viscosity-time curve indicates that the effect was greatly accelerated somewhere between 72 and 96 hours, the curve rising more rapidly than an exponential.

Figure 2B gives evaporation-time graphs. No great variations in evaporation rates were observed between the control runs and those in the presence of metals, as shown by the narrow cross-hatched band. Only lead greatly accelerated the evaporation rate; antimony and tellurium caused much smaller increases. As with the viscosity changes, the evaporation rate increased rapidly between 72 and 96 hours. The gradual decrease in evaporation rate after 120 hours is attributed to gelation.

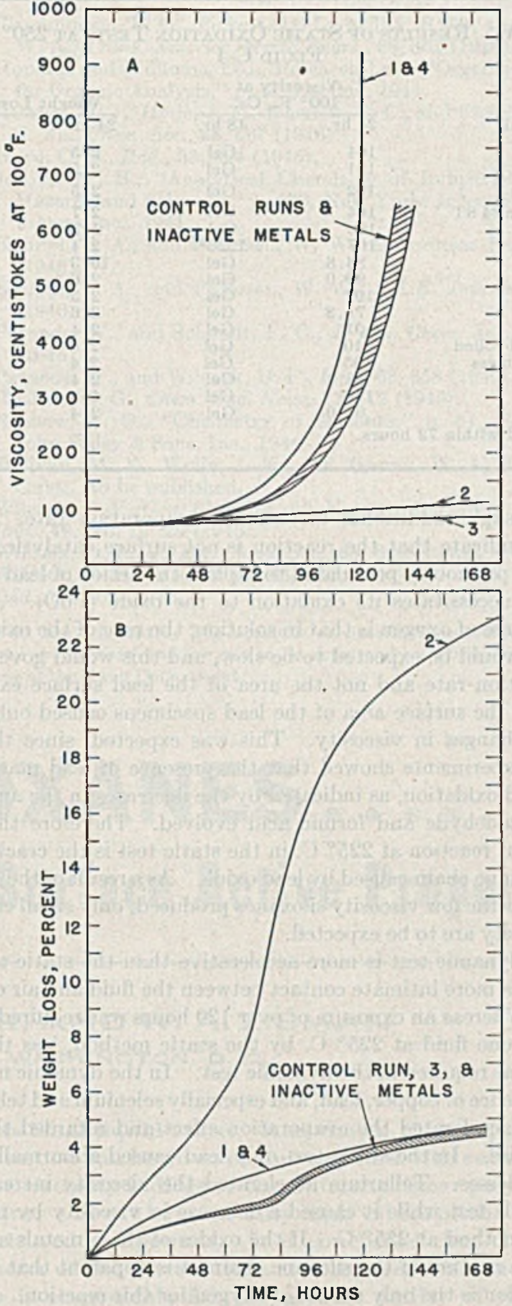


Figure 2. Influence of Metals on Static Oxidation Stability of Polymethylsiloxane C-4 at 225° C.

1 = antimony; 2 = lead; 3 = selenium; 4 = tellurium. Inactive metals: copper, nickel, platinum, silver, zinc, duralumin 24 ST, cold-rolled steel, stainless steel

Metal specimens of lead, zinc, and tin having ten times the surface area of the standard specimens and 20 grams of the granular metals having even larger surface areas were run in the silicone. Increasing the surface area of tin and zinc had no appreciable effect on the vicosity changes, and the evaporation rates were increased only slightly. Increasing the surface area of the lead specimen by a factor of 10 increased the evaporation rate by a factor of 2. The granular lead of much larger surface area caused

Table IV. Results of Static Oxidation Tests at 250° C. on Fluid C-4

Metal	Viscosity at 100° F., Cs. 24 hr.	Viscosity at 100° F., Cs. 48 hr.	Weight Loss, % 24 hr.	Weight Loss, % 48 hr.
None	104	Gel	2.5	5.6
None	101	Gel	2.5	5.4
Average	102	Gel	2.5	5.5
Duralumin 24 ST	104	Gel	2.7	5.5
Antimony	103	Gel	2.7	5.2
Copper	107	1226[a]	2.4	4.9
Lead	83.8	Gel	10.3	16.9
Nickel	90.0	Gel	2.6	5.7
Platinum	102	Gel	2.5	5.5
Selenium	75.8	Gel	3.6	6.3
Silver	101	Gel	2.4	5.4
Steel, cold-rolled	110	Gel	2.6	5.3
Steel, stainless	105	Gel	2.4	5.1
Tellurium	88.4	Gel	2.4	4.7
Tin	116	Gel	2.8	5.3
Zinc	91.0	Gel	2.4	5.0

[a] Gelled within 72 hours.

only a slight additional increase in evaporation rate. These results indicate that the reaction is not surface catalytic. The reaction previously postulated to explain the action of lead on the silicone necessitates its oxidation to the oxide (PbO). As the only source of oxygen is that in solution, the rate of the oxidation of lead would be expected to be slow, and this would govern the evaporation rate and not the area of the lead surface exposed. Varying the surface area of the lead specimens caused only negligible changes in viscosity. This was expected, since the dynamic experiments showed that the presence of lead materially inhibited oxidation, as indicated by the decreases in the amounts of formaldehyde and formic acid evolved. Therefore the predominant reaction at 225° C. in the static test is the cracking of the siloxane chain caused by lead oxide. As a result of the evaporation of the low viscosity siloxanes produced, only small changes in viscosity are to be expected.

The dynamic test is more accelerative than the static test, as there is a more intimate contact between the fluid and air or oxygen. Whereas an exposure of over 120 hours was required to gel the silicone fluid at 225° C. by the static method, less than 24 hours was required in the dynamic test. In the dynamic method the presence of copper, lead, and especially selenium and tellurium greatly accelerated the evaporation effect and retarded the viscosity rise. In the static test only lead caused abnormally high weight losses. Tellurium accelerated the viscosity increases in the static test while it caused a decrease in viscosity by the dynamic method at 225° C. If the oxides of these metals accelerates the rupture of the siloxane chain, it is apparent that the air in solution is the only source of oxygen for this reaction. In the dynamic test fresh air continually sweeps over the metal surface, agitates the liquid, and hastens the evaporation of the volatile reaction products. As in the dynamic test, the fluid containing lead was cloudy even after 24 hours of exposure to the static test, and the turbidity increased with time. Similarly, selenium caused a slight pink color to develop in the fluid which faded as the fluid cooled.

Table IV gives the results of the static oxidation of silicone C-4 at 250° C. At this temperature the silicone gelled somewhere between 24 and 48 hours of exposure. As the silicone fluid gelled so rapidly at this temperature, it was difficult to ascertain the effect of metals. Copper was the only metal that inhibited gelation. After 24-hour exposure only selenium, lead, tellurium, nickel, and zinc inhibited the viscosity increase, the effect being very marked for the first two. No such effect was observed with nickel and zinc at the lower temperatures. As the oxidation stability of the silicone is very sensitive to temperature in this range, it is possible that the apparent inhibitive action observed is due to variations in temperature control. The evaporation rate in the presence of lead was four times as great as in the control after 24 hours and was three times as great after 48 hours. The decrease in the evaporation rate after 24 hours is probably due to the gelation of the sample. The presence of selenium also caused an increase in the evaporation rate, but it was only 50% greater than the control. After each of the runs lasting 48 hours, a small amount of white powder was observed on the walls of the beakers and on the top of the gel. This was believed to be silica or a highly cross-linked siloxane network.

Although the static oxidation experiments were less accelerated the results are in substantial agreement with those of the dynamic type. Both show that the oxidation stability of the polymethylsiloxane fluid decreases rapidly as the temperature is raised above 200° C.

THERMAL STABILITY

It has been shown (*11, 17*) that the polymethysiloxanes undergo thermal rearrangements at 350° to 400° C. with the rupture of the siloxane chain to form products which are predominately cyclic siloxanes of low molecular weight. The dynamic experiments at 225° C. revealed that the presence of some metals, notably lead, selenium, and tellurium, in an oxidizing atmosphere greatly accelerated the rupture of the siloxane chain with the formation of cyclic products. As the cyclic products of low molecular weight are volatile at 200° C. and above, viscometric evidence of the thermal instability of the silicone would probably be masked by the viscosity increases due to oxidation and the evaporation of the low-molecular-weight siloxanes originally present in the fluid. To obtain some indication of the thermal stability of the polymethylsiloxanes, silicone C-4 was sealed in a Pyrex vial with the various gases, as described under "Stability Tests," and heated at 250° C. The viscosities of the fluids were determined after 24, 72, and 168 hours of exposure (Table V). These data reveal that cracking does occur and that equilibrium has not been reached at 168 hours. The viscosity decreases were greater for the samples under an atmosphere of air. Atmospheres of helium and nitrogen resulted in smaller rates of viscosity change. Probably the control runs under the inert gases would approach the same limiting value at equilibrium. Under an atmosphere of helium none of the metals affected the rate of the viscosity change significantly, as compared to the control run. Copper, nickel, and cold-rolled steel were also inactive under atmospheres of air and nitrogen. The metals (lead, selenium, and tellurium) which accelerated the evaporation of the silicones and inhibited the viscosity increases in the dynamic experiments were also found to affect the thermal stability of the silicones as reflected by the decreases in viscosity. Lead caused only a slight acceleration in the viscosity decrease as compared to the control run under these atmospheres. In the presence of selenium the viscosity of the

Table V. Effect of Metals on Thermal Stability of Fluid C-4 in a Sealed Glass System at 250° C.

Atmosphere	Metal	Viscosity at 100° F., Centistokes 24 hr.	Viscosity at 100° F., Centistokes 72 hr.	Viscosity at 100° F., Centistokes 168 hr.
Air	None	67.3	64.8	62.4
	Copper	67.4	64.8	63.8
	Lead	66.5	64.2	59.5
	Nickel	...	64.9	...
	Selenium	55.9	57.3	57.9
	Steel[a]	67.6	64.3	62.4
	Tellurium	65.9	64.9	52.1
Helium	None	71.4	70.6	67.4
	Copper	71.0	70.4	65.4
	Lead	71.9	70.1	67.3
	Nickel	70.8	68.2	...
	Selenium	71.7	69.9	69.7
	Steel[a]	71.7	70.5	66.0
	Tellurium	71.9	67.4	63.6
Nitrogen	None	72.3	70.9	69.2
	Copper	72.2	70.2	69.2
	Lead	64.1	62.7	62.9
	Nickel	72.4	70.9	...
	Selenium	56.9	65.5	56.8
	Steel[a]	72.4	71.4	69.1
	Tellurium	71.9	69.1	48.8

[a] SAE 1020 cold-rolled.

silicone decreased greatly during the first 24 hours of exposure, and thereafter there was little change. With tellurium the great viscosity change generally occurred between 72 and 168 hours of exposure. However, variable results were obtained with tellurium under an atmosphere of nitrogen. In some experiments the equilibrium viscosity was obtained after 24 hours.

ACKNOWLEDGMENT

The authors would like to express their appreciation to C. E. Cox for many of the viscometric determinations and to D. C. Smith for his cooperation in making the essential spectroscopic analyses discussed here.

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Received April 9, 1947. The opinions or assertions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

POLYORGANOSILOXANES . . .

Surface Active Properties

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A STUDY has been made of the densities, the surface tensions and their temperature coefficients, the interfacial tensions against water, the spreading pressures, and the force-area and potential-area relations of monolayers on water of various types of linear polyorganosiloxanes. The McLeod constants and parachors have been calculated, and their application to the type analysis of the silicones is discussed. Relations have been found between the critical spreading pressure, the spreading coefficient, and the viscosity. A study of the force-area curves revealed that the polymethylsiloxanes and the related polymers containing a small proportion of phenyl substituents are able to coil reversibly into helices made up of about six monomers per turn. Conclusions relative to the molecular structures in thin films have been carried over to the three-dimensional liquid state. It is shown that a qualitative explanation can be given of the variation with substituents in the viscosity indices of the different linear polyorganosiloxanes and of the unusually high values of the methyl-substituted compounds. It is concluded that the larger diameter of the silicon atom as compared with the carbon atom is responsible for the greater ability of the polymethylsiloxanes to coil, as compared with analogous linear polymers of the hydrocarbon or ether types. At low film pressures each helix uncoils, and the molecule adsorbs with the long axis in the water. The length of the helix increases with the temperature. The potential-area changes with molecular packing were unusual. The electric moment per monomer has been obtained, and its significance is briefly discussed.

MANY of the physical and chemical properties of the polyorganosiloxanes (or silicones) have been described recently (*1, 2, 4, 9, 10, 11, 12, 17, 19, 22*). Relatively few data have appeared concerning the surface active properties and their relation to molecular structure. This discussion deals with some of the properties of polyorganosiloxane films when adsorbed at the gas-silicone and water-silicone interfaces.

The linear polymethylsiloxanes from the dimer to the heptadecamer were carefully purified compounds having trimethylsiloxy end groups. Many of the properties of the dimer through the octamer have been described by Hunter *et al.* (*10*). The DC 500 series fluids are commercial mixtures of homologous linear polymethylsiloxanes, those under 5 centistokes (cs.) in viscosity apparently being distillation cuts. The samples of this series having lower viscosities than 5 cs. comprised a small range of molecular weights approaching pure compounds at the lowest viscosities (0.65, 1.0, and 1.5 cs.). This is evidenced by the close agreement of the surface tensions and densities with those measured for the linear dimer, trimer, and tetramer. The polyethylsiloxanes and polymethylphenylsiloxanes used were producers' samples of mixed homologous compounds. The type classifications of these fluids given in Table I are based on the analyses of this laboratory. Almost all of the measurements were made in a constant temperature room held at 20° ± 0.2° C. The relative

Table I. Type Classification[a] of the Polyorganosiloxanes Studied

Identification	Viscosity, Cs. at 25° C.	Organic Substituents: On terminal Si atoms	Organic Substituents: On other Si atoms	Estimated[b] Ratio, Phenyl/ Methyl
Linear polymethylsiloxanes, DC 500	All visc.	Trimethyl	Methyl	0
Linear polyethylsiloxanes				
A1	13	Triethyl	Ethyl	0
A2	50	Triethyl	Ethyl	0
A3	158	Triethyl	Ethyl	0
Linear polymethylphenylsiloxanes				
B1	3.5	1 phenyl, 2 methyl		0.60[d]
B2	27	Trimethyl	Methyl & phenyl	0.63
B3	50	Trimethyl	Methyl & phenyl	0.14
B4	50	No trimethyl[c]	Methyl & phenyl	0.53
B5	102	Trimethyl	Methyl & phenyl	0.49

[a] These type classifications are approximate and do not completely exclude the presence of other siloxane structures.

[b] A rough estimate based on the ratio of intensities of infrared absorption maxima.

[c] Probably terminal group has methyl and phenyl substitution.

[d] Actual ratio of phenyl to methyl groups is 0.5.

humidity was held between 50 and 60%. A Cenco-Du Nouy interfacial tensiometer was used for measuring the surface tensions of the materials which were available in sufficient quantity, the usual corrections (*8*) being applied. The surface tensions of the rarer materials and all the interfacial tensions were measured with a drop-weight apparatus, and the appropriate corrections (*5*) were made. The measurements on the same materials using both instruments agreed within 0.1 dyne per cm. A modified Cenco hydrophil balance was used to measure the spreading pressures and force-area relations. Film potential measurements were made with the vibrating electrode method (*23, 24*) using an electrically driven gold electrode 4 cm. in diameter and a cathode ray oscillograph (instead of a telephone) to detect the null point. Such potentials were easily measured to ±3 millivolts.

It was essential to remove any traces of more surface active compounds present as impurities by percolating each fluid through a suitable selective adsorbent. The equilibrium spreading pressures of the DC 500 fluids were found to be decreased permanently by this procedure and were used to indicate the relative effectiveness of removal of adsorbable impurities by the various adsorbents. As Florisil was the most effective of the adsorbents tested, it was chosen for use in purifying all of the silicones discussed here.

GAS-SILICONE INTERFACE

The surface tensions in air are given in Tables II and III. No change exceeding a few tenths of one per cent was found in the densities or surface tensions due to percolation. When surface tension was plotted against density, a linear graph was obtained for all of the polymethylsiloxanes of Table II. The data for all of the ethyl- and phenyl-substituted polymers fell well off the line and did not lie on any other straight line. This was expected, since these polymers were not homologous. These surface tensions, and especially those of the polymethylsiloxanes, are very low for materials of such densities and boiling points. It is illuminating to note that the data for the series of normal aliphatic hydrocarbons lie on a linear curve which is displaced by over 10 dynes per cm. more than the curve for the polymethylsiloxanes. At room temperature the silicone fluids dissolve roughly 25% of their volume of air. A series of surface tension measurements were made in a helium atmosphere after stripping the air from the fluids by evacuation and subsequent bubbling of helium through them. However, the surface tensions were found to be the same as in air.

The corrected surface tensions and densities in air at several temperatures are given in Table III. The surface tension of the DC 500, 35-cs. fluid was found to change linearly with the temperature. The Eötvös constant was calculated using the data on the polymethylsiloxane heptadecamer. The resulting value of 3.6 is much higher than the "normal" value of 2.1. The Eötvös constant calculated for the phenyl-substituted dimer (fluid B1) is 2.8. It is usually considered that a high constant is indicative of a linear molecular structure, and this is obviously true here.

Sauer (*16*) derived the group and bond refractions of a wide variety of organosilicon fluids and showed they can be used for determining the average composition of the polymethylsiloxanes. A more limited, although similar, analysis employing the atomic parachors was made and used by the present authors during the recent war for the identification of silicones. An example may be given for a linear polyorganosiloxane containing only methyl and ethyl group substituents. If *m* and *e* are the ratios of the number of methyl and ethyl groups to the number of silicon atoms *n*, the polymer may be represented as follows:

$$(CH_3)_m\ (C_2H_5)_e\ Si\ O\left(\frac{4-(e+m)}{2}\right) \tag{1}$$

Assuming additivity of the parachors, the specific parachor is then:

$$p = \frac{mP_{CH_3} + eP_{C_2H_5} + P_{Si} + \frac{1}{2}\,[4-(e+m)]\,P_O}{mM_{CH_3} + eM_{C_2H_5} + M_{Si} + \frac{1}{2}\,[4-(e+m)]\,M_O} \tag{2}$$

where P, M = group or atomic parachors and weights, respectively

Using Sugden's figures (*18*) for the parachors of C_2H_5, CH_3, O, and our own figure for silicon (30.2), the expression reduces to

$$p = \frac{46.1m + 85.1e + 70.2}{7.03m + 21.06e + 60.06} \tag{3}$$

Table II. Surface Tensions, Interfacial Tensions against Water, Densities, McLeod Constants, and Parachors for Some Linear Polymethylsiloxanes

(All measurements at 20° C.)

Substance	Surface Tension, Dynes/ Cm.	Interfacial Tensions against Water, Dynes/Cm.	Density, d_4^{20}	McLeod Constant	Parachor	Parachor for Si
Pure compounds						
Dimer	15.7	...	0.7636	2.608	423	33.3
Trimer	16.96	...	0.8200	2.475	585	32.1
Tetramer	17.60	...	0.8536	2.400	745	31.1
Pentamer	18.10	...	0.8755	2.356	906	30.6
Hexamer	18.45	...	0.8910	2.326	1067	30.3
Heptamer	18.60	...	0.911[a]	2.280[a]	1215[a]	28.2[a]
Octamer	18.82	...	0.913[a]	2.281[a]	1385[a]	29.3[a]
Nonamer	19.24	37.0[b]	0.9173	2.283	1554	30.3
Dodecamer	19.56	30.4[b]	0.9314	2.258	2040	30.1
Heptadecamer	19.87	27.3[b]	0.9428	2.239	2852	30.2
DC 500 series						
0.65 cs.[c]	15.7	39.9	0.7631	2.608	...	...
1.0 cs.	16.8	42.5	0.8199	2.469	...	...
1.5 cs.	17.5	42.4	0.8538	2.395	...	...
3.0 cs.	18.5	40.0	0.8939	2.319	...	...
5.0 cs.	19.0	42.2	0.9177	2.291	...	...
10 cs.	19.4	39.9	0.9392	2.234	...	...
35 cs.	19.9	43.1	0.9560	2.214	...	...
56 cs.	20.2	...	0.9643	2.202	...	...
70 cs.	20.3	...	0.9683	2.196	...	...

[a] These values are approximate.

[b] Unpercolated.

[c] All viscosities at 25° C.

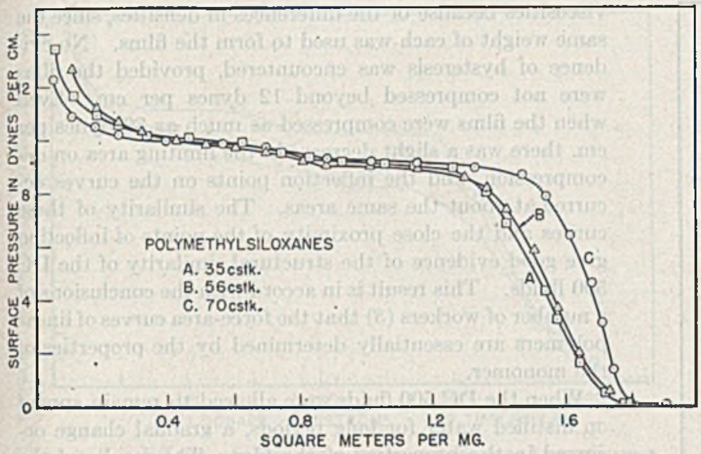


Figure 1. Force-Area Curves for DC 500 Fluids

When $e = 0$

$$m = \frac{p - 1.169}{0.7676 - 0.1170p} \qquad (4)$$

Since

$$m = \frac{2 + 2n}{n} \qquad (5)$$

Equations 4 and 5 may be used to calculate n as well as the molecular weight of a linear polymethylsiloxane. However, as the molecular weight becomes large, m approaches 2 as a limit and p changes very slowly. This makes it difficult to compute accurately the mass of a high-molecular-weight polymer.

The values for m are high when calculated using Sugden's early value (*18*) of 27.8 for the parachor of silicon. Hunter *et al.* (*9*) concluded that, in four of the low-molecular-weight cyclic polymethylsiloxanes, the parachor of silicon varied between 25.8 and 27.1. Hunter and another group of workers (*10*) recently reported surface tension and density data for some linear polymethylsiloxanes. From these we have computed the parachors for silicon and found them varying from 27.8 to 31.1. Our own data are closer to the latter, the parachor for silicon becoming constant at 30.2 for linear polymethylsiloxanes containing more than five silicon atoms in the molecule. Equations 4 and 5 appear to discriminate the chain length satisfactorily up to the heptadecamer.

DISTILLED WATER-SILICONE INTERFACE

When in two nonmiscible liquids $\gamma_B > \gamma_A + \gamma_{AB}$, liquid A will spread on liquid B. The quantity $\gamma_B - \gamma_A - \gamma_{AB}$ has been called the initial spreading coefficient (*7*). Washburn and Keim (*20*) have shown experimentally that this coefficient is equal to the equilibrium spreading pressure for a number of liquid organic compounds on water. Their method was used in this study with eicosyl alcohol serving as the "piston film" material. Preliminary trials showed that there was no pressure at which a bulk lens of a polymethylsiloxane fluid was in equilibrium with a monolayer of the same substance. However, a pressure which we call critical spreading pressure (S_1) could be observed experimentally where a thin disk showing interference colors increased or decreased in size rapidly with little change in pressure. This pressure was reproducible and represented a highly compressible and reversible state of the silicone film as confirmed by the force-area studies.

Table IV shows the effect of the various adsorbents on the value of S_1 for the 70-cs. DC 500 fluid. Of all the adsorbents tried, Florisil produced the largest effect. After the first percolation of each silicone sample a yellow ring was left at the top of the column of adsorbent. No such residue was left after the second percolation. On simply standing in contact with the atmosphere in a clean Pyrex container, the silicone fluids developed higher values of S_1 than were exhibited by freshly percolated materials, the greatest change taking place in the first few hours. However, the critical pressure S_1 did not revert back to the values for the unpercolated fluids. For example, in several experiments the fluid was taken directly from the delivery tube of the adsorption column, and S_1 was found to be as small as 7.9 dynes per cm. Within two hours after percolation the same batch of silicone was tested, and S_1 had become about 10.0 dynes per cm. Table V shows that S_1 increased with decreasing molecular weight (or viscosity). When the logarithm of the viscosity at 25° C. was plotted against the critical pressure S_1, a straight line was obtained, provided the graph points for the fluids of 3.0 cs. or less were disregarded. This is not unreasonable, since it is shown later that the silicones below the octamer (4 cs.) do not have critical spreading pressures.

The spreading pressures of the silicones are greater than those of all but the very volatile hydrocarbons, but are less than those of most hydrocarbon derivatives containing a single hydrophilic substituent. The polyethylsiloxane fluid (A2) showed no evidence of possessing such a critical spreading pressure. The phenyl-substituted compounds showed a critical pressure similar to S_1, but it was less well defined depending on the degree of phenyl substitution.

The interfacial tensions for the most part were more difficult to measure because of the small density differences between the silicones and water. It was impossible to use the ring method, and some difficulty was experienced with the drop-weight method. Therefore, the interfacial tensions are uncertain to ±0.5 dynes per cm., and no measurements were made on the silicones having viscosities over 35 cs. The best value from Table II is 42.5 dynes per cm. Percolation caused changes in the interfacial tensions, as would be expected from the fact that the surface tensions were

Table III. Effect of Temperature on Surface Tension and Density of Various Polyorganosiloxanes

Fluid & Viscosity at 25° C.	Temp., ° C.	Density	Surface Tension	Coefficient of Cubical Expansion × 10^3	$\frac{-d\gamma}{dt}$
Linear polymethylsiloxanes					
Heptadecamer	20	0.9428	19.9	1.07	0.067
	35	0.9283	18.9		
DC 500, 35 cs.	5	0.9689	21.10		
	10	0.9646	20.65		
	15	0.9602	20.38		
	20	0.9557	20.00	1.00	0.067
	25	0.9514	19.67		
	30	0.9649	19.35		
	35	0.9425	19.00		
Linear polyethylsiloxanes					
A1, 13 cs.	20	0.9535	23.3	0.87	0.060
	35	0.9418	22.4		
A2, 50 cs.	20	0.9909	23.7	0.80	0.060
	35	0.9795	22.8		
A3, 158 cs.	20	0.9941	25.7	0.67	0.073
	35	0.9840	24.6		
Linear polymethylphenylsiloxanes					
B1, 3.5 cs.	20	0.9809	29.6	0.87	0.080
	35	0.9686	28.4		
B2, 27 cs.	20	1.0735	28.6	0.72	0.08
	35	1.0612	27.4		
B3, 50 cs.	20	0.9955	22.2	0.93	0.12
	35	0.9827	20.4		
B4, 50 cs.	20	1.0704	27.2	0.69	0.11
	35	1.0586	25.5		
B5, 102 cs.	20	1.0787	26.1	0.71	0.11
	35	1.0665	24.4		

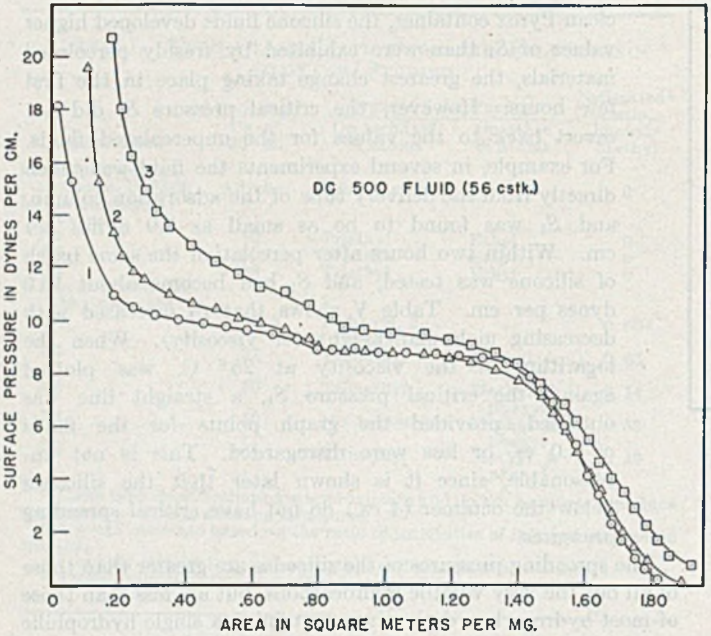


Figure 2. Force-Area Curves for 56-Cs. DC 500 Fluid

1. Initial curve
2. After 90 minutes
3. After 4 hours

not affected while the spreading pressures were. For example, the interfacial tension of the 35-cs. DC 500 fluid was 36.9 dynes per cm. when unpercolated and 43.1 dynes per cm. after percolation. Allowing the silicone to stand after percolation for lengths of time up to several hours did not affect the interfacial tension, although the experimental uncertainty in the measurement may have obscured minor effects.

It is interesting to calculate the initial spreading coefficient (S_{AB}) of Harkins and Feldman (*7*) from the surface and interfacial tension data of Table II. Column 3 of Table V gives the values of S_{AB} calculated from the observed surface and interfacial tensions of Table II, and column 4 gives the results when the best interfacial tension of 42.5 dynes per cm. is used instead. The surface tension of water at 20° C. was taken to be 72.8 dynes per cm. The agreement of columns 2 and 4 is as good as could be expected for all but three of the fluids. This gives support to our treatment of the critical pressure S_1 as analogous or equivalent to the equilibrium spreading pressure. Applying to the silicone-water interface, the well known relation for the work of adhesion between two liquids *A* and *B*

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \qquad (6)$$

it is found that the value of W_{AB} for the polymethylsiloxanes ranged from 47 to 53 ergs per square cm., the higher values being obtained for greater molecular weights. This is only 10 to 15% higher than the value for nonpolar hydrocarbons.

FORCE-AREA RELATIONS FOR POLYMETHYLSILOXANES

Monolayers spread on water were studied of all but the lowest members of the series of polymethylsiloxanes of Table II. It was not possible to purify the hexamer, heptamer, and octamer by percolation because not enough was available. The silicone material (0.04 mg. dissolved in C.P. benzene) was spread on the film balance with the Harkins' pipet (*21*). The accuracy of the film balance was checked by measuring the equilibrium spreading pressure of benzene, 9.5 dynes per cm. (*20*).

Figure 1 shows the force-area curves for a series of DC 500 fluids on distilled water at 20° C. The limiting areas of the film would be expected to be slightly different for silicones of different viscosities because of the differences in densities, since the same weight of each was used to form the films. No evidence of hysteresis was encountered, provided the films were not compressed beyond 12 dynes per cm. Even when the films were compressed as much as 30 dynes per cm. there was a slight decrease in the limiting area on decompression, and the inflection points on the curves occurred at about the same areas. The similarity of these curves and the close proximity of the points of inflection give good evidence of the structural similarity of the DC 500 fluids. This result is in accord with the conclusions of a number of workers (*3*) that the force-area curves of linear polymers are essentially determined by the properties of the monomer.

When the DC 500 fluids were allowed to remain spread on distilled water for long periods, a gradual change occurred in the properties of the film. The results of the effect of such aging are shown in Figure 2. After 24 hours of contact with the water the plateau of the force-area curve disappeared. This corresponds to the disappearance of the critical pressure S_1. The same results were obtained by using either well waxed troughs of Pyrex or stainless steel and by using water which had been triply distilled in an all-tin still. These effects of varying the pH and the aqueous ions present were investigated but are not reported here. For the present it is sufficient to point out that the effect of aging the film on water is not significant in the length of time involved in obtaining the force-area curves reported here.

Force-area curves were taken at 5° and 38° C. for the heptadecamer to determine the effect of temperature (Figure 3). Rise in temperature caused the limiting areas to increase slightly, the effect being little more than the uncertainties in the experimental method. The pressure S_1 (represented by the plateau) decreased linearly with increase in temperature, in agreement with the results of Cary and Rideal (*14*) from their work on liquid fatty acids and esters. The kink in the plateau of the force-area curve occurred at larger specific areas with rise in temperature.

Fischer-Hirschfelder atom models of the polymethylsiloxanes were made using silicon atom models which were constructed assuming (*a*) tetrahedral symmetry in the valence angles, (*b*) a

Table IV. Critical Spreading Pressure of a Polymethylsiloxane after Percolation through Various Adsorbents[a]

Adsorbent	Spreading Pressure S_1 of 70-Cs. DC 500 Fluid after Percolation, Dynes/Cm.
None	15.0
Filter paper	14.9
Charcoal (granular Nuchar)	14.3
Alumina (Aluminum Ore Co.)	12.7
Silica gel (Davison Chemical Co.)	13.9
Florisil 100/200 mesh (Floridin Co.)	9.6
Florisil 40/60 mesh (Floridin Co.)	10.1

[a] The adsorbents were activated by a 4-hour baking at 250° C. They were used immediately after cooling to room temperature.

Table V. Critical Spreading Pressure of Various Polymethylsiloxanes

(DC 500 fluids percolated through Florisil)

	Critical Spreading Pressure S_1, Dynes/Cm. at 20° C.		
		Calcd. spreading coefficient	
Viscosity at 25° C., Cs.	Obsvd., S_1 measured 2 hr. after percolation	From data of Table II	From data of Table II and interfacial tension of 42.5
0.65	14.6?	17.2?	14.6?
1.0	13.0?	13.4?	13.5?
1.5	13.2?	12.9?	12.8?
3.0	13.3	14.3	11.8
5.0	12.0	11.6	11.3
10	11.6	13.4	10.9
35	10.5	9.6	10.2
56	10.2	..	10.1
70	10.0	..	9.9

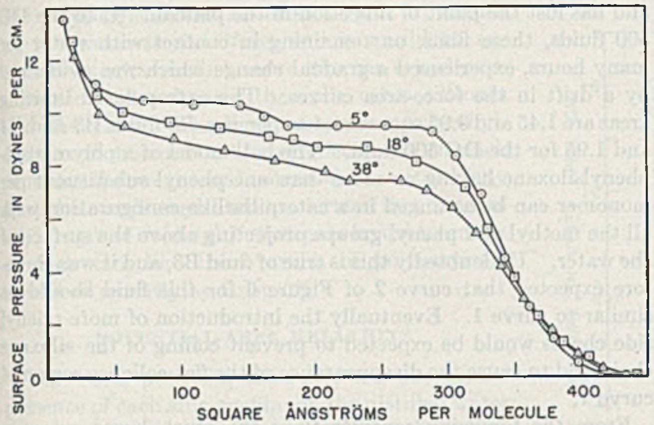


Figure 3. Effect of Temperature on Force-Area Curve of Linear Polymethylsiloxane Heptadecamer

valence bond radius of 1.17 Å. (*13*), and (*c*) the usual calculated atom diameter of 0.8 of the sum of 1.6 Å. plus twice the covalent bond radius. Inspection of the molecular model offered explanations for many of the peculiarities of the force-area curves. The polymethylsiloxanes can be arranged in a caterpillarlike configuration with all of the silicon atoms in line in the same plane and all of the hydrocarbon groups on one side of that plane. Such a molecule can adsorb so that all the silicon (and oxygen) atoms are in the water surface at low film pressures. Hurd (*11*) measured the molar volumes at 20° C. of the polymethylsiloxanes and obtained a value of 75.5 ± 0.2 ml. per gram molecular weight of monomer. The contribution of the end groups may be disregarded for the higher molecular weight polymers used here. On the basis of Hurd's measurements, the volume occupied by a single monomer is 125 cu. Å. Measurements on the caterpillarlike atom model showed that each monomer occupied a parallelepiped having a volume of 132 cu. Å., a height of 5.6 Å., and an area of 22.7 sq. Å. This value of the volume per monomer is in reasonable agreement with Hurd's, considering the fact that adjacent molecules can insinuate themselves a small distance inside the outer boundaries of the parallelepiped. On the basis of these measurements the abscissas of the force-area curves for the DC 500 fluids could be expressed in square Ångström units per monomer. The force-area curve of Figure 8 for the polymethylsiloxane fluid (35 cs.) shows that the limiting area is actually 22.9 sq. Å., which is in good agreement with the value derived from measurements on the molecular ball model.

The changes in the molecular packing and orientation involved in compressing a polymethylsiloxane film can now be outlined. The close-packed phase with every oxygen and silicon atom still adsorbed at the surface appears at pressures of less than 1 dyne per cm. This phase has a moderate compressibility, a measure of the ease with which some of the oxygen and silicon atoms can be squeezed out of the surface. If no large segments of molecules are pushed out of the monolayers, a change in the arrangement of the atoms takes place which ends at an area of approximately 16 sq. Å. per monomer. In this state of compression the average thickness of the film is computed to be 7.9 Å., but no disposition of the atoms with all the silicons lying in the surface will produce a thickness of 7.9 Å. However, a regular zig-zag arrangement of the atoms of the molecule is possible for which the area occupied by each monomer is only slightly smaller than in the flat caterpillar configuration, and the height of the molecule is then approximately 7.9 Å. The new configuration is such that only every other silicon (or oxygen) atom is adsorbed at the air-water interface. Here the molecule is much more flexible, and can be considerably twisted and bent without strain. This may explain what goes on in the region of high compressibility beginning at 16 sq. Å. per monomer, where the molecules are able to coil or fold up more easily, and portions can eventually be pushed out of the interface. The flatness of the curve in this region indicates the occurrence of some important molecular transformation. It was considered possible that the siloxane chain was being coiled up to form a helix whose axis was parallel to the surface of the water.

It is noteworthy that, even when the films were subjected to pressures as high as 45 dynes per cm., no collapse of the film was observed. At the average thickness of 70 Å. the film became relatively incompressible. In fact, careful inspection of the film showed striations due to varying thicknesses in different portions of the film. In the highly compressible region there is a small change in the slope of the curve which disappears after a small rise in pressure. This occurred with each DC 500 fluid tried at about 0.80 square meter per mg., which corresponds to about 10.0 sq. Å. per monomer and a film thickness of 12.5 Å. This discontinuity occurred in every force-area curve, whether stainless steel or Pyrex troughs were used, and also with two different torsion heads.

Figure 4 gives the force-area curves at 20° C. of the heptadecamer and nonamer, and those of the dodecamer and octamer are in Figure 5. It was possible to express the abscissas in square Ångström units per molecule because the molecular weights of these compounds were known. The curve for the heptadecamer resembles closely those of the higher-molecular-weight polymethylsiloxane mixtures shown in Figure 1. An important difference was that the heptadecamer film became rigid at about 12.5 dynes per cm. On further compression the film crumpled, and it did not spread again on decompression. The lack of reversibility of the highly compressed film may be due to a chemical reaction at the interface.

The points of interest have been indicated by letters on the curve for the heptadecamer (Figure 4). At specific areas larger than that indicated by point *A*, the film is apparently gaseous. Around pressures corresponding to point *A* the film is a close-packed monolayer with every silicon and oxygen atom in the surface of the water, since the limiting area agrees closely with that calculated from the caterpillar-ball model. Extrapolating the linear portion of the curve near point *A* to zero pressure results in an area of 395 sq. Å. per molecule, which corresponds to an average film thickness of 5.9 Å. This is to be compared with the area of 415 sq. Å. per molecule and the thickness of 5.6 Å. measured on the ball model. It is not surprising that the measured

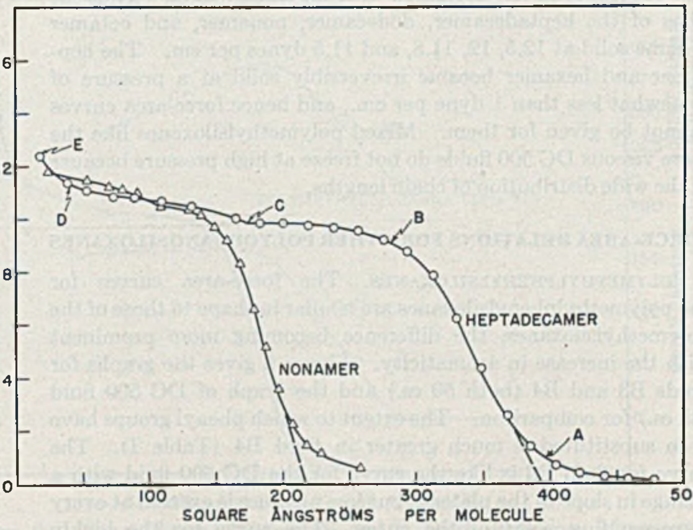


Figure 4. Force-Area Curves of Polymethylsiloxane Heptadecamer and Nonamer

specific area is smaller than the calculated, since the latter corresponds to the area of the enveloping parallelepiped. At point *B* the monolayer is 7.9 Å. thick, which corresponds to the zig-zag configuration described earlier. The change in slope (*C*) occurs at an area per molecule of 175 sq. Å., which corresponds to a film thickness of 12.7 Å. A horizontal helical ball model coiled into turns containing six monomer units each has a height of 12.5 Å. It was not possible by manipulating the ball model to wind it into a close-wound helix having a smaller diameter. Point *D* marks the location where the area per molecule (40 sq. Å.) approximately equaled the cross-sectional area of the straight caterpillar molecule taken at right angles to its long axis. At *E* the film became solid.

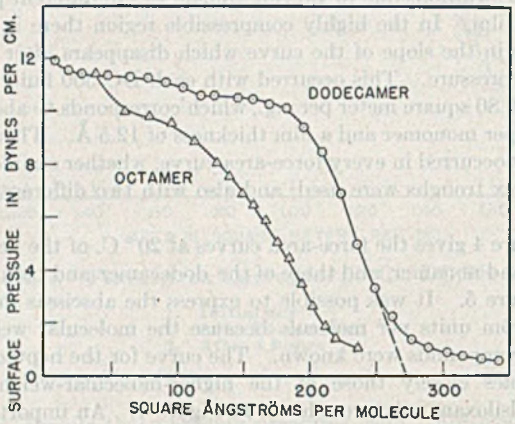


Figure 5. Force-Area Curves for Polymethylsiloxane Dodecamer and Octamer

From this interpretation of the behavior of the film of the heptadecamer it would be expected that the nearest homologs of shorter chain length would behave similarly, but the similarity should eventually disappear when the number of silicon atoms in the chain becomes too small to permit coiling into a helix. This was found to be true, and the octamer was the lowest homolog to show any similarity. The region *BC* decreased as the chain length decreased until it was no longer evident in the curve for the octamer. The area for the dodecamer and nonamer molecules (*A*) was found with the data of Figures 4 and 5 to be 270 and 216 sq. Å., respectively, and the corresponding heights were 6.0 and 5.6 Å. These are to be compared with areas of 294 and 221 Å. and a height of 5.6 Å. calculated from the straight ball models. From these graphs the heights found for the coiled helical molecule (at *C*) are 13.1 and 12.5 Å., respectively. The pressure at which the film became solid (*E*) decreased with the chain length. Thus the films of the heptadecamer, dodecamer, nonamer, and octamer became solid at 12.5, 12, 11.8, and 11.5 dynes per cm. The heptamer and hexamer became irreversibly solid at a pressure of somewhat less than 1 dyne per cm., and hence force-area curves cannot be given for them. Mixed polymethylsiloxanes like the more viscous DC 500 fluids do not freeze at high pressure because of the wide distribution of chain lengths.

FORCE-AREA RELATIONS FOR OTHER POLYORGANOSILOXANES

POLYMETHYLPHENYLSILOXANES. The force-area curves for the polymethylphenylsiloxanes are similar in shape to those of the polymethylsiloxanes, the difference becoming more prominent with the increase in aromaticity. Figure 6 gives the graphs for fluids B3 and B4 (both 50 cs.) and the graph of DC 500 fluid (35 cs.) for comparison. The extent to which phenyl groups have been substituted is much greater in fluid B4 (Table I). The curve for fluid B3 is like the curve for the DC 500 fluid with a change in slope in the plateau, but less pressure is exerted at every corresponding point of the curve. The curve for the highly phenyl-substituted fluid B4 shows a great loss of compressibility and has lost the point of inflection in the plateau. Like the DC 500 fluids, these films, on remaining in contact with water for many hours, experienced a gradual change which was evidenced by a drift in the force-area curves. The extrapolated limiting areas are 1.45 and 0.95 square meters per mg. for fluids B3 and B4 and 1.95 for the DC 500 fluid. The ball model of a polymethylphenylsiloxane having no more than one phenyl substituent per monomer can be arranged in a caterpillarlike configuration with all the methyl and phenyl groups projecting above the surface of the water. Undoubtedly this is true of fluid B3, and it was therefore expected that curve 2 of Figure 6 for this fluid should be similar to curve 1. Eventually the introduction of more phenyl side chains would be expected to prevent coiling of the siloxane chain and to cause the disappearance of the flat collapse region of curve 1.

From the foregoing considerations the much lower area per molecule for the fluid B4 is understandable, for the presence of the phenyl side chains would cause the film to be thicker than that of the methyl-substituted compound, and the number of oxygen and silicon atoms in the surface is smaller in the given weight of material. Since no accurate information was available on the proportion of phenyl and methyl groups in these polymers, a comparison based on the ball models could not be made of the area occupied by each monomer.

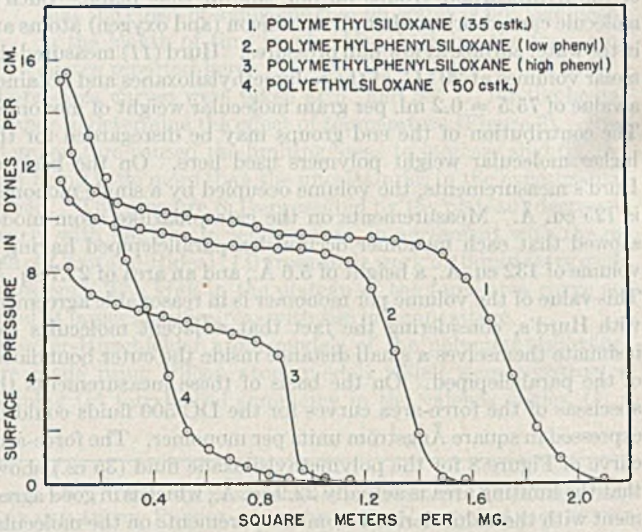


Figure 6. Force-Area Curves for Different Types of Linear Polyorganosiloxanes

POLYETHYLSILOXANES. The force-area curve obtained with polyethylsiloxane fluid A2 (50 cs.) is given in Figure 6 and again in Figure 9. Like the other polyorganosiloxanes already described, the force-area curves were reversible but did change slowly as the film aged while spread out on the water. Force-area curve 4 of Figure 6 is different from the others. It is similar to the curves obtained by Harkins, Carman, and Ries (6) from polymers of ω-hydroxydecanoic acid, which were shown to lie flat on the water surface at low pressures. The polyethylsiloxane films did not collapse at high pressures but became thicker and more viscous until, at pressures of 17–18 dynes per cm., striations appeared. At the highest pressures obtained (18.5 dynes per cm.) the films were liquid and viscous.

The ball model of a polyethylsiloxane was impossible to arrange in the caterpillarlike configuration described earlier because of hindrance to the rotation of the ethyl side chains about the Si—C bond. However, the ball model could be arranged so that some but not all of the silicon and oxygen atoms could emerge from the surrounding sheath of ethyl groups to contact the surface of the water. Therefore, only an occasional silicon or oxygen atom of the polyethylsiloxane molecule is able to adsorb at the water-air interface, and it would be expected to behave much more like the ω-hydroxydecanoic acid polymers than the other silicones described here. The limiting area per polyethylsiloxane monomer is not known because of the lack of molecular weight and volume data. It is likely that the compressed films are formed by a random buckling and folding of the monolayers to create a thick film like the overfilm of polyacrylates described recently by Crisp (*3*).

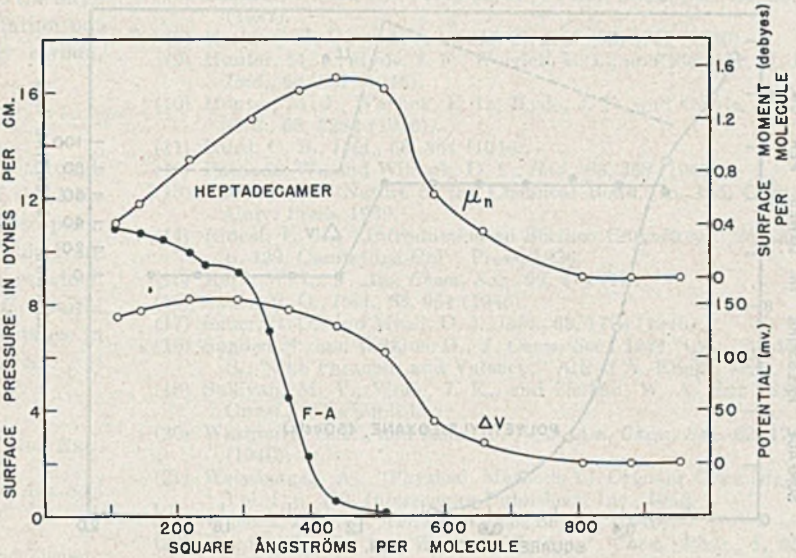


Figure 7. Force-Area, Potential-Area, and Surface Moment-Area Curves for Polymethylsiloxanes Heptadecamer

POTENTIAL-AREA RELATIONS

The Volta potential difference ΔV due to the presence of each silicone film on the distilled water of the film balance is expressed as a function of the degree of packing in Figures 7, 8, and 9. The corresponding force-area curves are given for comparison. The ordinate of the curve marked μ_n is the normal component of the dipole moment for that degree of packing. Because of limitations set by the units used in plotting the abscissas in each figure, the ordinate in Figure 7 was given in Debye units per molecule; in Figure 8 it was in Debye units per monomer; and in Figure 9 it was expressed in arbitrary units which are equivalent to Debye units per monomer multiplied by an unknown constant. The curve of Figure 9 was obtained by multiplying ΔV by each corresponding value of the abscissa A in square meters per milligram. For each substance studied on distilled water the ΔV-A and μ_n-A curves were reproducible and free from hysteresis.

As would be expected, the force-area and μ_n-A curves are similar for the heptadecamer and the DC 500 fluid, both revealing that μ_n is zero for all values of A for which the molecules are not in close proximity. It rises rapidly to a maximum value as A approaches and equals the area of closest packing of the flat caterpillar-shaped molecules. As buckling of the film occurs at higher film pressures, μ_n decreases nearly linearly, and it approaches zero as the greater portion of the monolayer collapses into a thick film showing striations. The previously described geometrical rearrangements, which occur in the film after buckling starts, do not cause changes of slope in the ΔV-A or μ_n-A curves. The maximum value of μ_n per monomer calculated from Figure 7 is 1.5/17 or 0.089 Debye unit. This is to be compared with the value of 0.087 Debye unit per monomer as read from the maximum of Figure 8. This is a good agreement for results obtained for a pure compound and a mixture of homologs. It is evident from the μ_n-A curve of Figure 9 that the polyethylsiloxane fluid behaves quite similarly to the polymethylsiloxane fluids. The linear drop in the μ_n-A curve after buckling commences is quite common in other types of films, and it is also assumed to be caused by disorganization of the dipoles during the formation of the overfilm. The low pressure electrical behavior observed is different from anything reported heretofore. One cause may be that electrical compensation in the caterpillar-shaped molecules exists unless forces arising during close packing can disturb the situation. These effects may be due to (*a*) bond strains, (*b*) induction effects between molecules, or (*c*) compensating effects due to the orientation of adsorbed molecules of water or dissolved ions, which may disappear during close packing and buckling as the silicon and oxygen atoms are lifted out of the water.

DISCUSSION

The collapse phenomena found in studying the force-area relations in the silicone monolayers explain some of the effects described earlier in connection with the search for the equilibrium spreading pressure. In no instance could a drop of any silicone fluid exist on water in equilibrium with the silicone monolayer. The remarkable phase transition discovered in monolayers of the polymethylsiloxane of higher molecular weight (point C in Figure 4) is responsible for the critical spreading pressure. The conditions of the polymethylsiloxane molecules in the adsorbed film at high pressures (points D and E in Figure 4) and at very low pressures (point A) are apparently not found in the bulk liquid. However, the coiling of the molecule encountered at B and C is believed to be characteristic of the configuration of the molecules in the three-dimensional liquid state. As evidence it should be noted that the critical spreading pressure S_1 has been shown to be approximately equal to the spreading coefficient S_{AB}, which is calculated from the surface and interfacial tensions. Also it has been shown that S_1, like the equilibrium spreading pressure of many of these liquids, decreases linearly as the temperature rises. The logarithmic decrease in S_1 as the viscosity rises is also indicative.

From the calculation of W_{AB} using Equation 6 it was concluded that the silicones had only 15% more energy of adhesion to water than the hydrocarbons and were therefore not strongly

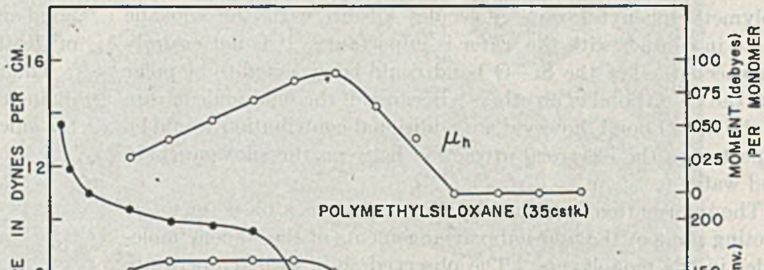


Figure 8. Force-Area, Potential-Area, and Surface Moment-Area Curves for DC 500 Fluid

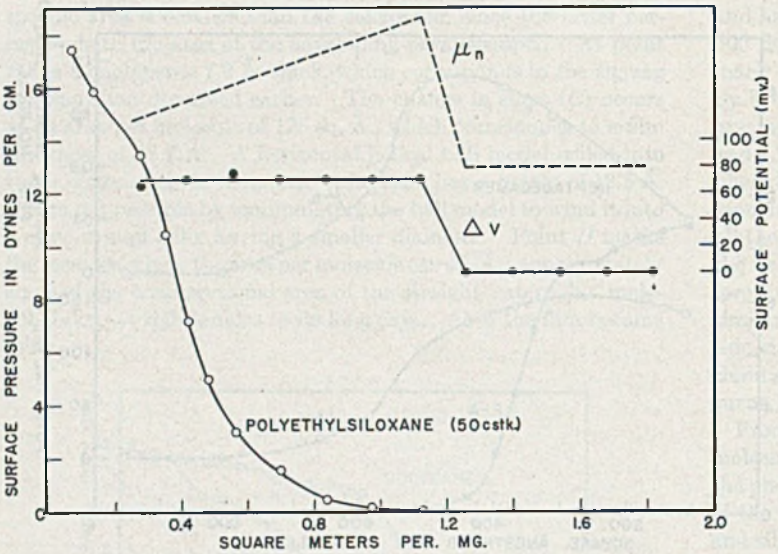


Figure 9. Force-Area, Potential-Area, and Surface Moment–Area Curves for Linear Polyethylsiloxane Fluid A2

adsorbed on water. The force-area curves of the polymethylsiloxanes show this conclusion to be erroneous. The contradiction is only apparent, for W_{AB} measures the adhesional energy between bulk silicone fluid and water. The arguments given above lead to the conclusion that, in the three-dimensional liquid state, the methyl-substituted linear silicones are coiled into helices. The net energy of adhesion would be smaller the lower the proportion of silicon and oxygen atoms per molecule capable of reaching the water. Hence the energy of adhesion would be a maximum when the silicone molecules at the interface are completely uncoiled and adsorbed with the long axis parallel to the water, and it will be at a minimum when arranged as in states *D* to *E* of Figure 4. When the molecule is in the coiled state characteristic of bulk liquid, the energy will have some intermediate value corresponding to the molecular orientations existing in states *B* and *C*. Therefore W_{AB}, although correct for bulk liquid, is by no means fully indicative of the surface activity on water of polyfunctional or other hydrophilic molecules, which are hindered from full orientation and adsorption in the three-dimensional state. The shorter the average lifetime of adsorption of each of the hydrophilic groups, the more unreliable will W_{AB} become as a measure of the adsorptivity of the whole molecule for water.

The fact that at low pressures the polymethylsiloxane and the polymethylphenylsiloxane molecules adsorb with the siloxane chain in contact with the water is important. It is not entirely unexpected, since the Si—O bond could be expected to be polar like the C—O bond of an ether. Because of the semi-ionic nature of the Si—O bond, however, an additional contribution would be expected to the electrical attraction between the siloxane chain and water.

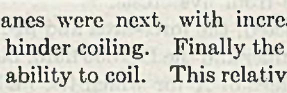
The information furnished by Figure 3 gives a basis for interpreting some of the unusual rearrangements of the silicone molecules in the monolayers. The observed shift with temperature of kink point *C* of Figure 4 as shown in Figure 3 means that each horizontally oriented helical molecule lengthens considerably as the temperature rises. An order-of-magnitude calculation can be made of the thermal expansion of the helix by assuming that the temperature change of the radius can be neglected. From Figure 3 it was calculated that the linear coefficient of thermal expansion of the helix along its axis is approximately 25 times the linear coefficient of expansion of the bulk liquid.

It will be noted further that the compressibility of the monolayer at low pressures as defined by the slope of the curves (region *A–B*) increases with increase in temperature. The apparent thickness of the film at the kink point increases with decrease in temperature, as does the extent of the collapse of the film in the transition region *B–C*. These two effects are to be expected from the increase with increase of temperature in the effect of thermal agitation in hindering the compact coiling of the molecules. At 5° C. the compact helix has a diameter corresponding roughly to seven monomers per turn (14 Å.) as compared to the value of six (12.5 Å.) at 20° C.

The ability of the molecules, in monomolecular films of the polymethylsiloxanes and low aromaticity polymethylphenylsiloxanes, to coil and uncoil reversibly as helices is remarkable as a phenomenon of surface chemistry. But this phenomenon can furnish a rational explanation of some of the little-understood properties of the silicones in the bulk liquid state. It is suggested that the remarkably high viscosity indices of the methyl-substituted silicones (or the low temperature coefficients of viscosity) are caused by the opposing actions of two molecular mechanisms: (*a*) the effect of increased temperature in separating the molecules causing the viscosity to decrease, and (*b*) the effect of increasing temperature in lengthening the helically coiled polymers causing the viscosity to increase. Effect *a* is common to all liquids, whereas effect *b* is more evident in long chain molecules, being most pronounced in the linear polymers so bonded and free from steric hindrances as to be most able to coil. The polymethylsiloxanes have just been shown to have the most pronounced ability to coil of the polyorganosiloxanes studied. The low aromaticity polymethylphenylsiloxanes were next, with increase in the aromaticity operating to hinder coiling. Finally the polyethylsiloxanes exhibited the least ability to coil. This relative order agrees with the order of decreasing viscosity indices. An evident conclusion is that the high viscosity indices of the silicones are due to the tendency of the siloxane chain to coil into a helix. This property is most pronounced in the methyl-substituted compounds, because they have the most compact hydrocarbon side chains and cause the least steric hindrance to the coiling of the chain.

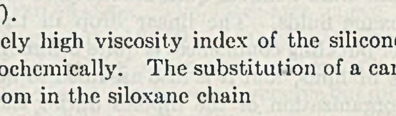
The conclusion that the helical coil contains from six to seven silicon atoms is given support by recent work of Wilcock (*22*) who estimated from the Kauzmann-Eyring theory of the activation energy for viscous flow that the flow units involved in the linear polymethylsiloxanes consisted of six to seven silicon atoms, the former value being preferred. The flexibility of the polyorganosiloxane chains may be increased even more than is evident in studying Fisher-Hirschfelder ball models, if the silicon-carbon bond angle is as variable as has been suggested by the x-ray work of Roth (*15*).

The uniquely high viscosity index of the silicones can be explained stereochemically. The substitution of a carbon atom for the silicon atom in the siloxane chain



$$\begin{array}{ccccccc} & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} & \\ & | & & | & & | & \\ - & \mathrm{C} & -\mathrm{O}- & \mathrm{C} & -\mathrm{O}- & \mathrm{C} & -\mathrm{O}- \\ & | & & | & & | & \\ & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} & \end{array}$$

results in a space model that is fairly rigid and cannot coil because of the small size of the carbon atom as compared with the silicon atom. A further substitution of methylene groups for the oxygens, thus,



$$\begin{array}{cccccccccccc} & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} \\ & | & & | & & | & & | & & | & & | \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}- \\ & | & & | & & | & & | & & | & & | \\ & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} \end{array}$$

results in a nearly completely rigid molecule. This leads to the conclusion that the high viscosity index of the polyorganosiloxanes as compared to ether and hydrocarbon analogs is due to the large size of the silicon atom, which permits freedom of rotation not found in hydrocarbons or molecules containing only carbon, hydrogen, and oxygen.

ACKNOWLEDGMENT

The pure linear polymethylsiloxanes were made available through the cooperation of Shailer Bass and M. J. Hunter of the Dow Corning Corporation. The conclusions from infrared absorption studies used in preparing the type classfications of Table I are excerpts from a larger spectroscopic study of the silicones which were made available through the cooperation of D. C. Smith. Acknowledgment is due to Edwin M. Solomon for assistance in obtaining many of the force-area and potential-area curves.

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Received April 12, 1947. The opinions or assertions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

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Shapes and Extruded Articles Made from Silicone Rubber

END OF SYMPOSIUM

Behavior of Silastic on Aging

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Silicone rubbers possess combined resistance to a wide variety of conditions which normally cause deterioration in organic elastomers. Under some of these conditions, such as exposure to heat, silicone rubber is serviceable at temperatures considerably above that of any other natural or synthetic rubber formulation. Moreover, these tests give further support to the hypothesis that stability is inherent in the silicone polymer because resistance to one set of conditions is not developed by special formulation at the expense of resistance to other kinds of aging. Both high and low temperature stability, together with weather and oil resistance, are found to be characteristic of silicone elastomers.

THE general properties of various silicone rubbers have been described in other publications (*7*, *8*, *9*). The most important of these, on which most commercial uses depend, are heat resistance, low temperature flexibility, weather resistance, and oil resistance. Data are presented here to evaluate the stability of silicone rubbers after exposure to heat, cold, weather, and oil.

Silicone rubbers, in common with other silicone compounds, are based on molecular skeletons which are chains of alternate silicon and oxygen atoms. In contrast, most other elastomers are composed of carbon-to-carbon linked molecular chains. On the basis of their bond energies, the structure of these silicone elastomers could be expected to produce compounds of exceptional stability. The bond energy between carbon atoms, for example, is 59 kg.-cal. per mole. The bond energy between the silicon and oxygen atoms in a silicone rubber chain is 89.3 kg.-cal. per mole, approximately 50% greater (*6*). That silicone elastomers bear out this prediction of greater stability is shown by their ability to withstand conditions which cause carbon-based elastomers to undergo temporary or permanent change.

The inherent stability of the silicone polymer is further emphasized by the fact that special compounding is not necessary to produce stocks resistant to many conditions. It is, on the contrary, common practice to vary the formulation of rubber stocks to meet varying specifications. Certain desired properties are developed and enhanced, usually at the expense of others less important to the particular application requirements. Thus, carbon-based natural and synthetic rubbers compounded for heat resistance could not be expected to be especially effective at low temperatures. Conversely, most low temperature rubber formulations are of little use at elevated temperatures. Rubber compounds can be altered by an almost infinite number of techniques and additions, but no single formulation combines resistance to more than a few of the conditions which usually cause elastomers to deteriorate.

The properties of silicone rubber can also be varied to a certain extent by compounding. Silicone rubber contains a dimethylsiloxane polymer and suitable fillers. All of the present Silastic stocks contain the same polymer. The individual properties of the various stocks are gained by varying the kind and amount of filler. The fillers used in compounding the Silastic stocks referred to in the subsequent data are listed in the following table; the filler constitutes approximately 60% by weight of each of the compounded stocks:

Silastic Stock No.	Filler
160	50% ZnO + 50% TiO_2
167	TiO_2
180	50% SiO_2 + 50% TiO_2
181	SiO_2

Although the fillers affect some properties of silicone rubber, others are characteristic of the polymer itself. These properties are common to all the various stocks and require no special development. The most important are resistance to change when exposed to heat, cold, weathering, and oils.

Most of the silicone rubber formulations tested show a remarkable degree of resistance to all of these conditions. The Silastic stocks used in the stability tests were molded in a press at 500 pounds per square inch pressure and 260° F. for 5 minutes. The Silastic was then cured for 4 hours at 482° F. in a circulating air oven. The test strips and dumbbells were cut from these cured sheets. The test strips were approximately 4 inches long and 0.125 inch thick.

RESISTANCE TO HEAT

The most significant characteristic of a silicone rubber is its retention of properties after exposure to heat. Tests were run at elevated temperatures to determine the maximum temperature at which Silastic could be considered to be stable for extended periods.

Test samples were aged in circulating air ovens held at 302°, 392°, or 482° F. At intervals the samples were removed and tested for weight loss, shrinkage, hardness (*3*), and flexibility. The tests were discontinued only when the samples could no longer be flexed about 60° without breaking.

After 50-day heating at 302° F., all the Silastic samples were still flexible enough to be bent 180° without cracking or breaking. The average weight loss of three representative formulations was 2.5%. The average shrinkage was 1.7%. The increase in hardness, as measured with the Shore A durometer, averaged 15 points. Tests are being continued on these samples.

A commercial GR-M stock, specially compounded for heat and oil resistance, was used as a basis of comparison of the stability of Silastic with that of more conventional elastomers. This same

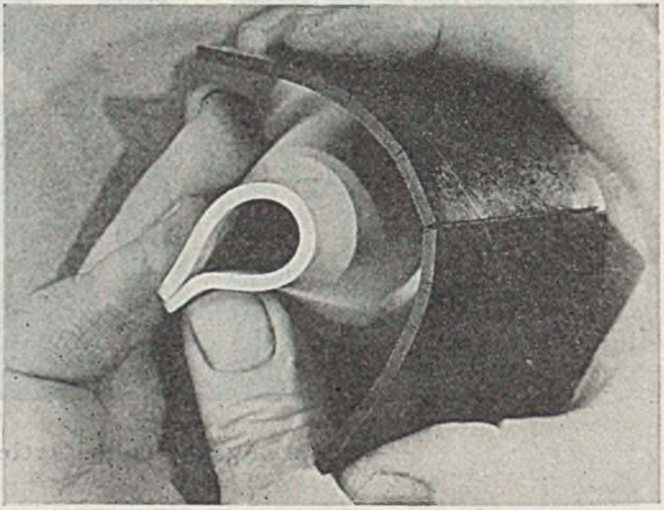

Figure 1. Silastic (*left*) after 90 Days and GR-M (*right*) after 1 Day at 300° F.

GR-M stock was used throughout the entire series of exposure tests. GR-M was exposed along with the Silastic samples at 302° F. and tested in the same way. Figure 1 shows the sample of GR-M being bent after 1-day exposure. The white sample is Silastic 160 exposed to 302° F. for 90 days. The organic rubber has cracked badly, while the silicone rubber is withstanding a much more severe bend with no visible effect. Figure 2 shows graphically the weight loss of three Silastic stocks and the GR-M stock. The weight loss of the GR-M in 1 day is twice the maximum weight loss of any of the Silastic samples after 75 days. All the Silastic stocks have approximately the same weight loss in spite of the difference in fillers. This indicates that weight loss is independent of the filler and is the result only of slight decomposition of the polymer.

Figure 3 shows the change in Shore A hardness on aging at 302° F. The silica- and titania-filled Silastic 180 increases least in hardness, evidently because its original hardness was greater and, therefore, nearer the top of the Shore scale. All stocks follow the same general pattern of hardness increase. The original durometer reading of Silastic 160 and GR-M were about equal. At the indicated rate of hardness increase, however, almost 4 months would be needed for Silastic 160 to reach the same durometer reading attained by GR-M in 1 day.

After 50-day heating at 392° F., all of the Silastic samples were still flexible enough to be bent 180° without cracking or breaking. The average weight loss was 6.3% and the shrinkage was 4.0%. The increase in hardness averaged 23 points.

At 482° F. the Silastic samples failed the flexing test at 50 days, the 42-day inspection showing no failure. The weight loss was 11.0%, the shrinkage 7.1%, and the hardness increase 29 points.

Since all present Silastic stocks contain the same polymer and since the changes in properties on aging at elevated temperatures are evidently independent of the type of filler used, the behavior can be said to be characteristic of all present Silastic stocks. In general, silicone rubbers can successfully withstand considerably higher temperatures than other natural or synthetic heat-resistant rubber formulations. These tests indicate the usefulness of Silastic for long periods at temperatures above 302° F. (150° C.) which is well beyond the useful range of other heat-resistant rubber formulations. At temperatures near 392° F. (200° C.) a 3–6 month life can be expected for a silicone rubber. A temperature of 482° F. (250° C.) would cause failure in 1 to 2 months. These predictions are based on data obtained from aging test samples in circulating air ovens. Actual service life depends, to a great extent, on the conditions of exposure and the physical requirements of the rubber. In less extreme service conditions, where the rubber is protected, the life of the silicone rubber would be considerably longer.

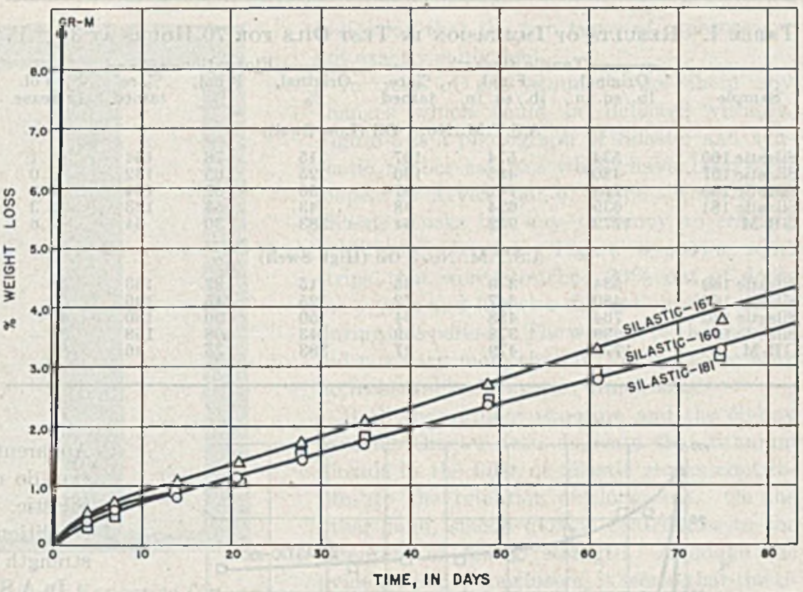

Figure 2. Weight Loss of Silastic and GR-M after Oven Aging at 300° F.

LOW TEMPERATURE BEHAVIOR

The same Silastic formulations were tested at temperatures from +32° to −100° F. (0° to −73° C.) for brittleness (*5*) and hardness change as measured on the Shore durometer. Temperatures were obtained in a machine which recirculated air through solid carbon dioxide. Specified temperatures were maintained within ±2° F. throughout the entire range.

In the brittleness test, standard tensile dumbbell specimens were exposed to low temperatures for 5 hours and were then bent double in a prescribed manner; any fracture or cracking was noted. Two samples of each stock tested were used at each temperature, and both samples had to show no signs of failure to pass the test. Brittle points of three commercial types at intervals of 10° F. follow: Silastic 167, −80° F.; Silastic 180, −90° F.; Silastic 181, −80° F. Evidently the kind of filler has little influence on the brittle points of Silastic stocks. The conclusion is that low temperature flexibility, like the high temperature behavior, is an inherent property of Silastic.

Several samples exposed to the lowest temperature at which it was possible to flex them were tested for such properties as tensile strength (*1*), elongation, and hardness after return to room temperature. In all cases no change in these properties could be detected, an indication that flexure at low temperature did not harm the elastomer until the brittle point was reached.

The hardening of Silastic at low temperatures was measured by operating the Shore durometer inside the test chamber. Exposure periods at each temperature were varied to ensure that samples were at equilibrium by testing at each temperature until check readings of hardness were obtained. The time required for readings to become constant at temperatures down to −67° F. was 30 minutes. However, hardness equilibrium at lower temperatures was not reached until after 3.5 hours of exposure.

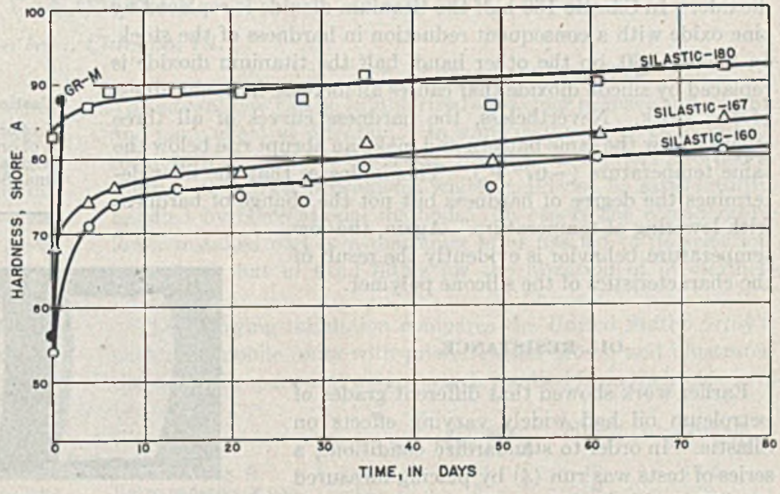

Figure 3. Effect of Oven Aging at 300° F. on Hardness of Silastic and GR-M

Table I. Results of Immersion in Test Oils for 70 Hours at 350° F.

Sample	Tensile Strength: Original, lb./sq. in.	Tensile Strength: Final, lb./sq. in.	Tensile Strength: % retained	Elongation: Original, %	Elongation: Final, %	Elongation: % retained	% Vol. Increase
A.S.T.M. No. 1 Oil (Low Swell)							
Silastic 160	534	574	107	115	178	154	6.1
Silastic 167	480	485	100	125	165	132	6.0
Silastic 180	764	741	97	50	67	134	7.2
Silastic 181	639	624	98	43	53	123	6.3
GR-M	1772	952	54	383	130	34	2.6
A.S.T.M. No. 3 Oil (High Swell)							
Silastic 160	534	349	65	115	187	163	53
Silastic 167	480	347	72	125	245	196	55
Silastic 180	764	488	64	50	90	180	41
Silastic 181	639	378	59	43	68	158	38
GR-M	1772	479	27	383	175	46	81

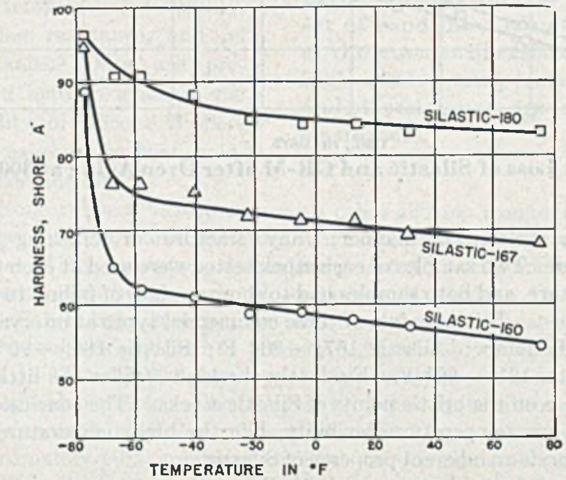

Figure 4. Effect of Low Temperature on Hardness of Silastic

After the 3.5-hour exposure at −76° F. the temperature was raised to −67° F. and held there for 1.5 hours. All samples tested at that time showed a return to the durometer readings previously obtained at this higher temperature. This indicates that equilibrium conditions had been reached during the test. Figure 4 shows the effect of low temperatures on the hardness of three Silastic stocks. The rise in hardness is very gradual as the temperature is lowered to −67° F. Below this temperature the rise is abrupt, and at −76° F. all of the formulations show durometer readings of 90 to 100 points.

It is important to observe that these hardness-temperature curves have the same slope. The filler in Silastic 167 is titanium dioxide. In Silastic 160 half the titanium dioxide is replaced by zinc oxide with a consequent reduction in hardness of the stock. In Silastic 180, on the other hand, half the titanium dioxide is replaced by silicon dioxide that causes an increase in the hardness of the stock. Nevertheless, the hardness curves of all three stocks follow the same pattern and make an abrupt rise below the same temperature (−67° F.). This indicates that the filler determines the degree of hardness but not the change of hardness with lowering of temperature. Again, the low temperature behavior is evidently the result of the characteristics of the silicone polymer.

OIL RESISTANCE

Earlier work showed that different grades of petroleum oil had widely varying effects on Silastic. In order to standardize conditions, a series of tests was run (*4*) by placing measured tensile dumbbells in a test tube of oil, heating in a controlled oven for the prescribed period of time, and then breaking the samples in a tensile tester immediately after removal and cooling. The tests were run using A.S.T.M. No. 1 (a low swell oil) and A.S.T.M. No. 3 (a high swell oil). The volume change of the stocks was determined by a water displacement method before and after exposure to the test oil. Table I summarizes the data obtained. The conditions were 70-hour immersion at 350° F., a higher temperature than is ordinarily used in testing rubber.

A.S.T.M. No. 1 oil has little effect on the tensile strength or the volume of any of these silicone rubber formulations. The maximum decrease in tensile is 15%, the maximum swell 7.2%. The elongation is actually increased by the oil immersion. Apparently the oil acts as a plasticizer. Variations in the formulation do not have a great effect on the over-all oil resistance of Silastic. The volume increase of GR-M exposed under identical conditions is lower than that of Silastic. However, the tensile strength and elongation are appreciably lowered.

In A.S.T.M. No. 3 oil the effects are more pronounced on all of the stocks tested. In general, silicone rubber formulations showed a 30 to 40% decrease in tensile strength. There was, however, 50 to 100% increase in the elongation. On the basis of the efficiency of elastic materials (tensile strength × elongation) this would more than compensate for the loss in tensile. The increase in volume, between 38 and 55%, was more than can be tolerated for some applications.

The GR-M was deteriorated to a greater extent in No. 3 oil than Silastic. Its retention of tensile strength was only 27% of the original value. Instead of increasing, elongation decreased to less than half that of the original. The volume increase also was almost twice that of Silastic.

Table I shows there is little variation in the capacity of the various Silastic stocks to resist the effects of hot oil. The titania-filled stocks retain their original properties slightly better than do the other stocks. In general, it can be said that at elevated temperature (350° F.) silicone rubber swells in oil, but to a lesser extent than do most organic rubbers. It deteriorates only slightly and does not discolor the oil.

WEATHERING RESISTANCE

Ultraviolet light, moisture, ozone, and oxygen all take part in the attack on rubber when it is exposed to weather. To determine how they affect Silastic, several samples were exposed on a

Table II. Effect of Exposure on Silastic

	12 Months Out of Doors			50 Days in Weather-Ometer	
Silastic No.	160	167	180	167	181
% of original elongation retained	81	82	71	98	68
% of original tensile strength retained	92	74	81	73	98
Original Shore hardness	51	63	76	67	80
Final Shore hardness	55	68	77	68	82

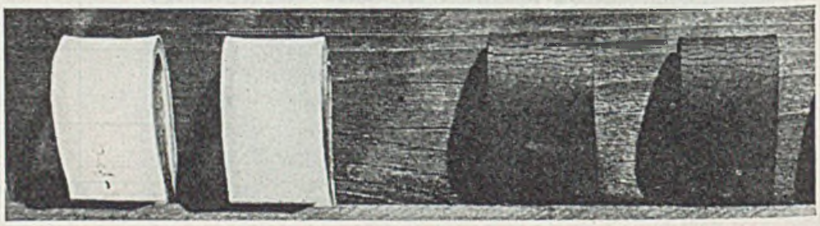

Figure 5. Silastic (*left*) and Synthetic Rubber (*right*) Samples after Outdoor Exposure for One Year

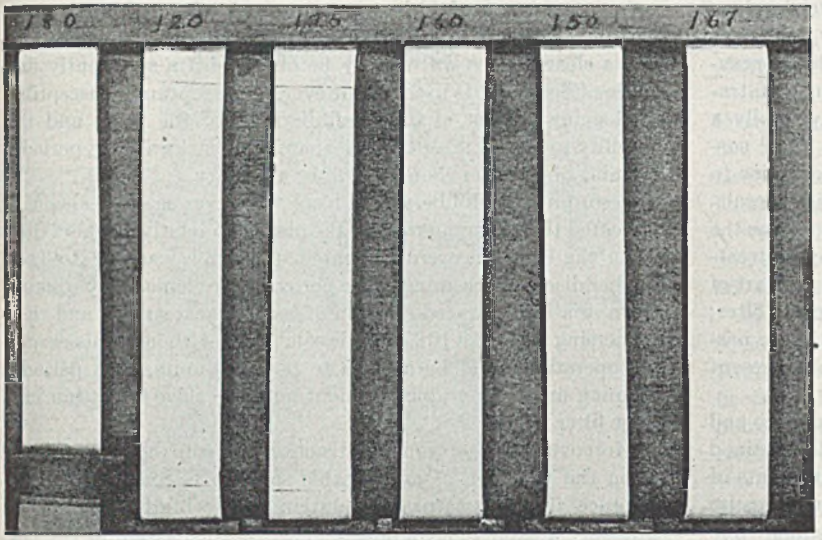

Figure 6. Stretched Silastic Samples after Outdoor Exposure for One Year

60° exposure rack facing south at Midland, Mich. Some other samples were placed in an Atlas single-arc Weather-Ometer designed to intensify the conditions of moisture and ultraviolet light encountered in outdoor weathering. A.S.T.M. procedure (*2*) was followed in testing flexed pieces and stretched pieces of Silastic. Flat moldings for use in tensile testing were exposed at the same time.

Table II shows the effects of outdoor exposure on Silastic. Both tensile strength and elongation are somewhat reduced, while durometer values increase only slightly. Table II also shows that the effects of 50-day Weather-Ometer aging on tensile strength and elongation are of the same order of magnitude as those obtained in a year of outdoor exposure. However, the Weather-Ometer aging had little effect on durometer hardness, an indication that the two types of exposure are not exactly equivalent.

In none of the samples were there any changes which could be detected visually. Figure 5 is a photograph of Silastic and synthetic rubber samples which have been held looped for a year out of doors. None of the Silastic stocks has any tendency to crack if held under tension. Figure 6 shows some strips that were stretched 20% out of doors for a year and likewise did not check or crack during this period. The weights of the samples did not vary more than 0.1%, and there were no measurable changes in dimensions.

Both the outdoor exposure and the 50-day Weather-Ometer tests indicate that titanium dioxide in the filler of Silastic stocks contributes to the retention of elongation. On the other hand, silicon dioxide contributes to the retention of tensile strength. Although the evidence is not conclusive, it seems that the titania-filled stocks have slightly better over-all weather stability than the silica-filled stocks.

These tests are being continued at Midland and any further changes will be recorded every 6 months.

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RECEIVED June 10, 1947. Presented before the Spring Meeting of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, Cleveland, Ohio, 1947.

Industrial Applications of Diatomite Filters

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Diatomite filters are finding wide industrial application because of the advantages of saving in space and weight and more effective filtration. Operating rates as high as 8 gallons per minute per square foot can be employed, and, as precoagulation is not required, sparkling-clear filtrate can be obtained in handling many aqueous or nonaqueous solutions. Operating costs are higher than the cost of sand filtration, but there are many cases where over-all evaluation favors installation of diatomite filters when the installed cost and the space requirements are taken into consideration.

DIATOMITE filters, like many other new or improved types of industrial equipment, were given their first tests on the battle fronts of World War II. It was these tests that brought out the many advantages of diatomite filters which are as important in many respects to industry as to the armed forces. The advantages can be summarized as savings in space and weight and more effective filtration. In some instances, as cited in test results which are later discussed, the diatomite filters afforded a solution to filtration problems which could not be satisfactorily handled by conventional methods. In others the considerably lower installed cost of a diatomite filter has led to its selection instead of that of sand filters for the filtration of preclarified water.

The following tabulation compares the United States Army's pack and mobile units with pressure sand filters, and illustrates the saving in space and weight which resulted from their use:

	Pack Unit	Pressure Sand Filter	Mobile Unit	Pressure Sand Filter
Filter area, sq. ft.	3.6	7.1	10	19.6
Rated capacity, g.p.m.	15	15	50	50
Weight, lb.	30	2860	350	8050
Diameter, in.	8	36	18	60
Over-all height, in.	22	73	30	82
Floor space, in.	10 × 10	37 × 49	24 × 24	61 × 78

In addition to the fact that the saving in space and weight alone would justify the use of diatomite filters, an equally important benefit is derived from their use in that chlorine-resistant organisms are removed, as are all suspended solids, by means of filtration through diatomaceous earth. A sand filter is virtually a strainer which will catch only particles of silt and other suspended matter unless the water is properly coagulated prior to filtration. The accumulation of coagulum or floc particles resulting from precoagulation forms a gelatinous mat which retains the mud, bacteria, etc., removed by the filter. The proper pretreatment of the water required considerable technique on the part of the operator, as an excessive amount of coagulum will clog a filter; whereas the formation of an exceedingly fine floc will cause passage of some of the floc and the contaminating substances present in the raw water through the filter (*5*).

Whereas a sand filter requires an operator with experience and knowledge of filter operations, excellent filtration is obtained through the use of diatomite filters even when no refinements of coagulation technique are employed in the pretreatment, because the diatomaceous earth forms a porous cake with exceedingly fine openings. It thereby filters out considerably smaller impurities than could be removed with a sand filter.

Black and Spaulding (*1*) reported that, in a series of sixty-three filter cycles, the diatomite filtered water after coagulation and settling could be expected to approximate the United States Public Health Service standard, even though chlorination was not employed. It was further found that, while rapid sand filtration failed to remove cysts of *Endamoeba histolytica*, diatomite filters effected virtually complete removal of cysts under most severe tests. United States Army Engineers reported that the diatomaceous earth filters removed not only cysts of amoebic dysentery but also the cercariae of schistosomia (blood flukes) which were prevalent in Philippine waters. These advantages led to the adoption of the diatomite filter as the standard for the pack and mobile purification units of the United States Army.

TYPES OF DIATOMITE FILTERS

Several types of diatomite filters are being manufactured, the primary difference among them being in the construction of the filter elements. Diatomaceous earth requires a permeable base to support the filter cake. Although many materials are suitable for this purpose, including porous paper filter pads, filter cloths, wire screens, wire-wound tubes, porous stones, and rubber tubes, the material differ with respect to durability, response to backwash, and liability to plugging.

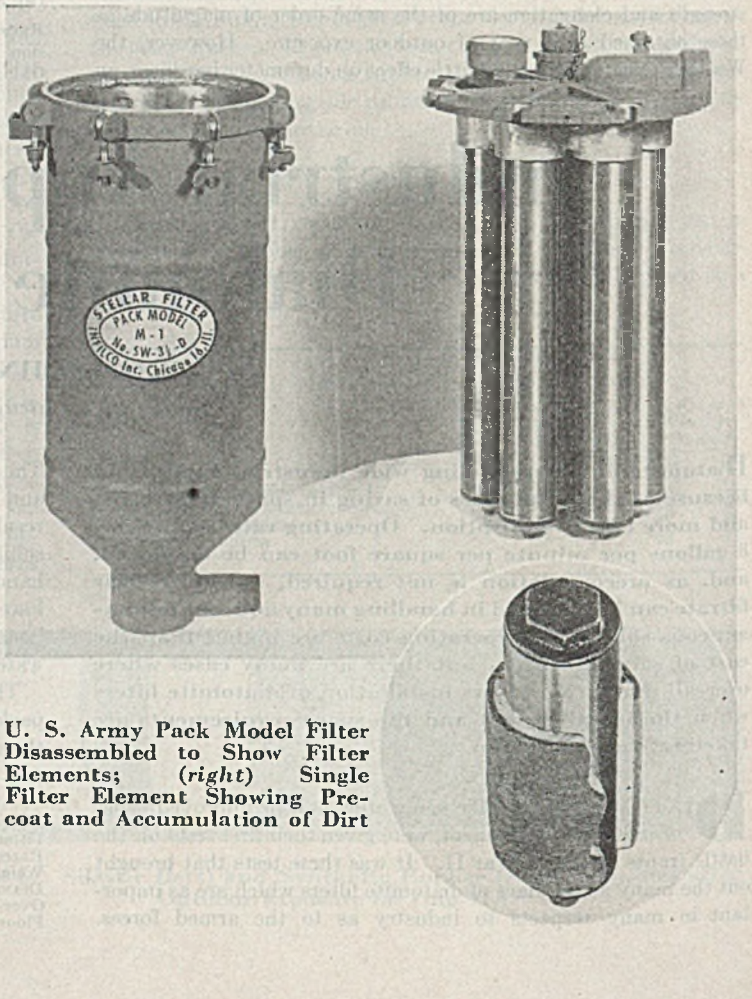
The helically wire-wound elements and the porous refractory elements were found to be the most satisfactory for the mobile units. The former were used in the purification units of the United States and British Armies and the latter in United States Navy units. The wire-wound elements used by the British Army consisted of a wire winding over a fluted hollow metal core, whereas the units used by the American Army utilized plastic for the core of the elements to reduce weight further. The wire-wound elements had a spacing of 0.0027 inch between the wires, and the fact that the space opened rapidly from this minimum in both directions made it practically impossible for anything to lodge between the wires. A further advantage of this construction is the fact that no backwash is necessary with wire-wound elements except to flush out the spent diatomite. Moreover, as the elements have smooth surfaces with relatively wide spacing between the wires, plugging of the elements is a remote possibility.

Any porous and rigid base or septum satisfactory for the support of the diatomite will be effective for the filtration operation, and a clear filtrate will usually be obtained if a sufficiently fine grade of diatomite is used. However, if the septum is susceptible to clogging because of the small diameter of the pores and the inability to clean the septum adequately by backwashing, periodic cleaning of the filter elements will be necessary.

According to Hollberg (*4*), tests with porous stone elements indicated that clogging would take place in a relatively short time when the elements were precoated using raw water. Hollberg further discussed cleaning of the porous stone elements by soaking them in a concentrated solution of sodium acid sulfate and then immersing them in a 10% caustic solution. Although this cleansing operation could be applied to portable units, such periodic cleaning might be an inconvenient and expensive operation in a large filter plant.

Moreover, the septum construction is even more important when the filtration of an unstable solution is considered. For instance, if a supersaturated solution were being filtered, a considerably greater tendency would exist for deposition in the fine pores of a porous stone element than in the wire-wound element. In any event, unless it would be possible to run long term pilot tests with a liquid which was considered as being unstable, it would be advisable to make provisions for a periodic cleaning of the filter elements.

TYPICAL FILTER. Figure 1 illustrates a typical diatomite filter. The filter shell which houses the elements is usually of plastic or glass in the smaller sizes. In larger sizes the shell is of steel or other metal, depending on the character of the liquid to be filtered, and an observation port is provided so that formation of the filter cake can be observed. The elements are mounted vertically on a removable plate and are inserted as a unit in the filter shell. The usual inlet, outlet, drain, and rewash connections are provided



U. S. Army Pack Model Filter Disassembled to Show Filter Elements; (*right*) Single Filter Element Showing Precoat and Accumulation of Dirt

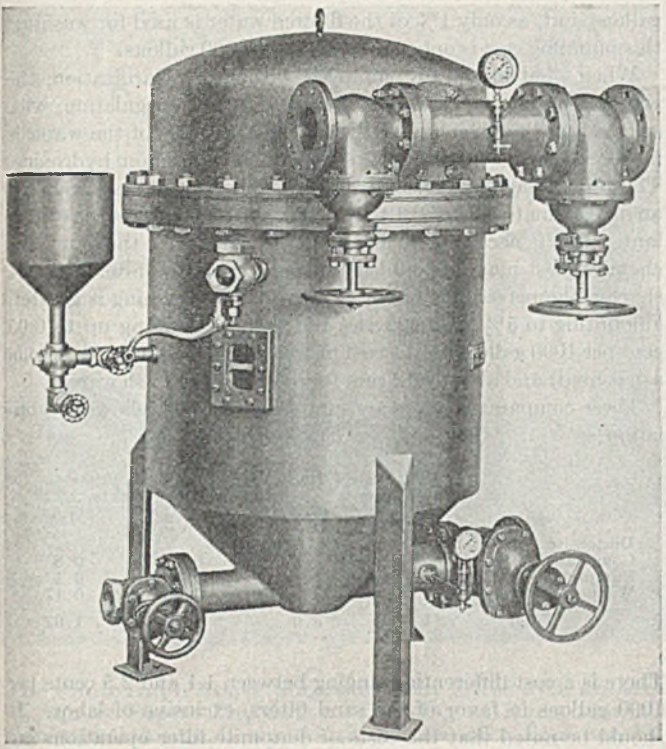


Figure 1. Large Filter with Area of 80 Square Feet

with a backwash release valve in place of a wash valve on a sand filter. The filter is backwashed by releasing the pressure in the shell by opening this valve; this pressure release reverses the flow for about 30 seconds and cleans the elements. The spent diatomite settles in the conical bottom of the tank, from which it can be conveniently drained. The diatomite for the new precoat is added as slurry through the diatomite charger attached to the side of the tank. The raw liquor is then added through the inlet at the bottom of the tank, the liquid and filter aid being forced upward around the elements. The precoat develops within a few seconds, and, after a short period of filtering to waste or recirculating the filtrate, a sparkling clear filtrate is obtained.

SELECTION OF FILTER AID

Elsenbast and Morris (*2*) tabulated the following particle sizes for Celite 503 and Filter-Cel:

Particle Size, Microns	Celite 503, %	Filter-Cel, %
>40	12.0	2.5
40–20	25.5	8.0
20–10	33.5	14.0
10–6	22.0	19.0
6–2	21.5	37.5
<2	1.5	19.0

With a spacing between the wires of 0.0027 inch, or about 69 microns, the individual diatomite particles are not held back by the septum, but rather the septum supports an interlaced mat of thousands of particles over each opening. Although a certain amount of diatomite passes through the element before the filter cake is formed, no further passage of diatomite through the septum is apparent during the operating run.

The selection of the optimum grade of filter aid for a filtration problem must usually be decided by experiment. The size of the particles determines the flow rate under a given set of conditions, but, as the particle size also determines the clarity of the filtrate in many instances, it is necessary to select as "fast" a filter aid as will produce a clear filtrate under all conditions. The Johns-Manville Corporation and The Dicalite Company manufacture a variety of grades of diatomite, and it is generally a relatively simple matter to select the filter aid best suited to a particular filtration problem.

In some instances, where a liquor having a high pH is to be filtered, and where silica contamination is to be avoided, a purified wood cellulose can be used to advantage as a filter aid. The Brown Company offers a series of grades of a purified wood cellulose from which all lignin, ash, and chemical salts have been removed. This has been used to advantage in the filtration of dilute caustic soda solutions. Asbestos powder is also used to advantage in some applications.

In filtration of pretreated water, a precoat of 0.5 to 1 ounce per square foot of filter area is usually used. As the water is relatively clear prior to filtration, and as the suspended particles are flocculated, the accumulated suspended matter is sufficiently porous to permit long filter runs without an excessively rapid increase in pressure drop through the filter. On the other hand, if the suspended solids are exceedingly fine, or if they tend to form an impervious mat over the precoat, it is necessary to feed diatomite continuously. By this means a porous cake is deposited on the precoat; this results in a less rapid increase in pressure drop and, consequently, in longer filter runs. In cases where continuous diatomite feed is employed, the dosage will approximate a total of 3 ounces per square foot; but this will vary, depending upon the characteristics of the suspended matter in the water.

COMPARISON OF COSTS

The amount of filtrate obtained per filter run and the amount of filter aid required depend upon the nature and the amount of solids in the water to be filtered:

Influent Turbidity, P.P.M.	Diatomite, Lb./1000 Gal.	Approx. Cost/ 1000 Gal., Cents
2–3	0.04	0.2
10	0.1–0.2	0.5–1.0
50	0.25–0.5	1.25–2.5

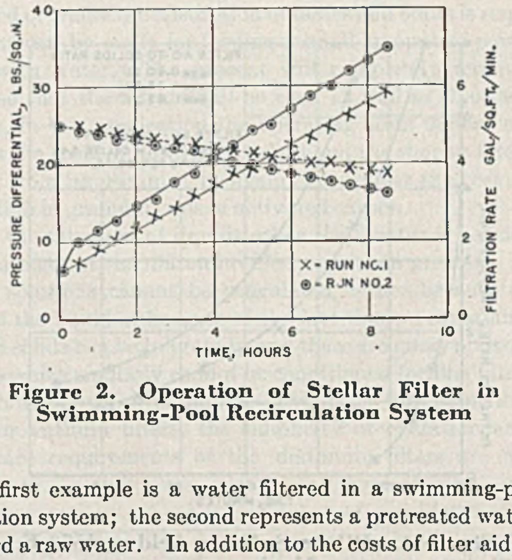


Figure 2. Operation of Stellar Filter in Swimming-Pool Recirculation System

The first example is a water filtered in a swimming-pool recirculation system; the second represents a pretreated water, and the third a raw water. In addition to the costs of filter aid, power consumption for pumping is an important consideration. The accompanying graphs show that the pressure drop through the filter depends upon the filter aid, the characteristics of the liquid, and the operating rate. When pretreated water is being filtered, the average pressure drop is about 25 pounds per square inch, with a maximum of 50 pounds per square inch, although the latter depends, within limits, upon the length of run desired.

Figuring on the basis of a maximum head loss of 50 pounds per square inch, the power required for pumping 1000 gallons is approximately 0.56 kilowatt, based on an over-all pump and motor efficiency of 65%. Assuming 2 cents per kilowatt-hour for power,

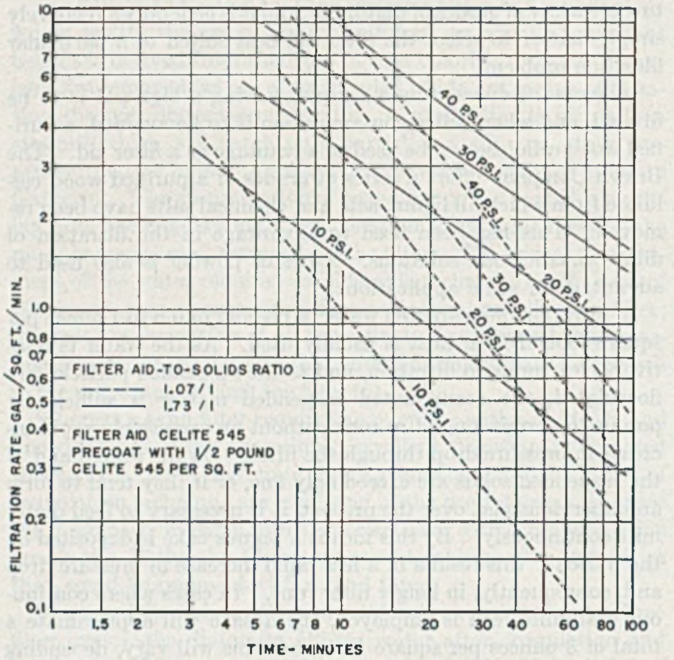


Figure 3. Dilute Sulfuric Acid at 157° F. Maximum

the pumping cost will be about 1.1 cents per 1000 gallons, an over-all cost ranging from 1.3 to 3.6 cents per 1000 gallons, depending on the water characteristics and predicated on a power cost of 2 cents per kilowatt-hour. Contrasting these costs with the costs of sand filter operations, the power costs are nominal as the maximum pressure drop through a sand filter is about 5 pounds per square inch, a power cost of approximately 0.1 cent per 1000 gallons. In addition, there is the cost of backwash water and, where preclarification is not employed, the cost of coagulant for pretreatment.

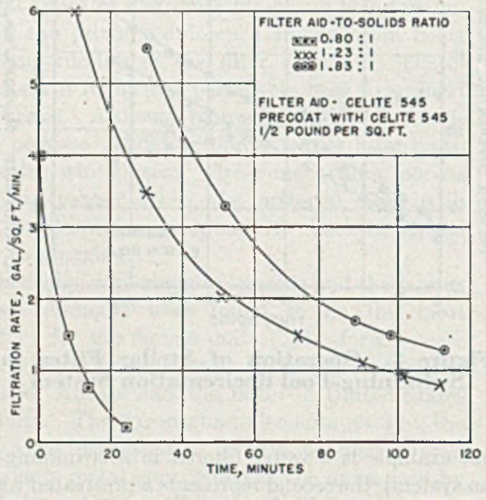


Figure 4. Dilute Sulfuric Acid at 157° F. Maximum

In a gravity filter plant where effective preclarification is maintained, filter runs of about 60 hours will be obtained when the filters are operated at a rate of 2 gallons per minute (g.p.m.) per square foot. It is customary to backwash for about 5 minutes at a rate of 15 g.p.m. per square foot, so that about 1% of the filtered water is used for backwashing the filter. The cost of this water will depend upon the pretreatment employed, but it would rarely exceed 0.03 cent per 1000 gallons based on the filtered water. The cost of pumping backwash water is about 0.25 cent per 1000 gallons, but, as only 1% of the filtered water is used for washing, this pumping cost is only 0.0025 cent per 1000 gallons.

When sand filters are employed without preclarification, the water is usually treated with alum for partial coagulation, with soda ash or lime being added when the alkalinity of the water is insufficient for the complete precipitation of aluminum hydroxide. The alum dosage will usually vary from 0.5 to 2.0 grains per gallon an approximate cost of 0.1 to 0.4 cent per 1000 gallons for coagulant. If it is necessary to add soda ash along with the alum, the chemical cost may be doubled. Moreover, as the filter runs are shorter, the percentage of water used for backwashing is greater, amounting to 5% in some cases and therefore adding up to 0.05 cent per 1000 gallons to the cost of treatment (assuming that soda ash is used) and about 0.12 cent for pumping the wash water.

These comparative costs are summarized in the following tabulation:

	Diatomite Filter, Cents		Sand Filter, Cents	
	Min.	Max.	Min.	Max.
Diatomite	0.2	2.5	..	...
Coagulant	..	..	0.1	0.8
Pumping	1.1	1.1	0.1	0.1
Wash water	..	..	0.002	0.17
Total	1.3	3.6	0.20	1.07

There is a cost differential ranging between 1.1 and 2.5 cents per 1000 gallons in favor of the sand filters, exclusive of labor. It should be noted that the costs of diatomite filter operations are based on the maximum pumping costs. If, however, two pumps, each developing a pressure of 25 pounds per square inch, were operated in series, with the second pump cut in during the last half of the filter run, the pumping costs would be reduced about 0.2 cent per 1000 gallons; this would thereby reduce the cost differential to between 1.0 and 2.3 cents per 1000 gallons.

COMPARISON OF FILTER SIZES

Diatomite filters afford considerable savings in floor space, as shown in the following table:

Capacity, G.P.M.	Diameter of Stellar Diatomite Filter[a], In.	Diameter of Vertical Pressure Filter[b], In.	Size of Gravity Filter[c], Ft.
100	20	78	8[d]
200	28	120	10 × 10
300	36	2-96	10 × 15
400	42	2-120	14 × 15

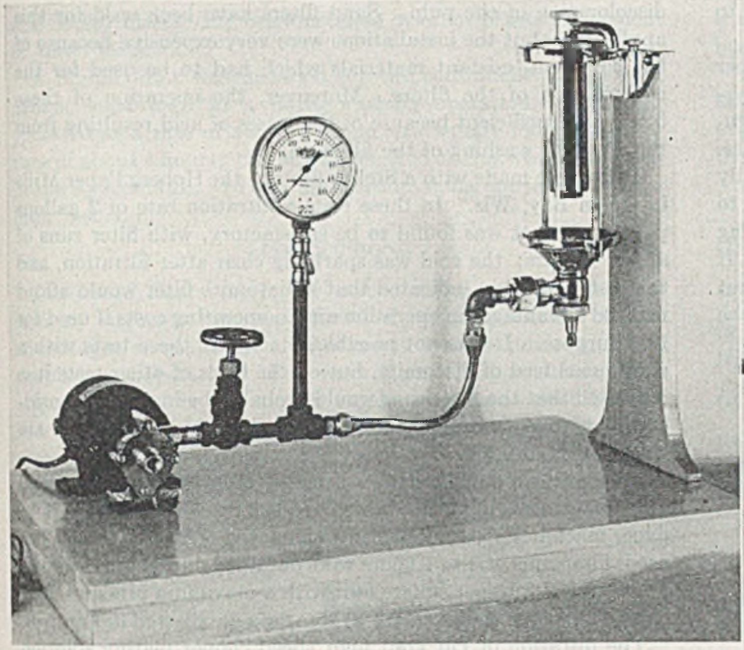
[a] Rate, 4 gallons per square foot per minute.
[b] Rate, 3 gallons per square foot per minute.
[c] Rate, 2 gallons per square foot per minute.
[d] Diameter.

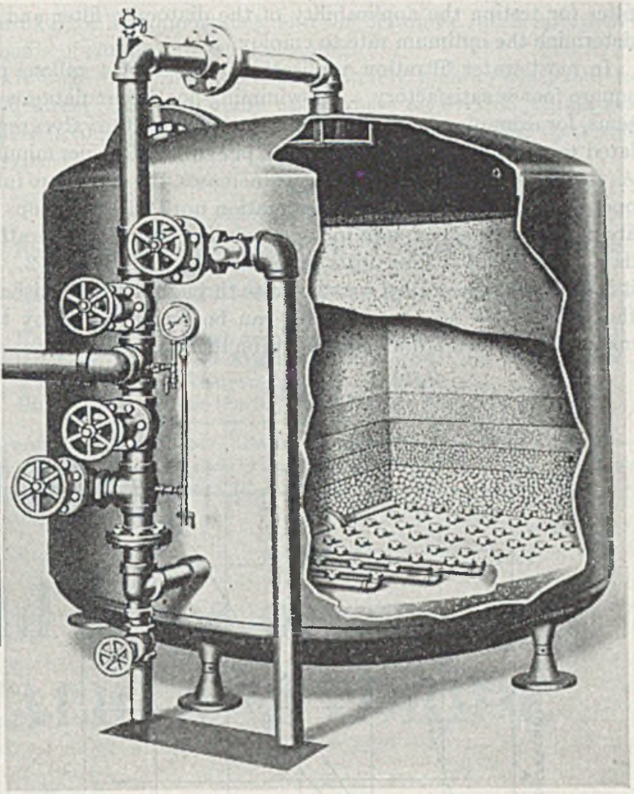
The pressure filters are rated at a rate of 3 g.p.m. per square foot and the gravity filter 2 g.p.m. per square foot., although both types of filters can be operated at a rate of 3 g.p.m. per square foot. However, as most state boards of health insist on the filtration of drinking supplies at the rate 2 g.p.m. per square foot, the relative sizes of the filters for the two rates have been included. In this regard it should be noted that many boards of health have approved the diatomite filters at a filtration rate of 4 g.p.m. per square foot or greater.

In view of the space saving made possible by the diatomite filters, it will be possible for many industrial plants to enlarge their water treatment facilities even though the space available would not permit installation of conventional sand filters.

INSTALLATION COSTS

It is difficult to estimate accurately the relative installation cost of the two types of filters in view of the variables involved. In general, the diatomite filters will cost about 10 to 15% more than pressure sand filters for a given capacity. However, when the cost of the land and the building to house the filters is evaluated,





The Photograph Above Shows a Small Filter with an Area of 1/8 Square Foot. The Cutway Drawing at Right Shows the Construction and General Appearance of a Pressure Filter

the installed cost of the diatomite filter will be 30 to 50% less than that of the sand filters. Because of this saving, there are several large diatomite filters being installed in the following places:

Location	Capacity, Gal./Hr.
Yankton, S. Dak.	75,000
Univ. of Fla., Gainesville, Fla.	60,000
Nacogdoches, Tex.	48,000
Mounds, Ill.	48,000
Highland, Ill.	38,400
Hoffman-LaRoche, Nutley, N. J.	36,000

DIATOMITE FILTER APPLICATIONS

One of the most important advantages of the diatomite filters for the Army and Navy was the removal of amoebic cysts and blood fluke larvae. Although these organisms are not widely prevalent in the United States, the Pacific Northwest and certain regions in Canada are troubled with the infestation of their water systems with blood worms or Chironomus larvae. Harrington (*3*) reported troubles at the Montreal water-treating plant with the larvae burrowing through the sand filter beds. Although these larvae are killed by pressure in the mains, they are objectionable in the water supply. The diatomite filters will provide a positive means for removal of these organisms. A large food-processing plant in Washington is now installing a water-conditioning plant with diatomite filters to ensure production of a clear uncontaminated process water.

In the filtration of condensate, cooling water, and recirculated process water, where the removal of a small amount of oil may be involved, the diatomite filters will produce an oil-free effluent when oil-adsorbent filter aids are employed. Johns-Manville Sorbocel will adsorb about 1 pound of oil per pound of filter aid and will produce an oil-free effluent, provided that the contamination is not excessive. For example, 50 parts per million of oil were removed completely by a Stellar filter operating at a rate of 3 g.p.m. per square foot at the Roseland pumping station in Chicago, Ill.

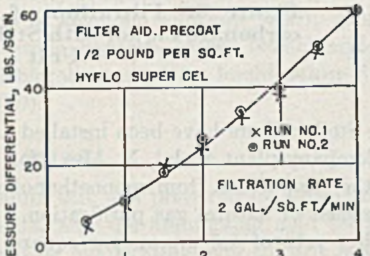


Figure 5. Filtration of Sulfite Cooking Acid

In cases where filtration and dechlorination of water supply are considered or where the adsorption of tastes and odors is required, provisions can be made for feeding a small amount of powdered carbon with water. The precoat will completely remove the carbon, so that the filtrate will be clear as well as chlorine-free. However, in this application the operating costs require careful study, as the costs of powdered carbon and the shorter filter runs resulting from its use must be evaluated against the cost of dechlorination in granular beds of activated carbon.

When the filtration of liquids other than water is considered, the advantages of the diatomite filters are even greater. Many aqueous solutions cannot be coagulated, either because of the nature of the liquid or because of the fact that no contaminating dissolved solids can be tolerated; and there are many nonaqueous solutions which similarly cannot be conditioned for fine filtration. Although these types of liquids have been filtered with filter presses or vacuum filters, the simplicity of operation and the small space requirements of the diatomite filters are advantageous and worthy of consideration.

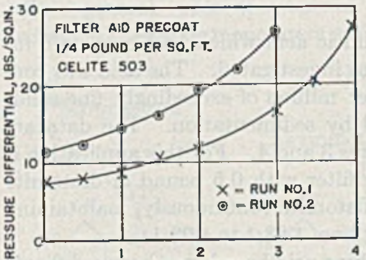


Figure 6. Filtration of Process Water

FILTRATION RATES

It is difficult to predict beforehand the rate at which a diatomite filter can be operated, because of variations in the nature of the suspended matter. It is therefore advantageous to use a small filter for testing the applicability of the diatomite filter and to determine the optimum rate to employ.

In most water filtration applications, a rate of 4 gallons per square foot is satisfactory. In swimming-pool recirculation systems, for example, the filter runs are started with the valves regulated to maintain a rate of 5 gallons per square foot per minute. As the pressure drop across the filter increases, the valves are fully opened, the filter being kept in operation until the rate drops to about 3 gallons per square foot per minute. Typical operating data from a Stellar filter installation are shown in Figure 2. If it is desired to maintain a constant rate through the filter without the attention of an operator, this can be accomplished by the installation of rate-of-flow controllers on the filter outlet.

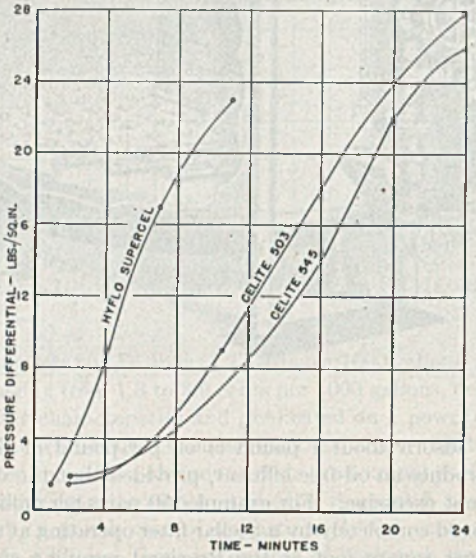


Figure 7. Filtration of Magnesium Bicarbonate Liquor

The wire-wound filter elements have been extensively used in England for process liquor filtration. The recommended filtration rates for various liquids are as follows:

Solution	Rate, Gal./Sq. Ft./1 Min.
Plating solutions	2.0
Beer	0.3
Varnish	0.2
Transformer oil	0.4
Cider	1.2

Although most of these rates are relatively low, primary advantages of the diatomite over the other types of filters were found to be ease of operation due to the short time required for cleaning the filter and the almost complete absence of liquor losses in the filter operation. For example, in the filtration of cider the time required to place the filter in operation was cut from 15 minutes to 30 seconds, and the wash losses were reduced from 8% to practically nothing. These tests were conducted by Lorna Doone Cider Vintage, Ltd., comparing the Stellar filter with a Seitz-Werke filter.

The filtration of dilute sulfuric acid which had been used for leaching minerals from ore was investigated. The acid was contaminated with 300 parts per million of exceedingly fine solids which could not be removed by sedimentation. The data are expressed graphically in Figures 3 and 4. For this application it was necessary to precoat the filter with 0.5 pound of diatomite per square foot and to feed diatomite continuously, maintaining a filter aid-solids rate ranging from 1.83:1 to 1.23:1.

The filtration of sulfate cooking acid has always been a difficult problem. The acid is contaminated with calcium sulfate and iron oxide scale which cause deposition in the system and partial discoloration of the pulp. Sand filters have been used for this application, but the installations were very expensive because of the corrosion-resistant materials which had to be used for the construction of the filters. Moreover, the operation of these filters was inefficient because of the losses of acid resulting from the frequent washing of the filters.

Tests were made with a Stellar filter at the Hoberg Paper Mills in Green Bay, Wis. In these tests a filtration rate of 2 gallons per square foot was found to be satisfactory, with filter runs of about 4 hours; the acid was sparkling clear after filtration, and the tests definitely indicated that a diatomite filter would afford marked advantages in operation and in operating costs if used for this purpose. It was not possible to conduct these tests with a continuous feed of diatomite, but on the basis of other tests it is indicated that the filter runs would probably be increased considerably with a continuous feed. Test data from two runs are shown in Figure 5.

Test runs were made with a process water containing a small amount of organic matter which tended to clog the showers in paper machines. Although continuous feed of diatomite was not used, filter runs of 3 to 4 hours were obtained during operation at a rate of 8 g.p.m. per square foot with a maximum pressure drop of 28 pounds per square inch. These data are plotted in Figure 6.

The filtration of Du Pont high speed copper plating solution indicated that Filterbestos was the most satisfactory filter aid. The tests indicated that an average rate of 2 to 3 g.p.m. per square foot could be maintained for 4 hours with a pressure drop of 20 pounds per square inch. The filter aid dosage required was 0.5 pound per square foot.

The filtration of a magnesium bicarbonate liquor with a Stellar filter indicated that a rate of 3.04 gallons per square foot per minute could be maintained, with a yield of 86 gallons of filtrate per square foot. By way of contrast, filter presses operating under the same conditions produced about 123 gallons per square foot at an operating rate of 0.256 g.p.m. per square foot. Hence, appreciable time was saved in the filtration operation, and the labor required to put the filter into operation for succeeding runs was reduced appreciably. The filtration characteristics of this solution are shown in Figures 7 and 8.

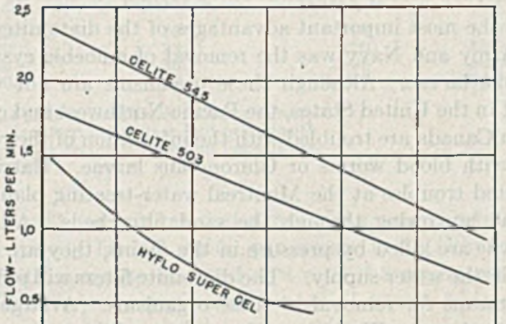


Figure 8. Filtration of Magnesium Bicarbonate Liquor with Stellar Experimental Unit

Stellar filters have been installed at the El Paso Natural Gas Company plant at Jal, N. Mex., for filtering ferrous sulfide and other impurities from monoethanolamine used in the Girbotol process of natural gas purification. Tests runs indicate that a filter rate of 1.5 g.p.m. per square foot could be maintained. Similar tests made at their Eunice, N. Mex., plant indicated that a rating of 0.5 g.p.m. per square foot was necesssary because of a difference in quantity and nature of the suspended solids. Several Stellar filters have been installed at other plants subsequent to these tests.

A Stellar filter was installed for the continuous filtration of caustic soda used in a bottle-washing operation. The filter operated at a rate of about 4 g.p.m. per square foot with filter runs of about 4 hours; thereby the desired clarity was maintained in the soaker tank. In this application alpha floc is used as the filter media.

CONCLUSIONS

Diatomite filters merit the consideration of chemical and sanitary engineers for many filtration problems because of their advantages of quality of effluent, small space requirements, and simplicity of operation. For water filtration applications diatomite filters can be practically employed without prohibitively short filter runs, if the suspended matter in the water does not exceed about 200 parts per million. With other liquids, which may be difficult to filter by any means, the length of operating run is usually of less importance, and the diatomite filters afford the benefits of simple and rapid cleaning.

Although operating costs are relatively high as compared to sand filters, there are many cases where an over-all evaluation proves favorable to diatomite filters when the installed costs and the space requirements are taken into consideration.

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Received February 7, 1947. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Ill.

Reactions and Uses of TETRACHLOROPHTHALIC ANHYDRIDE

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An extensive search of the literature on the chemical reactions and applications of tetrachlorophthalic anhydride has been made, and a review of the subject is given here. The material is treated in sections based, in the main, on the class of compounds involved. It is evident from the data presented in this review, that tetrachlorophthalic anhydride is a versatile intermediate and, since it is now commercially available, will find even more extensive use. In many of the reactions described, the yields are exceptionally good, probably because of the absence of replaceable hydrogen, thereby limiting side reactions. Active research is in progress on applications of the anhydride in many fields and should result in greatly extending the available literature on the subject.

TETRACHLOROPHTHALIC anhydride was first prepared by Graebe in 1868 (*34*). Some of its properties which have been studied by a number of workers (*15, 35, 59, 126*) include, for example, melting point, 254.9° ± 0.2° C. (*15, 59*); hydration of the anhydride to acid and its solubility at various temperatures and in the presence of inorganic acid (*15, 59*); boiling point at atmospheric pressure, 366° C. (*59*); density of solid anhydride at 20° C., 1.92 (*59*); conductivity of aqueous solutions at various temperatures (*118, 119*) and of alcoholic solutions (*120*); solubility of the anhydride in acetone, benzene, carbon tetrachloride, monochlorobenzene, and dichlorobenzene (*59*), liquid sulfur dioxide and liquid ammonia (*10*).

SALTS

A solution of the ammonium salt was prepared by dissolving the acid in aqueous ammonia, and the ammonium acid tetrachlorophthalate was obtained by evaporating over sulfuric acid. Upon addition of a solution of lead acetate or silver nitrate to the ammonium salt solution, the lead or silver salt was precipitated (*34*). By addition of a solution containing barium, cupric, or zinc ions, the corresponding slightly soluble metal salts were prepared (*35*). In a similar way the basic scandium salt was obtained and used to prepare scandia free from traces of yttrium and ytterbium (*13*). The sodium and potassium salts were made by neutralizing the acid or anhydride with the alkali hydroxide (*59*). The potassium salt was also formed when an alcoholic solution of the acid was treated with alcoholic potassium hydroxide (*85*). The solubilities of the sodium and potassium salts at various temperatures have been determined (*59*). The addition of solutions containing aluminum, calcium, cupric, or zinc ions to the neutral sodium salt solution resulted in the precipitation of the metal salt (*59*).

The sodium and potassium acid salt could not be obtained; instead there was formed the sparingly soluble "acid double salts" containing a mole of acid per mole of acid salt (*59*).

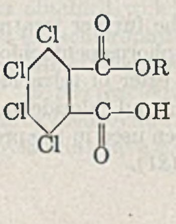
The aniline salt was prepared and used as an intermediate in the synthesis of *N*-phenyltetrachlorophthalimide (*38*).

The use of the normal salt of tetrachlorophthalic acid in treating animal fibers was proposed (*100*). The silver salt (*35, 68*) and the sodium salt (*16, 64*) were used in making the neutral esters by reaction with an appropriate organic halide.

ESTERS

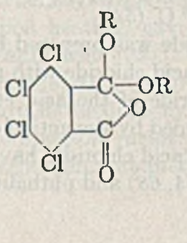
Two general types of esters of tetrachlorophthalic acid are formed—the acid or monoesters and the neutral or diesters:

MONOESTER

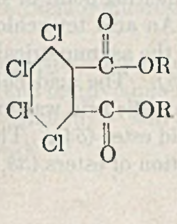


DIESTER

Asymmetrical



Symmetrical



The acid esters of methyl, ethyl (*35, 69*), *d*-amyl, isoamyl (*65*), and benzyl alcohols (*68, 104*) have been formed by direct esterification. Even at room temperature and without a catalyst, the acid esters were obtained (*59, 120*). No diester resulted from these reactions (*69, 99*). The acid esters of several primary alcohols of the neopentyl type were thus prepared for use as derivatives in identifying the alcohol (*96*). *tert*-Alkyl acid esters, formed by the reaction of the *tert*-alkoxy magnesium bromide with tetrachlorophthalic anhydride, were proposed as derivatives for the identification of the corresponding alcohols (*30*).

Upon being heated strongly, the acid esters yielded the alcohol and the anhydride (*35*) or, in some cases, such as the ester of benzyl carbinol, yielded the corresponding olefin (*104*). The acid ethyl ester was converted by treatment with thionyl chloride into the acid chloride ethyl ester (*54*).

Several investigators have prepared the neutral esters of tetrachlorophthalic acid by methods other than direct esterification. The dimethyl (*35*), diethyl (*35, 37*), dibenzyl, di-*p*-nitrobenzyl, and dicetyl (*68*) esters have been made using the silver salt of the acid and the appropriate organic halide. The di-*p*-phenylphenacyl (*16*) and di-*p*-nitrobenzyl esters (*64*) were derived in an analogous manner through the sodium salt.

The dimethyl, diethyl (*35*), and dibenzyl (*68*) esters resulted also from the reaction of the sodium alkylate with the acid chloride, but the yields were not high and some acid ester was also formed. The reaction was also carried out with the acid chloride and the alcohol, and in this way either the symmetrical or asymmetrical ethyl ester could be prepared (*35, 54*). The dimethyl ester was also made by the action of dimethyl sulfate on a solution of the sodium salt (*36*).

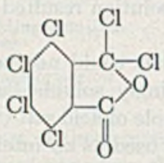
Tetrachlorophthalic acid heated with pinene and similar materials gave the dibornyl, di-isobornyl, and difenchyl esters which are useful in camphor synthesis (*25, 26, 41, 42, 51*).

A compound which was probably the di(*m*-dimethylaminophenyl) tetrachlorophthalate was formed as a by-product in the reaction of the acid with *m*-dimethylaminophenol (*6*).

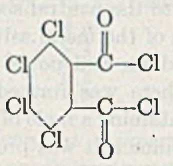
ACID CHLORIDES

Two isomeric acid chlorides of tetrachlorophthalic acid are known:

Asymmetrical



Symmetrical



The asymmetrical acid chloride, which is reported to be the stable form, has been prepared by the action of phosphorus pentachloride on the anhydride (*36, 52, 54, 81*), by the action of thionyl chloride on the anhydride in the presence of zinc chloride (*57, 58*), and by the chlorination of tetrachlorophthalide with iodine trichloride (*70*). It was once reported that the two acid chlorides had melting points of 118° and 137° C. (*52*). However, it was later shown that these were the asymmetrical acid chloride, the lower melting one differing only in having benzene of crystallization (*54*). The symmetrical acid chloride was obtained in low yield simply by rapidly distilling the asymmetrical form and extracting with petroleum ether, and was found to have a melting point of 48° C. (*54*).

An acid tetrachloride was prepared by the further treatment of the asymmetrical acid chloride with phosphorus pentachloride (*35*). The acid chloride of the acid ethyl ester of tetrachlorophthalic acid was formed by the action of thionyl chloride on the acid ester (*54*). The acid chlorides have been used in the preparation of esters (*35, 54, 68*) and phthalides (*81*).

TETRACHLOROPHTHALIMIDE AND OTHER NITROGEN COMPOUNDS

Tetrachlorophthalamidic acid in solution was prepared by heating the solution of ammonium salt and used for the synthesis of tetrachloroanthranilic acid (*111*). A number of *N*-substituted tetrachlorophthalamidic acids have been described, including the *N*-tolyl, *N*-phenyl, and *N*-β-naphthyl (*107*). They were made by alkaline hydrolysis of the corresponding imide or more readily by adding the amine to a solution of the anhydride. It is stated that the potassium and sodium salts of the *N*-phenyl derivative are colloidal and form lathers easily. These amidic acids changed readily into the corresponding imides, being converted slowly even at room temperature (*107*).

Tetrachlorophthalimide has been obtained from the anhydride by passing a stream of ammonia through the molten anhydride (*35, 40*), by warming the anhydride in formamide (*92*), and by heating a mixture of the anhydride and ammonium carbonate (*2*).

The imide was utilized in the preparation of tetrachloroanthranilic acid by the Hofmann reaction, and gave even better yields than the corresponding reaction of phthalimide (*40*). This acid was also prepared through the tetrachlorophthalamidic acid by treatment with alkali hypochlorite solution (*111*). From the tetrachloroanthranilic acid so obtained have been prepared the formyl, acetyl (*62*), formalid, and ω-cyanomethyl derivatives, and 2,3,4,5-tetrachloroaniline, the latter simply by heating the acid (*111*). Octachloroindigo was made through the monoacetyltetrachloroindoxylic acid acetate obtained from tetrachloroanthranilic acid (*83*). Octachlorothioindigo was also synthesized from tetrachloroanthranilic acid through the tetrachlorophenylthioglycolic-2-carboxylic acid (*62*).

The stability of tetrachlorophthalimide toward decomposition to form the corresponding benzonitrile was studied and found to be much greater than that of phthalimide or 4-chlorophthalimide (*67*).

Many substituted tetrachlorophthalimides are known. The *N*-phenyl derivative has been formed by heating the aniline salt of tetrachlorophthalic acid (*38*), by adding aniline to a solution of the anhydride in boiling acetic acid (*92*), or by dehydrating tetrachlorophthalophenylamidic acid, slowly at room temperature or more rapidly at higher temperature or in 50% alcohol (*107*). The *N*-*p*-hydroxyphenyl-, *N*-*p*-acetylaminophenyl-, *o*-, *m*-, and *p*-isomers of *N*-tolyl-, and *o*-, *m*-, and *p*-isomers of *N*-nitrophenyltetrachlorophthalimide were prepared by the second method. The *N*-β-naphthyl compound is also known (*107*). The corresponding derivative of ethyl *p*-aminobenzoate was prepared by the reaction of anesthesin and tetrachlorophthalic acid (*33*).

The *N*-potassium derivative, formed by the action of alcoholic potassium hydroxide on the imide, was reacted with various halogen compounds, including alkyl halides, α-halogen esters, chloroformates, halohydrins, haloketones, and haloethers, to form solid derivatives for the purpose of identification (*2*).

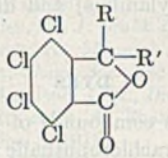
The *N*-amino derivative was prepared by reaction of the acid or the anhydride with hydrazine hydrate. Heated with further anhydride it forms octachloro-*N*-phthalimidophthalimide (*17*). By reaction of the anhydride with methyleneaminoacetonitrile, tetrachlorophthalamidoacetonitrile is obtained. The corresponding imidoacetic acid, its chloride, amide, and methyl and ethyl esters were made (*103*).

A number of hydrazine derivatives of tetrachlorophthalic anhydride were prepared, including the primary and secondary hydrazides and several salts of the latter (*90*).

Tetrachlorophthaloxime was obtained in good yield by reaction of the anhydride with hydroxylamine hydrochloride in the presence of sodium carbonate, and through its silver salt a number of oxime ethers were prepared (*91*). The oxime hydrate methyl ether was also made by the action of hydroxylamine hydrochloride in the presence of sodium methoxide (*83*). The corresponding phenylhydrazone (*91*) was obtained from phenylhydrazine and the anhydride.

TETRACHLOROPHTHALIDE AND ITS DERIVATIVES

Reduction of tetrachlorophthalic anhydride with zinc in acetic acid solution gives tetrachlorophthalide (*35*):



Catalytic reduction with hydrogen over nickel was claimed to yield the same product (*28*). The more vigorous reduction by means of hydriodic acid and phosphorus in a sealed tube resulted in the formation of tetrachloroxylylene oxide (*35*).

Numerous substituted tetrachlorophthalides have been described. When the anhydride was treated with an appropriate Grignard reagent, the dimethyl-, the monoethyl-, and a mixture of phenyl- and diphenyltetrachlorophthalides resulted (*5*). Di-*p*-bromophenyltetrachlorophthalide was similarly obtained by the action of the Grignard reagent of *p*-dibromobenzene on the anhydride (*115*).

Diphenyl- and ditolyltetrachlorophthalides have been prepared by the reaction of tetrachlorophthalyl chloride with benzene or toluene in the presence of aluminum chloride (*81*), and by the reaction of the anhydride with benzene or toluene in the presence of aluminum chloride followed by treatment with acetic anhydride (*61*). The diphenyl-, as well as the mixed phenyltolyl-, phenylphenol-, and phenylresorcinoltetrachlorophthalides were obtained by condensing the acetate of benzoyltetrachlorobenzoic acid with benzene, toluene, phenol, and resorcinol, respectively (*81*).

Many compounds of the phthalein type have been synthesized. Phenoltetrachlorophthalein was obtained in good yield by the reaction of phenol and the anhydride, some tetrachlorofluoran being formed simultaneously (*74*). Phenoltetrachlorophthalein is reported to be useful as an indicator less sensitive to carbon dioxide interference in acidimetric titrations than phenolphthalein (*74*). Studies of the light absorption spectra have been made (*31, 49, 105*). It was also proposed as a superior laxative (*71*). A large number of derivatives of phenoltetrachlorophthalein, including their nitration products, were studied (*79, 80*). Isophenoltetrachlorophthalein was obtained from the reaction of 2-hydroxybenzoyl-*o*-tetrachlorobenzoic acid with phenol (*84*). When resorcinol or pyrogallol was substituted for the phenol in the foregoing reaction, the resulting products were 3-hydroxytetrachlorofluoran or 3,4-dihydroxytetrachlorofluoran, respectively (*78*). Tetrachloro-α-naphthafluoran (*45*) was obtained from α-naphthol and the anhydride.

Resorcinol, condensed with the anhydride, yielded tetrachlorofluorescein and tetrachloro-*o*-fluorescein (*35, 72, 77*). From this compound was obtained a Phloxine dye, tetrachloroeosin (*8, 9, 72, 77*), and the closely related Rose Bengal 3B (*8, 9*). Mercury derivatives of these dyestuffs were proposed as pharmaceuticals (*116*).

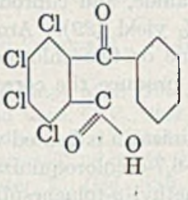
Pyrogallol, with tetrachlorophthalic anhydride, readily forms tetrachlorogallein (*35, 75, 76*). In a similar manner the three isomers of orcinoltetrachlorophthalein (*73*), *o*-cresoltetrachlorophthalein and its isomers (*3, 85, 87*), and thymoltetrachlorophthalein (*12*) and their derivatives have been prepared and studied. In the case of the orcinol and *o*-cresol compounds a study of the absorption spectra was made.

The anhydride is claimed to react with *m*-hydroxydiphenylamine to form a dye substance of the fluoran type (*32*). With dimethylaminophenol there was formed tetramethyltetrachlororhodamic tetrachlorophthalate (*72*). The free tetrachlororhodamine is obtained by treatment with a base, and this readily forms the hydrochloride with hydrochloric acid.

Disodium salicylate reacts with tetrachlorophthalyl chloride to give salicylic tetrachlorophthalidene ether ester (*52*).

BENZOYLTETRACHLOROBENZOIC ACIDS AND CORRESPONDING ANTHRAQUINONES

Benzoyltetrachlorobenzoic acid,



can be readily obtained from benzene, tetrachlorophthalic anhydride, and aluminum chloride (*53, 66*). This acid, its potassium, sodium, copper, and silver salts, as well as its methyl and ethyl esters, were prepared (*53*). Reduction with hydriodic acid and phosphorus yielded tetrachloroanthracene. Dehydrating agents, such as sulfuric acid and phosphorus pentoxide, caused ring closure with the formation of tetrachloroanthraquinone (*53*).

In a similar fashion toluene formed *o*-toluyltetrachlorobenzoic acid (, *60*), which upon ring closure gave 5,6,7,8-tetrachloro-2-methylanthraquinone (*21, 98*). This quinone serves as an intermediate for the preparation of 5,6,7,8-tetrachloroanthraquinoneisoxazole (*121*). Ethylbenzene and *o*-, *m*-, and *p*-xylene likewise yield *o*-aroyltetrachlorobenzoic acids which have been suggested as suitable derivatives for identification of these hydrocarbons. The product from *o*-xylene was further treated to form the corresponding anthraquinone (*110*). Naphthalene forms the α-naphthoyltetrachlorobenzoic acid (*39, 113*), which is also formed by the action of α-naphthyl magnesium bromide on the anhydride (*115*).

Mono- and dichlorobenzene (*47*), as well as trichlorobenzene (*22*), reacted with the anhydride to give the corresponding chlorobenzoyltetrachlorobenzoic acids, which on further treatment supply the penta-, hexa-, and heptachloroanthraquinones. Even nitrobenzene formed the nitrobenzoyltetrachlorobenzoic acid but did not yield an anthraquinone (*47*).

The aromatic hydroxy and amino compounds are quite reactive with tetrachlorophthalic anhydride in forming the substituted aroyltetrachlorobenzoic acids. With phenol there was formed 2'-hydroxybenzoyl-3,4,5,6-tetrachlorobenzoic acid, which by treatment with sodium hydroxide gives 5,6,7-trichloroxanthone-8-carboxylic acid (*84, 109*). Similar reactions were obtained with *p*-cresol (*108, 109*), *m*-cresol (*109*), *o*-cresol (*87, 109*), and β-naphthol (*97, 109*), each yielding the corresponding xanthonecarboxylic acid upon treatment with sodium hydroxide. β-Methoxynaphthalene (*97*) and anisole (*82, 115*) yielded the substituted aroyltetrachlorobenzoic acids but not the xanthones. α-Naphthol reacted to form the 2-hydroxynaphthoyltetrachlorobenzoic acid, along with some tetrachloro-α-naphthafluoran, and supplied 7,8,9,10-tetrachloro-1-hydroxynaphthacenequinone on ring closure (*45*).

Hydroquinone with tetrachlorophthalic anhydride gave 2',5'-dihydroxybenzoyl-3,4,5,6-tetrachlorobenzoic acid which, on ring closure, formed tetrachloroquinazarin (*4, 46, 113*). With resorcinol, 2',4'-dihydroxybenzoyl-3,4,5,6-tetrachlorobenzoic acid was obtained which, upon heating, gave tetrachlorofluorescein and tetrachlorophthalic anhydride (*72*).

m-Dimethylaminophenol (*6, 27, 43*) and *m*-diethylaminophenol (*27, 43, 86*) reacted to furnish the dimethyl- and diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acids. Dimethyl- and diethylaniline gave a corresponding product (*44*).

REACTIVITY OF AROMATIC CHLORINE

Ordinarily the chlorine in the aromatic ring is quite stable; however, the presence of two carbonyl groups adjacent to the chlorine atoms has a labilizing effect which is shown in a number of reactions of tetrachlorophthalic acid and its derivatives. The chlorine is quite stable, since a pyridine solution of silver nitrate did not remove chlorine from the aromatic nucleus (*93*). However, under certain conditions some, or even all, of the chlorine may be replaced by other groups. Thus, when tetrachlorophthalic acid was heated in an autoclave with aqueous potassium hydroxide, potassium cyanide, and cuprous cyanide, mellitic acid was produced in 60% yield (*29*). Aromatic amines, such as aniline, can replace one or two chlorine atoms of tetrachlorophthalic anhydride to produce the corresponding amino-substituted derivative (*92*).

When tetrachloroquinizarin is heated with aniline and sodium acetate, 5,8-dianilino-6,7-dichloroquinizarin (*113*) is formed. With toluidine or *N*-methyl-*p*-toluenesulfonamide, similarly substituted derivatives result (*112*). Tetrachloroquinizarin heated with *Naturkupfer C*, water, and lime yields dichlorotetrahydroxyanthraquinone; or heated with *p*-toluidine, *Naturkupfer C*, and sodium carbonate, yields 2,3,4-trichloro-1-*p*-toluidinoquinizarin (*46*). When 7,8,9,10-tetrachloro-1-hydroxynaphthacenequinone or 7,8,9,10-tetrachloro-1,6-dihydroxynaphthacenequinone is heated with aniline and boric acid, 8,9-dichloro-7,10-dianilino-1-hydroxynaphthacenequinone or 8,9-dichloro-7,10-dianilino-1,6-dihydroxynaphthacenequinone, respectively, result (*45*).

Part of the chlorine in tetrachlorophthalic anhydride may be replaced by reaction with bromine or hydrogen bromide to form the bromotrichloro- or dibromodichlorophthalic anhydrides (*7*). It is reported that chlorine in some of the substituted benzoyltetrachlorobenzoic acids is readily replaced. Thus in diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid one chlorine was replaced merely by boiling with 3% potassium hydroxide solution, and even ammonium hydroxide or sodium carbonate can remove the chlorine (*86*). The resulting materials are salts of trichloroxanthonecarboxylic acid. A number of other trichloroxanthonecarboxylic acids have been made (*97, 109*) (as described in the paragraph on benzoylbenzoic acids). Chlorine atoms in benzoyltetrachlorobenzoic acids are claimed to be replaceable by sulfonic acid groups through heating the salt of the acid with sodium sulfite or bisulfite (*106*).

Part of the chlorine in tetrachlorofluoran was removed by treatment with alcoholic potassium hydroxide and ethyl iodide (*74*).

PLASTICS AND PLASTICIZERS

Tetrachlorophthalic anhydride reacts with glycerol (*55, 114*) and ethylene glycol (*55*) to form resins. Some research has been done with these resins to determine their properties, the principal of which are self-extinguishment of its flame and compatibility with low viscosity cellulose acetate in diacetone (*48*). More extended research has been carried out to determine acid numbers, saponification numbers, degree of esterification, heat of activation, velocity constants, and average molecular weight when various ratios of tetrachlorophthalic anhydride and glycerol or ethylene glycol are used (*55*).

The anhydride was proposed for making waxlike flameproof chlorinated amide resins for electrical insulation by reaction with a diamine in acetamide solution (*101*).

The anhydride, acid, and its mono- and diesters, such as methyl, ethyl, amyl, cetyl, and benzyl, are proposed as plasticizers for organic derivatives of cellulose, of which cellulose acetate is an example (*18, 19*). Recently a patent was granted covering the use of esters of tetrachlorophthalic acid as plasticizers for cellulose esters, polystyrene, and methacrylates (*11*).

ADDITION COMPOUNDS

Numerous addition compounds of tetrachlorophthalic anhydride have been noted. Addition compounds with mesitylene, naphthalene, α-methylnaphthalene, acenaphthene, anthracene, phenanthrene, α-bromonaphthalene, α- and β-naphthol, α-naphthyl ethyl ether, β-naphthyl methyl ether, biphenylene oxide, carbazole (*89*), durene, hexamethylstilbene (*88*), diphenylbutadiene (*56*), dimethylaniline, and dimethyl-*p*-toluidine (*92*) are reported.

DYES

Among the numerous compounds of the phthalein type that can be derived from tetrachlorophthalic anhydride, several, such as Phloxine and Rose Bengal 3B, have been utilized as dyes (*8, 9*). The formation of substituted anthraquinones, quinizarins, and xanthones from various aroyltetrachlorobenzoic acids indicates its usefulness in the preparation of these dyes.

In addition, several novel dye preparations have been proposed. Blue vat dyes were obtained from dibenzanthrone derivatives and tetrachlorophthalic anhydride (*50*). Aminochloroanthraquinone dyes have been prepared from the tetrachloroquinizarin (*112*). A gray dye has been prepared by the reaction of *m*-hydroxydiphenylamine with the anhydride (*32*). Dyes are reported to result from the reaction of sulfur, resorcinol, and tetrachlorophthalic anhydride (*117*).

Chlorinated copper phthalocyanines have not been successfully prepared from tetrachlorophthalic anhydride (*14*) although there are patents covering the general field of halogenated phthalic anhydrides in the preparation of copper phthalocyanines (*123, 124, 125*).

MISCELLANEOUS REACTIONS AND USES

When tetrachlorophthalic anhydride was chlorinated over a long period of time at a high temperature in the presence of ferric chloride, it was largely converted to hexachlorobenzene (*20*). Similarly, at a high temperature and in better yield in the presence of chlorine, tetrachlorophthalyl chloride gave pentachlorobenzoyl chloride (*54*).

It was once reported that dry distillation of copper tetrachlorophthalate gave dodecachlorofluoran (*24*), but this was later reported to be in error (*23*).

The use of chlorinated phthalic anhydride, acid, esters, or salts has been proposed for lubricating compositions (*63, 94, 95*).

Tetrachlorophthalic anhydride has been suggested as a suitable filler in dusting powder containing halogenated amides (*102*) and as a component in a coating composition for motion picture screens (*122*).

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Received June 4, 1947.

Tetrachlorophthalic Anhydride, Acid, and Salts

PROPERTIES AND SOLUBILITIES

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A discussion is presented of the properties and solubilities of tetrachlorophthalic anhydride, of the corresponding acid, and of some of its salts. The literature on the subject is reviewed and new experimental data are submitted.

GRAEBE first prepared tetrachlorophthalic acid and some of its salts in 1868 and made a preliminary study of their properties (*4*). Later when it had become commercially available as a dye intermediate, he studied it in more detail and prepared many of its derivatives. These findings, published in 1887 (*5*), and the work of Delbridge in 1909 (*2*), have served as the principal sources of information on this compound. Unfortunately the product with which Graebe worked was not pure and was undoubtedly contaminated with lower chlorinated phthalic acid, which led to erroneous results in the determination of solubility and melting point. In the course of the development of a process for the manufacture of this product it became desirable to obtain more accurate data as well as to extend the field of information regarding this interesting compound.

PROPERTIES

Graebe gave the melting point of tetrachlorophthalic anhydride as 252° C. (*5*). Delbridge carefully purified the commercial product and obtained a compound melting at 254.8-255.2° C. (*2*). Determinations of the melting point of sublimed tetrachlorophthalic anhydride by the heating and cooling curve method, as well as by the capillary tube method indicate a melting point of 254.9° ± 0.2° C. which is in close agreement with Delbridge's figure.

Pure tetrachlorophthalic anhydride distills without appreciable decomposition at a temperature of 366° C. at 760 mm. pressure. Boiling under reflux for several hours shows that slow decomposition takes place and the neutralization equivalent of the product decreases. This is probably the result of decarboxylation, as the amount of alkali-insoluble material increases with the period of boiling. The presence of various inorganic and organic impurities greatly accelerates the decomposition.

The solid crystalline anhydride has a specific gravity of 1.92 at 20° C. The liquid has a density of 1.52 grams per ml. at 275° C.

Tetrachlorophthalic anhydride is insoluble or very slightly soluble in water, but hydrolyzes to the acid, slowly at room temperature and more rapidly at 100° C. (Figure 1). The solid crystallizing from the aqueous solution is the hemihydrate, $C_6Cl_4(COOH)_2 \cdot {}^1/_2H_2O$. This point went unnoticed by Graebe and undoubtedly accounts for some of the errors in his analytical data. Delbridge discovered this fact and noted that the water-free acid was rather difficult to prepare. It cannot be obtained by drying the hemihydrate in the usual way, but is obtained from the acid crystallized from dry acetone by driving off the acetone of crystallization. The pure acid is not stable as it absorbs moisture from the atmosphere to form the hemihydrate. In contrast to this, both the anhydride and the acid hemihydrate are completely stable under ordinary atmospheric conditions. Others have confirmed the fact that it is the hemihydrate which crystallizes from aqueous solutions (*14*). This hydrate of tetrachlorophthalic acid dissolves rapidly in water to form saturated solutions. The solubility of tetrachlorophthalic acid was determined at a variety of temperatures by titration with 0.1 *N* sodium hydroxide of a weighed portion of the saturated solution. The results (Table I and Figure 2) are at variance with the values given by Graebe. In the lower temperature range his higher results due to impurities are particularly noticeable. There is considerable difficulty in obtaining satisfactory data at temperatures approaching the boiling point because of the combined effect of high temperature coefficient of solubility and rapidity of evaporation of such solutions during the necessary manipulation of the samples. The solubility increases rapidly near 100° C.; in order to determine whether this trend continues beyond 100° C., several approximate determinations were made by adding a known excess of tetrachlorophthalic acid to a suitable glass pressure flask and noting the temperature at which all of the acid was dissolved. While the method is admittedly inaccurate, the experiment demonstrates that the solubility continues to increase rapidly with rise in temperature even above 100° C. (Figure 3).

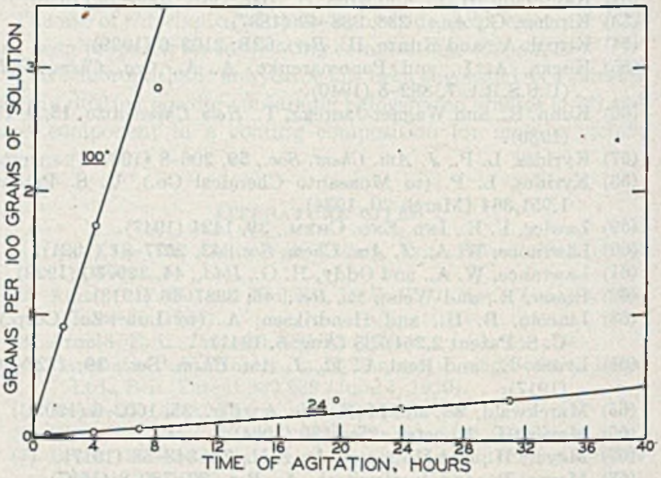

Figure 1. Hydrolysis of Tetrachlorophthalic Anhydride in Water

At 24° C.		At 100° C.	
Hours agitated	Grams $C_6Cl_4(COOH)_2$ formed/ 100 g. soln.	Hours agitated	Grams $C_6Cl_4(COOH)_2$ formed/ 100 g. soln.
1	0.03	2	0.91
4	0.06	4	1.74
7	0.09	8	2.74
24	0.27		
31	0.34		
Before 95	0.37		

Table I. Solubility of Tetrachlorophthalic Acid in Water and in Hydrochloric Acid Solutions

Temp., ° C.	Grams $C_6Cl_4(COOH)_2$/ 100 G. Soln.	Temp., ° C.	Grams $C_6Cl_4(COOH)_2$/ 100 G. Soln.
In Water		In 0.1 *N* HCl	
20	0.36	12	0.05
36	0.44	22	0.07
50	0.56	29	0.08
60	0.70	40	0.12
70	0.90	59	0.23
80	1.20	84	0.76
88	1.60	95	1.30
99	2.80		
Pressure above Atm.		In 0.6% HCl	
103	ca. 6	24	0.03
108	8	36	0.06
111	12	51	0.13
		61	0.20
		95	1.10

The presence of an inorganic acid exerts a depressing effect on the solubility of the acid in water. The results in Table I and Figure 2 were obtained by titrating weighed portions of the saturated solution with 0.1 *N* sodium hydroxide and 0.1 *N* silver nitrate solutions to obtain the total acidity and chloride content, from which the amount of organic acid was easily calculated. The practical value of this effect is realized in the recovery of the acid from waste water in processes in which it is used.

SOLUBILITY OF SALTS

The anhydride dissolves in alkali solutions to form the salts of the acid, which may be obtained even more readily by the reaction of the acid hydrate with the alkali solution. The solubilities of the sodium and potassium salts were determined by evaporating to dryness a weighed portion of the saturated solution. The solubility of the sodium salt (Table II and Figure 4) increases rather rapidly with elevation of temperature up to 63.5° C.; above this point further temperature increase has little effect. The solid phase crystallizing out below 63.5° C. was analyzed and shown to be the pentahydrate, $C_6Cl_4(COONa)_2.5H_2O$. Analysis of large, clear crystals formed by the slow atmospheric evaporation of saturated solutions at room temperature showed that they were also the pentahydrate. At temperatures above 63.5° C. the solid phase is probably not hydrated, but this point has not been proved.

Table II. Solubility of Sodium Tetrachlorophthalate in Water

Solubility of $C_6Cl_4(COONa)_2$				Sp. Gr. of Satd. Soln. of $C_4Cl_4(COONa)_2$	
Temp., ° C.	Grams/ 100 g. soln.	Temp., ° C.	Grams/ 100 g. soln.	Temp., ° C.	Sp. gr.
5.0	13.9	45.5	25.1	7	1.095
15.0	15.8	58.8	32.2	26	1.125
24.5	17.9	61.5	33.0	31	1.135
26.5	18.5	63.5[a]	34.0	77	1.188
34.0	20.8	75.0	34.6		
37.5	22.4	97.0	35.2		
40.0	23.0				

[a] Transition point.

The solubility of the potassium salt is somewhat greater than that of the sodium salt, but it has a lower temperature gradient so that the solubilities of the two salts are almost the same at 65° C. The solubility curve of the potassium salt shows no transition point in the interval 5-75° C. (Table III). The solid phase may be hydrated but loses water so rapidly in the atmosphere that it is difficult to determine definitely whether the solid is hydrated or has only adhering free water.

When a solution containing the cations of a metal other than the alkali group is added to a neutral or slightly acid solution of an alkali tetrachlorophthalate, the slightly soluble salt of the metal is precipitated. In this manner the aluminum, calcium, cupric, and zinc salts were prepared, washed, and dried. To determine their solubility in water portions of the saturated solution of the salt were subjected to analysis for the metal. Table III, giving the solubilities of these salts, shows that the zinc salt is less soluble in hot than in cold water, a fact which was also observed by Graebe (*5*).

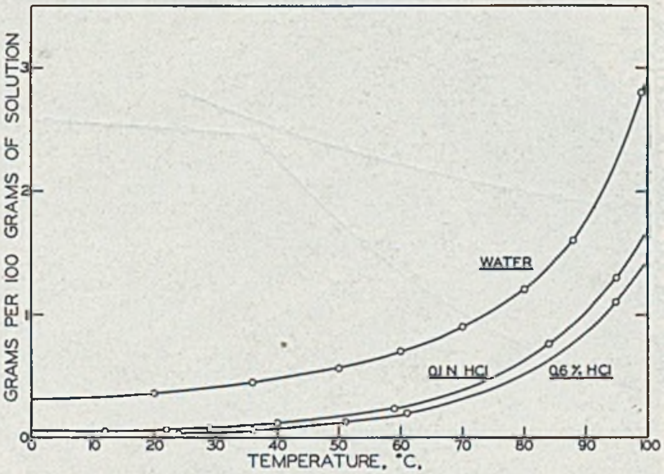

Figure 2. Solubility of Tetrachlorophthalic Acid in Water and in Hydrochloric Acid

ACID "DOUBLE SALTS"

Attempts to prepare the sodium acid salt of tetrachlorophthalic acid resulted in the formation of a sparingly soluble acid "double salt" having the composition corresponding to the formula $C_6Cl_4(COONa)(COOH).C_6Cl_4(COOH)_2$. The potassium acid "double salt" is completely analogous. These salts are similar in type to potassium tetraoxalate. When the theoretical amount of alkali hydroxide required to form the acid salt was added to a suspension of tetrachlorophthalic anhydride in water and heated to 100° C. with stirring, and just enough water added to bring the material into complete solution, a crop of crystals of the acid "double salt" separated on cooling. After filtration and evaporation of the filtrate, it was found to contain a relatively large quantity of the normal salt accompanied by some acid "double salt." The reaction which probably took place may be represented by the equation:

$$3C_6Cl_4(COONa)(COOH) \longrightarrow C_6Cl_4(COONa)(COOH).C_6Cl_4(COOH)_2 + C_6Cl_4(COONa)_2$$

When an inorganic acid, such as hydrochloric acid, is added to a solution of the normal salt, the acid "double salt" is precipi-

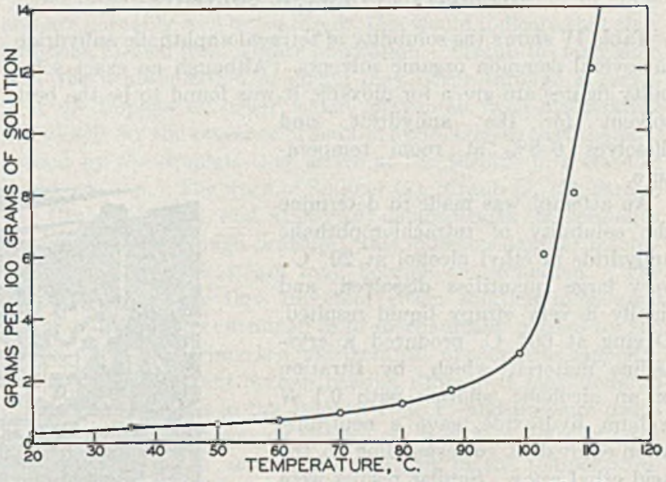

Figure 3. Effect of Temperatures above 100° C. on Solubility of Tetrachlorophthalic Acid in Water

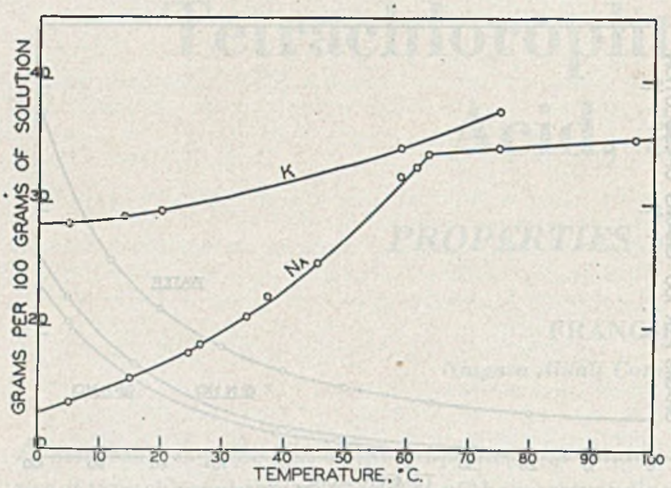

Figure 4. Solubility in Water of the Neutral Potassium and Sodium Salts of Tetrachlorophthalic Acid

tated. This type of acid "double salt" of 4,5-dibromo- and 4,5-dichlorophthalic acids was mentioned in the literature (*6*, *10*).

USES OF NORMAL SALTS

The normal silver and sodium salts have been used in the preparation of the normal esters of tetrachlorophthalic acid by reaction with an appropriate organic halide (*3*, *5*, *7*, *8*). The normal esters are not readily obtained by direct esterification (*9*, *14*); therefore, this method may be of considerable importance especially in view of the ease with which the anhydrous salts can be prepared. The normal salts were proposed for use in the treatment of animal fibers to impart "weight" (*12*). Scandium was purified from the accompanying traces of ytterbium and yttrium by precipitation of the basic salt of tetrachlorophthalic acid (*1*).

Table III. Solubility of Potassium and Other Salts of Tetrachlorophthalic Acid in Water

Soly. of $C_6Cl_4(COOK)_2$		Soly. of Other Tetrachlorophthalates		
Temp., ° C.	Grams/ 100 g. soln.	Salt	Temp., ° C.	Grams/ 100 g. soln.
5	28.3	Aluminum	25	0.35
14	28.9	Calcium	24	0.07
20	29.1	Cupric	25	<0.10
23	29.3	Zinc	25	3.0
59	34.5		75	2.0
75	37.5			

SOLUBILITY IN ORGANIC SOLVENTS

Table IV shows the solubility of tetrachlorophthalic anhydride in several common organic solvents. Although no exact solubility figures are given for dioxane, it was found to be the best solvent for the anhydride and dissolves 6–8% at room temperature.

An attempt was made to determine the solubility of tetrachlorophthalic anhydride in ethyl alcohol at 20° C.; very large quantities dissolved, and finally a very sirupy liquid resulted. Drying at 60° C. produced a crystalline material which, by titration of an alcoholic solution with 0.1 *N* sodium hydroxide, gave a neutralization equivalent corresponding to the acid ethyl ester. Similar results were obtained when the attempt was made to dissolve the anhydride in methyl, *n*-butyl, *n*-amyl, cyclohexyl, and tetrahydrofurfuryl alcohols. The dissolving rate is greatly accelerated by heating, but the resulting acid ester is also formed slowly at room temperature. The literature mentions that tetrachlorophthalic anhydride forms acid esters on dissolving in alcohols but not to the extent found in our experiments (*2*, *11*, *13*).

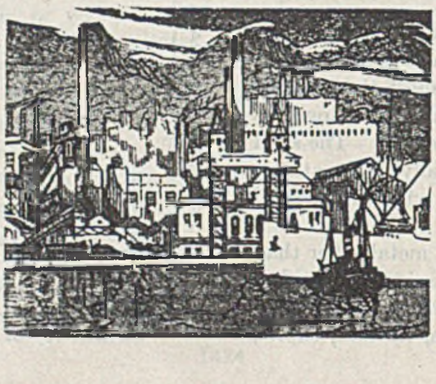

Table IV. Solubility of Tetrachlorophthalic Anhydride in Organic Solvents

	Soly. of $C_6Cl_4(CO)_2O$, Grams/100 G. Soln.			
Solvent	Temp., ° C.	Soly.	Temp., ° C.	Soly.
Acetone	25	3.1	49	5.6
Benzene	25	4.0	76	11.9
Carbon tetrachloride	24	0.15	76	0.68
o-Dichlorobenzene	25	4.0	76	9.1
Monochlorobenzene	25	2.7	76	8.6

The hemihydrate, obtained by crystallizing the acid from water is very different from the anhydride, since it is freely soluble in acetone, dioxane, and alcohol. In contrast to the anhydride, it is quite soluble in ether but is insoluble in benzene, carbon tetrachloride, and monochlorobenzene. However, upon addition of a small amount of methanol, it readily dissolves in these solvents and also in petroleum ether. In view of these observations it is evident that much of the information available in the literature on the solubility of tetrachlorophthalic acid and anhydride is not reliable because the acid hemihydrate can be readily dried to form the anhydride; hence the solubilities refer to various mixtures of the acid and anhydride rather than to either pure acid or anhydride. The fact that only the anhydride is soluble in benzene was noted by Delbridge (*2*).

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance rendered by the Research Staff of the Niagara Alkali Company, especially Gerald A. Thomas, Joseph L. Longo, and I. A. Hoekstra who carried out most of the analytical work in obtaining the data presented here.

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Received June 4, 1947. Presented before the Division of Organic Chemistry at the 111th Meeting of the American Chemical Society, Atlantic City, N. J.

X-Ray Diffraction Studies of Steam Turbine Deposits

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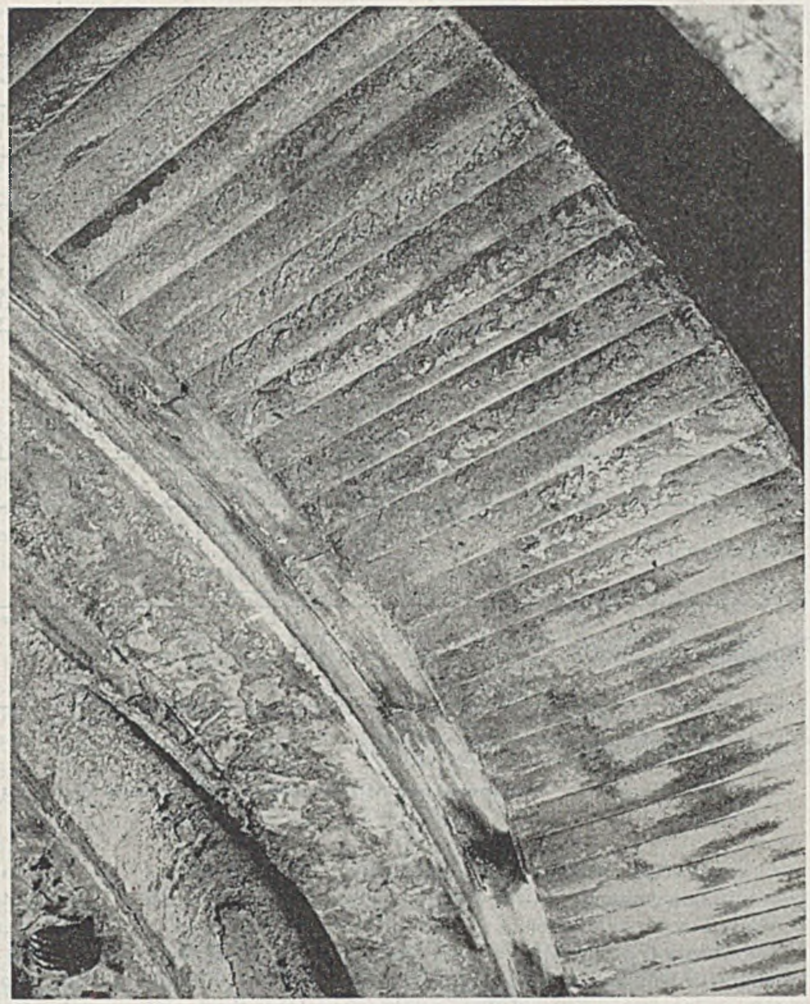

Deposits on Turbine Blading

The composition of a relatively large number of steam turbine deposits as determined by x-ray diffraction analysis is reported. An effort has been made to relate the composition of turbine deposits with the temperature at the point of deposition and with the pressure of the boiler supplying the turbine with steam. Certain compounds have been found to occur in sequence in steam turbine deposits.

THE appearance of deposits in steam turbines leads to serious reductions in turbine capacity and efficiency. The nature of these deposits, the mechanisms of their formation, and the means of avoiding their occurrence are problems of interest to all concerned with the operation of steam turbines. Soderberg (*7*) and Buckland (*1*) describe the appearance of deposits and their effect on turbine capacity and efficiency. Fitze and Long (*2*) recently published their experience with siliceous deposition at 1300 pounds per square inch. They show that siliceous deposition on the turbine blades is a function of the concentration of silica in the steam, but that the percentage of the silica carried by the steam that is deposited on the blades tends to reach a maximum at 60%. They observed a direct relation between the silica concentration of the boiler water in the range of 1.5–14 parts per million and the concentration of silica in the steam. The concentration of silica in the steam was found to be in the order of 1% of the silica concentration in the boiler water. This is in agreement with the results of Straub and Grabowski (*11*), who found the silica carry-over to be in the order of 1% of the silica concentration of the boiler water using an experimental boiler.

Efforts made to avoid the occurrence of turbine deposits should be guided by knowledge of the mechanism of their formation, which is as yet not fully known. The study of the complete mechanism of turbine blade deposits may be divided into two parts, (*a*) the manner in which the steam becomes contaminated with boiler water salts and (*b*) the manner in which the steam loses part of its contamination in passing through the turbine, producing the troublesome deposits.

The phases found in turbine deposits are largely crystalline and are normally well crystallized; this would indicate that they had been formed from a state of solution. Straub (*9*) suggested that the contamination of steam may occur through a carry-over of droplets of boiler water, prevented from evaporating completely by the presence of sodium hydroxide, so that the salts carried by the droplets thus arrive at the turbine in a state of liquid solution. The work of Spillner (*8*), Straub (*9, 10*), Straub and Grabowski (*11*), and Morey (*6*) demonstrates the solubility of salts in steam at high pressure; this indicates another mechanism by which the steam may become contaminated. The dissolved state may thus represent either solution in gaseous steam or in droplets entrained in or mechanically carried by the steam. A steam turbine is a "refrigerator" of enormous capacity, and any solute-solvent system passing through it may undergo temperature changes in the order of 700° F. and pressure drops in the order of 1000 pounds per square inch in a fraction of a second. Such large and sudden changes in the temperature-pressure conditions cause drastic changes in solubility relations

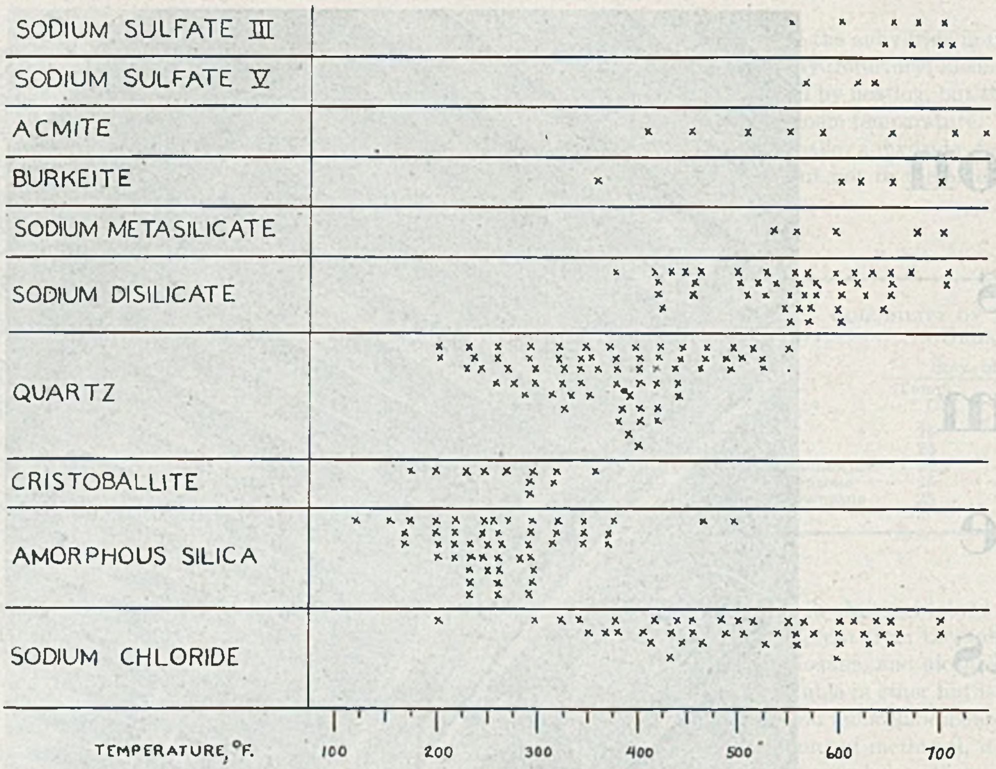

Figure 1. Temperature of Occurrence of Various Compounds

and throw certain of the salts out of solution. Since the solvent is in intimate contact with the turbine surfaces, supersaturation is relieved by crystallization of the salts on the turbine surfaces.

Identification of the solid phases and a correlation of these phases with temperature and composition of the steam contamination are necessary parts of the procedure in solving the *b* part of the problem on the complete mechanism of the formation of turbine deposits.

This study was begun as an attempt to establish a relation between the chemical species of a turbine blade deposit and the temperature at the point of occurrence of the deposit. Such an effort necessarily involves the identification of the various components of turbine deposits. Goerke (*3*) made a similar study, employing chemical analysis as a means of identification of the several components. Chemical methods of identification may be misleading, since they fail to distinguish such compounds as α-quartz and amorphous silica, or will indicate the presence of sodium sulfate and sodium carbonate when in reality burkeite is present. In this study x-ray diffraction methods were employed for the identification of the chemical species. Later the scope of the present study was extended to seek evidence of a relation between the compounds and the pressure of the boiler producing the steam from which the deposits formed. The study is now being continued to see if there is any relation between the compounds found in deposits and the average composition of the boiler water from which the steam was produced, and if there is any relation between the compounds found and the composition of the steam from which the deposits were produced.

CLASSES OF TURBINE DEPOSITS

Deposits occurring in steam turbines may be classified in the following fashion: (*a*) corrosion or erosion materials, (*b*) water-insoluble compounds of calcium and magnesium, and (*c*) silica, silicates, and water-soluble compounds.

Corrosion and erosion deposits consist primarily of metallic oxides and, occasionally, sulfides. Magnetite, Fe_3O_4, and hematite, Fe_2O_3, predominate in this group. The second class contains compounds such as calcium carbonate, calcium phosphate, and magnesium hydroxide. In the authors' experience these compounds have been almost invariably associated with oily materials. This suggests that the adherence of these compounds on turbine blades depends upon adhesive properties which oil in the steam imparts to the plastic mixture. The last group is made up of silica, both in the crystalline forms as α-quartz and cristobalite and the noncrystalline form as amorphous silica, water-soluble and -insoluble silicates, and water-soluble salts such as sodium chloride and sodium sulfate. This class of deposits has been the major concern of those interested in turbine blade deposits; the deposits examined in this study have been limited to this class.

SOURCES OF SAMPLES

A total of 199 samples was examined in this study. These were obtained from twenty-seven power plants. Fourteen of these were utilities, and thirteen were industrial plants. Difficulty is experienced in obtaining complete sets of samples from individual stages of a turbine. Composite samples have little value in this study, and samples from only badly fouled stages also give an incomplete picture. Frequently the amount of sample is small, less than 0.1 gram often being submitted. In many instances this is necessarily so, since the amount of deposit found on a given stage may be very small. Such small samples do not permit the number of tests which would often be desirable.

TECHNIQUES

Identifications were made by the x-ray powder diffraction method. Patterns were taken with unfiltered iron radiation, using circular cameras having a radius of 6.98 cm. Samples were mounted in open wedges and were protected by coating with a methacrylate lacquer when they appeared liable to change during the time of exposure. The methacrylate technique proved satisfactory with highly alkaline materials. Chemical analyses were also made of a number of the deposits. Many of the analyses are unfortunately incomplete because of the lack of sufficient sample. In general, chemical analyses are unsatisfactory for identification purposes, since they give no evidence for the presence of complex compounds such as burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$, or acmite, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$, and variations in composition from exact formulas make positive identification difficult. For example, samples containing sodium disilicate frequently show marked variation in the determined sodium oxide–silica ratio. Table I gives results obtained by chemical analysis of a number of turbine deposits shown to contain sodium disilicate by x-ray diffraction patterns.

The most serious difficulty with x-ray techniques is the lack of diffraction data. Two courses are being followed to meet this difficulty; first, diffraction data are being accumulated on all compounds that might possibly occur in steam turbines, either using natural minerals or by synthesizing compounds, and, second, chemical analyses of turbine deposits are being examined for suggestions as to possible compounds, and then attempts are being made to synthesize the suggested compounds, obtaining from them x-ray diffraction data which will permit their identification in deposits. Two factors tend to operate against the second course: The amount of sample ordinarily received is too small to permit complete chemical analysis, and the variations observed make it difficult to draw conclusions from chemical analyses.

CRYSTAL FORMATION

With the exception of amorphous silica, which is noncrystalline, and cristobalite, compounds found in turbine deposits are normally well crystallized; this indicates that the conditions surrounding their occurrence are favorable to crystal formation. Any mechanism postulated for the formation of turbine deposits is thus limited to conditions favorable to crystal formation.

COMPOUND-TEMPERATURE RELATIONS

The number of compounds thus far identified in this study is rather limited. Table II shows the frequency of occurrence, the temperature range, and average temperature of the various compounds found in the samples examined. This table clearly indicates the predominance of siliceous compounds. Silica-bearing compounds were found in 90.8% of the deposits examined. Next in frequency of occurrence is sodium chloride, which was found in 14.6% of the samples. The remaining compounds occur infrequently.

The temperature at the point of occurrence of the various compounds in the samples studied is shown in Figure 1. The data shown in this figure are arranged essentially in the order of descending average temperatures for the occurrence of the various compounds. Samples were examined from rows in turbines having a range in temperature from 125–810° F.

Sodium sulfate III and sodium sulfate V may be considered together. Both sodium sulfates are more commonly found as deposits in superheater tubes rather than as turbine deposits. Examples of the occurrence of the sodium sulfates are shown in Tables III, IV, and V. It seems probable that sodium sulfate is actually deposited as sodium sulfate III, the high temperature form, since the inversion temperature is only 465° F., and that in those instances where sodium sulfate V, the stable room temperature form, is found this represents a transformation from sodium sulfate III. Where sodium sulfate III is found, it would appear that it has been deposited with sufficient foreign material present, most probably in solid solution with it, to stabilize the high temperature form and thus prevent the inversion from taking place.

Acmite, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$, occurs somewhat rarely. The formation of acmite may be the result of a reaction between sodium metasilicate or sodium disilicate and hematite, Fe_2O_3. It has been prepared in the authors' laboratory by heating sodium metasilicate, hematite, and a small amount of water together in a bomb at 400° F. It may be noted that acmite has been found in the same temperature range as sodium metasilicate and sodium disilicate, and that its average temperature, 549° F., approximates the average temperature, 557° F., for these two compounds combined. An example of the occurrence of acmite is shown in Table V.

Burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$, is also rare. Like the sodium sulfates, burkeite is more commonly found as a deposit in superheater tubes rather than as a turbine deposit. Deposits which show, upon chemical analysis, an alkalinity relation suggesting the presence of sodium carbonate should be checked for sulfate content. All such samples examined here with x-ray diffraction methods to date have contained burkeite.

Table I. Partial Chemical Analyses of Deposits Containing Sodium Disilicate

	%	Equiv.	%	Equiv.	%	Equiv.	%	Equiv.	%	Equiv.	%	Equiv.
Sodium oxide (alkalinity)	25.4	0.82	24.8	0.80	21.5	0.69	25.7	0.83	10.9	0.35	29.8	0.96
Total silica	49.7	1.66	57.9	1.93	46.7	1.55	47.5	1.58	22.1	0.74	49.7	1.66
Soluble silica	25.0	0.83	32.5	1.05	12.7	0.41	40.2	1.34	16.6	0.55	32.0	1.07

Table II. Occurrence Data on Compounds Found

Compound	Formula	Temp. Range, ° F.	Av. Temp. of Locations Where Found	No. of Occurrences	Per Cent
α-Quartz	SiO_2	200–550	358	69	34.6
β-Sodium disilicate	$Na_2Si_2O_5$	419–710	546	51	25.6
Amorphous silica	SiO_2	120–490	274	48	24.1
Sodium chloride	$NaCl$	200–700	512	44	22.1
Cristobalite	SiO_2 ·	174–360	270	11	5.5
Sodium sulfate III	Na_2SO_4 III	625–700	673	9	4.5
Sodium sulfate V	Na_2SO_4 V	564–631	604	9	4.5
Acmite	$Na_2O.Fe_2O_3.4SiO_2$	410–744	549	8	4.0
Burkeite	$Na_2CO_3.2Na_2SO_4$	360–700	587	7	3.5
Sodium metasilicate	Na_2SiO_3	535–700	613	5	2.5
Unidentified	....	...	...	23	11.6

Table III. Composition of Turbine Deposits from Turbine Operating at 550-Lb. Throttle Pressure, 700° F. Throttle Temperature

Stage	Temp., ° F.	Composition
1	700	Sodium metasilicate, sodium sulfate III, unidentified
2	675	Sodium metasilicate, sodium sulfate III, unidentified
3	650	Sodium disilicate
4	625	Sodium disilicate
5	600	Sodium disilicate
6	575	Sodium disilicate
7	550	Sodium disilicate
8	525	Sodium disilicate
9	500	Sodium disilicate, sodium chloride

Table IV. Composition of Turbine Deposits from Turbine Operating at 400-Lb. Throttle Pressure, 680° F. Throttle Temperature

Stage	Temp., ° F.	Composition
1	618	Sodium sulfate V, unidentified
2	590	Sodium metasilicate, sodium chloride
3	562	Sodium metasilicate, sodium chloride
4	535	Sodium metasilicate, sodium chloride
5	508	Sodium chloride, unidentified
6	482	Sodium chloride, unidentified
7	546	Sodium chloride, unidentified
8	430	Sodium chloride, unidentified
9	404	Sodium chloride, unidentified
10	378	α-Quartz, sodium chloride
11	352	α-Quartz, sodium chloride
12	324	α-Quartz, sodium chloride

Table V. Composition of Turbine Deposits from Turbine Operating at 1250-Lb. Throttle Pressure, 900° F. Throttle Temperature, with Turbine Steam Washed Twice during Run in Which Deposits Formed

Stage	Temp., ° F.	Composition
5 moving	550	Acmite
6 moving	510	Acmite
7 moving	450	Acmite
7 stationary	450	Acmite, unidentified
8 stationary	410	Acmite, unidentified
9 moving	350	α-Quartz
10 moving	285	α-Quartz
11 moving	259	Amorphous silica
11 stationary	259	α-Quartz
12 moving	219	Amorphous silica
12 stationary	219	Amorphous silica
13 stationary	198	Amorphous silica
14 moving	166	Amorphous silica
14 stationary	166	Amorphous silica

Sodium chloride occurs rather frequently: Sodium chloride was found across the widest temperature range of any of the compounds. Whereas the other compounds found in this study have been found at least occasionally in a comparatively pure state, sodium chloride has thus far always been found associated with some other compound.

Figure 2. Combinations Observed in the Sodium Silicate–Silica Sequence in Blade Deposits

Metasilicate——Disilicate
Metasilicate——Quartz——Amorphous silica
Disilicate——Quartz——Amorphous silica and cristobalite
Disilicate——Quartz——Amorphous silica
Quartz——Amorphous silica and cristobalite
Quartz——Amorphous silica

Trona, $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$, was found in two turbine deposits. One sample was a composite from five stages having a temperature range of 400–700° F.; the other was from two stages having a range of 400–450° F. Unfortunately the deposits were several years old before they were examined. Since it is possible that this compound was formed by a reaction between alkaline components of the sample and carbon dioxide of the air, this compound cannot as yet be definitely placed in the list of those formed in turbines.

The compounds sodium metasilicate, β-sodium disilicate, α-quartz, cristobalite, and amorphous silica should be considered as a group, since they occur in a sequence in the order given, with sodium metasilicate in the higher temperature stages and amorphous silica in the lower temperature stages. In no instance thus far in this study have these compounds been found in any order than that given. After the individual members of this group are discussed, evidence of their tendency to occur in series will be given.

Sodium metasilicate is relatively rare. Deposits containing sodium metasilicate are hygroscopic and strongly alkaline. Chemical analysis is liable to suggest the presence of sodium hydroxide when in reality sodium metasilicate is present in the deposit.

β-Sodium disilicate, β-$Na_2Si_2O_5$, the low temperature form of sodium disilicate, was found in 25.6% of the samples studied. The samples are normally well crystallized. They are strongly alkaline and dissolve in water to form a milky solution, the milky appearance being due to colloidal silica formed through the decomposition of the disilicate by water. As in the case of sodium metasilicate, the alkalinity of samples containing sodium disilicate may erroneously suggest the presence of sodium hydroxide. Chemical analysis usually shows some approximation of the sodium oxide–silica ratio indicated by the sodium disilicate formula. Some time elapsed between the authors' first observation of β-sodium disilicate and its final identification with the aid of a sample of the low form sodium disilicate supplied by G. W. Morey of the Geophysical Laboratory of the Carnegie Institute of Washington, D. C. Diffraction data on β-sodium disilicate are given in Table VI.

α-Quartz, the stable low temperature form of crystalline silica, was found in 34.6% of the samples examined. Quartz forms a tightly adherent deposit. It is normally well crystallized and frequently makes up more than 90% of a sample.

Amorphous silica was observed in 24.1% of the deposits. Like quartz, it also forms a tightly adherent deposit. Since amorphous silica is noncrystalline, it yields no x-ray pattern, but evidence of its presence may be obtained by igniting the sample at 950° C. for about a half hour, after which a diffraction pattern is taken. This treatment converts amorphous silica to cristobalite, the high temperature form of crystalline silica, which does yield a pattern. Occasionally heating fails to bring about the conversion to cristobalite. In this case the addition of a mineralizer, such as a trace of sodium hydroxide, followed by ignition will cause the conversion to take place.

Cristobalite has been found associated with amorphous silica in turbine deposits. Cristobalite crystallizes poorly in these deposits and therefore yields a poor x-ray pattern. For some time the authors considered its identification questionable; however, the finding of strong lines of cristobalite in samples (Tables VII and VIII) containing over 90% silica renders this identification certain. In several of the instances where cristobalite was found, the turbine from which the samples were obtained was operated with considerable variation in load and hence variation in stage temperature. It would appear that cristobalite is derived from amorphous silica under conditions which are sufficient to initiate crystallization but insufficient to carry the crystallization to the stable state, which in this case would be quartz.

Considerable overlap of temperature ranges is observed among the compounds sodium metasilicate, sodium disilicate, α-quartz, and amorphous silica and cristobalite. Despite the temperature range overlap, in deposits from any given turbine the change from one of these compounds to another usually occurs across a stage or two and frequently occurs between two adjacent stages. The change from sodium metasilicate to sodium disilicate (Table III) is sharp, as is the change from sodium disilicate to quartz (Table IX). The change from α-quartz to amorphous silica is often not so sharp as that between the other members of the series.

Figure 2 shows the combinations of these compounds which have been observed thus far in this study. As yet the authors have not observed the complete series in samples from any one turbine. Hankison and Baker (*5*) report the analysis of a series of deposits which appears to contain the whole series. In this same series quartz is reported as occurring before sodium silicate, a situation the authors have not encountered. To date, except in those instances where the temperature of the last stage of the turbine was too high, no instance has been observed where sodium disilicate was not followed by quartz and amorphous silica, or where quartz was not followed by amorphous silica. Table IX illustrates a series of deposits in which sodium disilicate is followed by quartz, which in turn is followed by amorphous silica.

TABLE VI. X-RAY DIFFRACTION DATA ON β-SODIUM DISILICATE

d	*I*	*d*	*I*
6.61	vw	1.61	m
3.98	ms(4)	1.57	vw
5.46	vw	1.53	w
4.72	vw	1.52	wm
4.57	vw	1.49	wm
4.26	m	1.46	w
4.13	w	1.45	wm
3.94	m	1.445	vw
3.76	w	1.42	wm
3.63	ms(6)	1.399	wm
3.52	vw	1.377	vw
3.36	w	1.334	vw
3.07	m(5)	1.322	vw
2.96	s(2)	1.307	vw
2.85	w	1.297	vw
2.67	m(7)	1.287	w
2.58	m(8)	1.269	vw
2.52	w	1.259	vw
2.42	m(9)	1.232	vw
2.35	vw	1.203	m
2.27	w	1.184	m
2.19	vw	1.175	w
2.14	m(10)	1.166	w
2.08	w	1.155	s(3)
2.05	w	1.142	w
1.99	w	1.134	w
1.94	w	1.111	vw
1.93	w	1.087	vw
1.89	w	1.083	vw
1.87	w	1.071	vw
1.82	s(1)	1.057	vw
1.78	w	1.044	vw
1.77	w	1.039	vw
1.74	wm	1.030	vw
1.70	vw	1.023	vw
1.65	vw	1.014	vw
1.62	vw		

This series of deposits shows an interesting feature. At the eleventh stage, where the transformation from sodium disilicate to quartz takes place, the stationary element shows the higher temperature phase, β-sodium disilicate, whereas the moving element shows a considerable amount of the lower temperature phase, α-quartz. A similar situation is seen in the fifteenth stage where the transformation from α-quartz to amorphous silica takes place. Here α-quartz, the higher temperature phase predominates in the deposit from the stationary element, whereas amorphous silica, the lower temperature phase, predominates in the deposit from the moving element. Another example of this division of phases across stationary and moving elements is shown in Table V. In this series of deposits, α-quartz appears in the deposit from the stationary element of the eleventh stage, whereas amorphous silica appears in the moving element of the same stage. Table III shows the sequence of sodium metasilicate and sodium disilicate. In another series, illustrated in Table IV, sodium metasilicate was not followed by sodium disilicate. However, in this series of deposits, a gap is found between the occurrence of sodium metasilicate and that of quartz in the region where sodium disilicate would be expected. An unidentified compound was found in this gap.

In some instances where sodium disilicate was not found previous to the occurrence of quartz and amorphous silica, inquiry revealed that a deposit had occurred in the stages previous to the first one from which samples were removed, but that these deposits had not been sampled because of the small amount present. In one case samples were received from a plant and on analysis were found to contain quartz and amorphous silica. Some time later samples from the same plant were received from another but identical turbine, and this series of deposits contained sodium disilicate followed by quartz and amorphous silica. Correspondence in an effort to find a possible cause for the difference in the two sets of samples revealed that, in the first instance, deposits had occurred which were probably sodium disilicate but had not been sampled. Cases such as this show the necessity of sampling every stage on which any deposit appears, if a full picture of the nature of the deposits in a turbine is to be obtained. In other instances, Table V shows, steam washing appears to have removed the soluble sodium metasilicate and disilicate together with any other soluble salts that might have been present.

Table VII. Composition of Turbine Deposits from Turbine Operating at 850-Lb. Throttle Pressure, 900° F. Throttle Temperature

Row	Temp., ° F.	Composition
5	710	β-Sodium disilicate, sodium sulfate III
6	665	β-Sodium disilicate, sodium sulfate III
7	616	β-Sodium disilicate, sodium chloride
8	565	β-Sodium disilicate, sodium chloride
9	515	β-Sodium disilicate, sodium chloride
10	454	β-Sodium disilicate, sodium chloride
11	419	Quartz, sodium chloride β-sodium disilicate
12	376	Quartz, sodium chloride
13	337	Quartz, sodium chloride, amorphous silica
14	295	Amorphous silica, quartz, cristobalite
15	261	Amorphous silica, cristobalite, quartz
16	227	Amorphous silica, cristobalite
17	198	Amorphous silica, cristobalite
18	174	Amorphous silica, cristobalite

Table VIII. Chemical Analyses of Deposits Shown in Table VII

Row	Sodium Oxide (Alkalinity), %	Total Silica, %	Soluble Silica, %	Sodium Chloride, %	Sodium Sulfate, %
5	24.1	43.1	21	...	29.1
6	27.8	46.4	20	...	3.9
7	31.5	46.8	24	4.0	...
8	29.5	54.2	40	19.0	...
9	29.8	49.7	32	27.6	...
10	19.1	38.8	25	43.5	...
11	5.5	75.5	16	19.0	...
12	1.7	94.9	4	4.0	...
13	1.2	97.3	3	3.0	...
14	...	96.8	..	...	...
15	...	96.1	..	...	...
16	...	94.6	..	...	...
17	...	95.5	..	...	...
18	...	92.8	..	...	...

An interesting series of deposits is shown in Table VII, with chemical analyses of these deposits shown in Table VIII. This series of deposits was taken from the same turbine as the series shown in Table IX, after a 2-year operating interval. Operating conditions were similar during the turbine runs that produced both series of deposits, with one exception. During the course of the run that produced the deposits shown in Table VII, a plugged blowdown line caused evaporator priming, and the resultant carry-over brought about a total dissolved solids concentration which persisted for about a week. It appears that this condition accounts for the presence of sodium sulfate and sodium chloride found in the series of Table VII. This set of samples shows an interesting variation in the crystal size of the sodium disilicate found in rows 5 to 11. This variation is shown in Figure 3. The crystal size of the sodium disilicate increased to a maximum in row 8 and then decreased in succeeding rows. Maximum crystal size was observed at a temperature of 565° F., which is not far from the average temperature of deposition, 546° F., found for sodium disilicate.

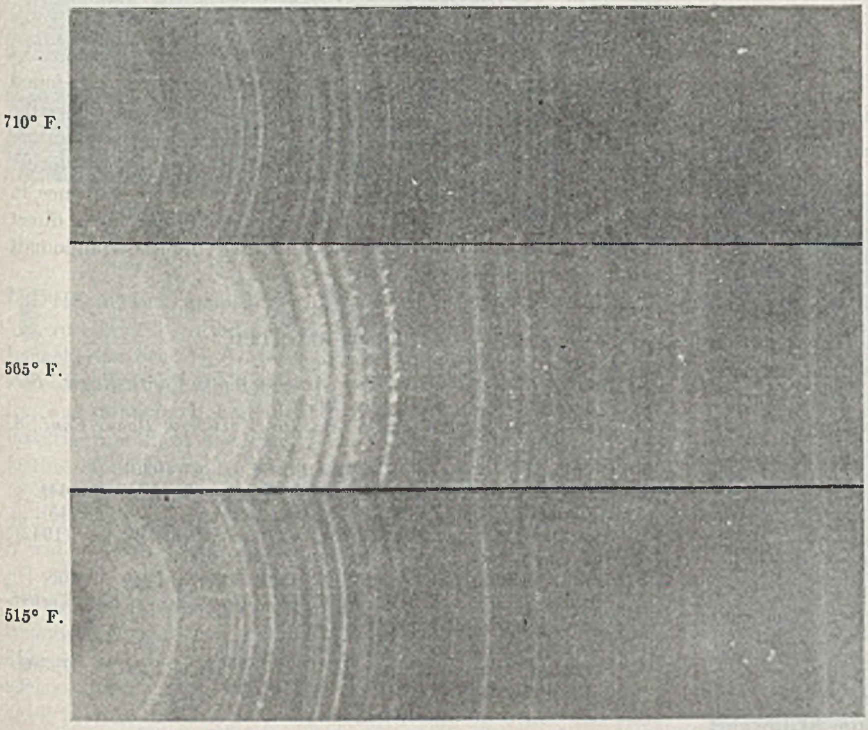

Figure 3. Variation of Particle Size of Sodium Disilicate at Various Temperatures

Further study of the behavior of the sodium silicate–silica system at elevated temperatures in the presence of steam should contribute much to our under-

Table IX. Composition of Turbine Deposits from Turbine Operating at 850-Lb. Throttle Pressure, 900° F. Throttle Temperature

Stage	Temp., ° F.	Composition
10 stationary	454	Sodium disilicate
10 moving	454	Sodium disilicate
11 stationary	419	Sodium disilicate
11 moving	419	Sodium disilicate, α-quartz
12 stationary	376	α-Quartz
12 moving	376	α-Quartz
13 stationary	337	α-Quartz
13 moving	337	α-Quartz
14 stationary	298	α-Quartz
14 moving	298	α-Quartz
15 stationary	261	α-Quartz, amorphous silica
15 moving	261	Amorphous silica, α-quartz
16 stationary	227	Amorphous silica, α-quartz
16 moving	227	Amorphous silica

Table X. Analysis of Material Containing Unidentified Component

Ionic	%	As Sodium Salts	%
Total silica	29.9	Sodium sulfate	23.4
Soluble silica	17.8	Sodium disilicate	29.9
Na_2O (alkalinity)	13.9	Sodium chloride	21.6
Cl	12.8	R_2O_3	4.6
SO_3	13.2	Total	93.4
R_2O_3	4.6		

Table XI. Comparison of Compounds Found in Turbine Blade Deposits with Boiler Operating Pressures

Compound	Boiler Pressure Range, Lb./Sq. In.	Av. Boiler Pressure, Lb./Sq. In.
Sodium chloride	300- 600	409
Sodium sulfate III	300- 550	450
Sodium metasilicate	400- 550	460
Burkeite	360- 900	502
Sodium disilicate	400-1200	692
Sodium sulfate V	400- 900	730
Amorphous silica	350-1325	980
Quartz	350-1325	1012
Acmite	1200-1250	1237

standing of the mechanism of the formation of these compounds in turbine deposits. Hall (*4*) offered some suggestions in regard to this mechanism based on analogy with the better understood potassium oxide-silica-water system.

UNIDENTIFIED COMPOUNDS

Considerable evidence for the occurrence of a number of unidentified compounds is at hand. This is in the form of diffraction patterns which do not conform to any compound on which data are available, and also in the form of lines which cannot be accounted for in patterns containing identifiable compounds. Although most of these instances have occurred in cases where the sample was too small for further investigation, an example of this situation is shown in Table X. Beside the pattern for sodium chloride, the pattern from this material shows lines which have some similarity to those from sodium disilicate as well as additional lines which do not correspond to those from sodium disilicate, sodium sulfate III, or sodium sulfate V. The efforts being made to identify these compounds have already been described.

Hankison and Baker (*5*), using optical and x-ray diffraction methods, report the occurrence of magnesium chloride, magnesium phosphate, magnesium sulfate, sodium phosphate, potassium chloride, potassium phosphate, potassium sulfate, and potassium tetrasilicate. As yet the present authors have not observed these compounds in turbine deposits.

Three compounds which might be expected in turbine deposits, sodium hydroxide, sodium carbonate, and sodium bicarbonate, have not as yet been found in this study. Sodium hydroxide, which has frequently been reported on the basis of chemical analysis, might be present in an amorphous condition and thus escape detection by x-ray methods. Thus far, however, all of the highly alkaline hygroscopic deposits examined have given good diffraction patterns with no evidence of either sodium hydroxide or its hydrates. Published analyses of turbine deposits such as those of Straub (*10*) which might be interpreted as containing sodium hydroxide, usually contain considerable silica, which suggests the presence of sodium silicates rather than sodium hydroxide. Other analyses, both published and made in this laboratory, contain an alkaline material which cannot be accounted for by either sodium silicates or burkeite. To date, no sample of this type has been available for x-ray diffraction studies.

COMPOUND-BOILER PRESSURE RELATION

The boiler pressure ranges, together with the average boiler pressure at which the various compounds have been found, are given in Table XI. The data shown in this table indicate that little direct relation exists between the operating pressure and the type of compound found. There is evidence that boiler pressure, together with other factors such as concentrations of salts in the boiler water, may have a relation to the type of compound found in the turbine. The deposition of sodium metasilicate and sodium disilicate appears to occur in greater quantity at lower pressure, whereas quartz and amorphous silica tend to predominate in quantity at higher pressures. These tendencies may be related to the decreasing total dissolved solids concentration with increasing operating pressures.

In the data from this study to date sodium chloride appears to be associated with lower pressure operation. The authors are aware of evidence of the occurrence of sodium chloride in high pressure operation, although samples were not available for this study in these instances.

Sodium sulfate III and burkeite both appear to be associated with low pressure operation. The appearance of sodium sulfate V, at considerably higher pressures than that at which sodium sulfate III is found, is interesting, as it suggests that at higher pressures sodium sulfate is found in a purer state than at the lower pressures.

Acmite has thus far been observed only at higher pressures.

SUMMARY

With the exception of amorphous silica, the compounds found in turbine deposits are normally well crystallized. Most of the compounds found appear to bear a relation to the temperature at which they are found. Sodium metasilicate, sodium disilicate, quartz, and amorphous silica appear to occur in sequence in turbine deposits. Little evidence has been found for a direct relation between boiler operating pressures and the compounds found in turbine deposits.

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Received November 27, 1946. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Ill.

Automatic pH Control in Water and Industrial Waste Treatment

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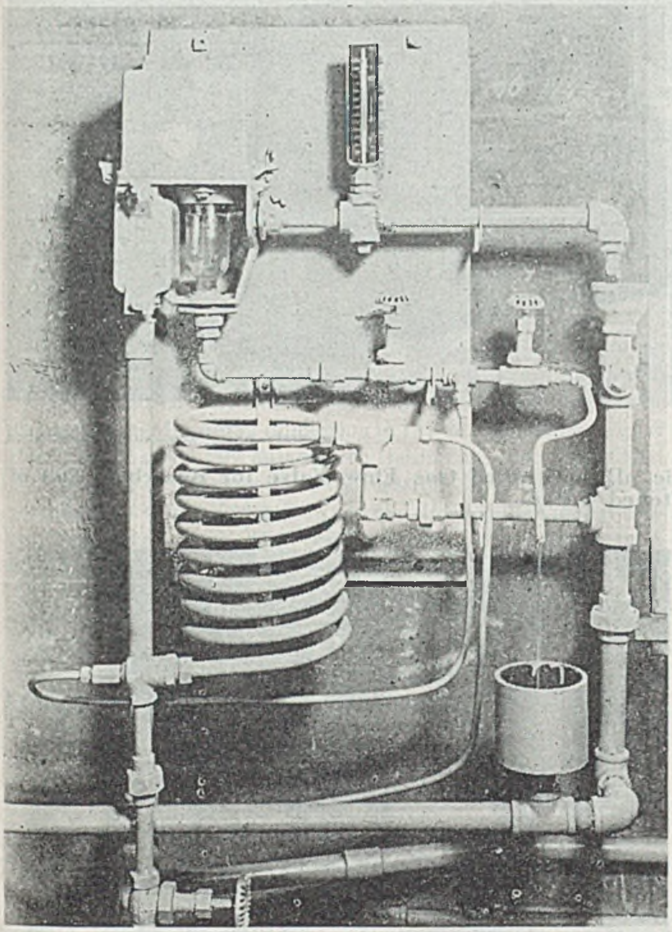
Automatic pH control is of increasing value in water treatment systems for prevention and control of corrosion, and for prevention of scale deposits. It is also used in the neutralization of excess alkalinity following lime-soda softening, in maintaining optimum pH for proper coagulation, and in automatic blending of hydrogen and sodium zeolite softened water to obtain desired residual alkalinity. In waste disposal systems, automatic pH control is frequently required to control neutralization of acid and alkaline wastes and to assure maintenance of proper pH for satisfactory coagulation. The elements of design are described. The buffer action of the system is important. The rate and degree of change of pH of the raw liquid must be evaluated and the system designed accordingly. Retention period, proper mixing of reagent with the liquid, choice of sampling point must be considered. The mechanics of automatic pH control are described; the three elements required being the pH meter, the controller, and the chemical feed or regulation device. Where two variables are present such as variable flow with changing variable composition, correction for each variable is desired, and the control system and chemical feed device must be designed to compensate for the changes in either or both variables. Several typical installations of automatic pH control are described.



COURTESY, LEEDS & NORTHRUP COMPANY

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Figure 1. Sample Cooling for pH Measurement of Boiler Feed Water

THE importance of pH control in water treatment has been receiving increasing attention during the last ten years. Langelier's work (*1*), showing the correlation of pH with calcium ion concentration, alkalinity, temperature, and total ionic activity, was important at the start of this trend, and a number of investigators since have published papers on this subject, with further applications or modifications of the Langelier theory (*2, 6, 7, 11*). Prevention of corrosion or of scaling is therefore directly correlated to pH control. Some of the excess alkalinity of water softened by lime and soda must be reduced and also the pH value must be decreased, for prevention of afterprecipitation, although certain chemicals now on the market—namely, sodium hexametaphosphate—have considerable value for preventing afterprecipitation, particularly in the cold. Various coagulants, such as alum, ferric chloride, ferric sulfate, and sodium aluminate, work best at definite pH ranges, depending on other materials present in the water. Therefore pH control for good coagulation is required to assure proper results with a minimum of coagulant and afterprecipitation, following filtration.

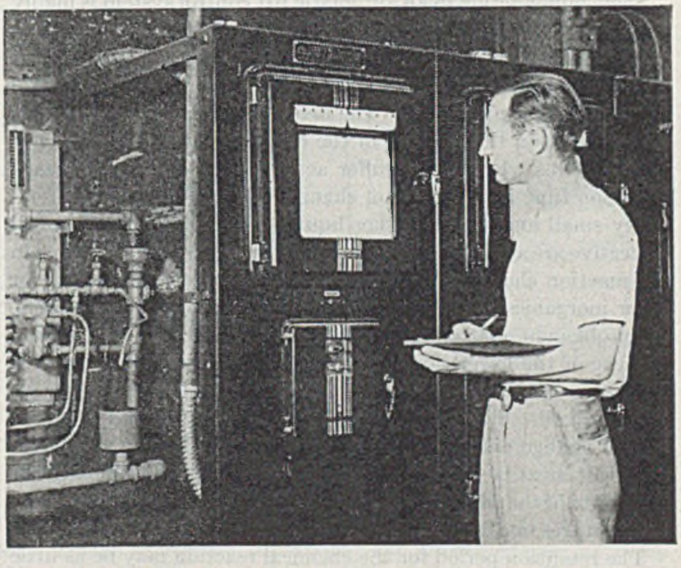

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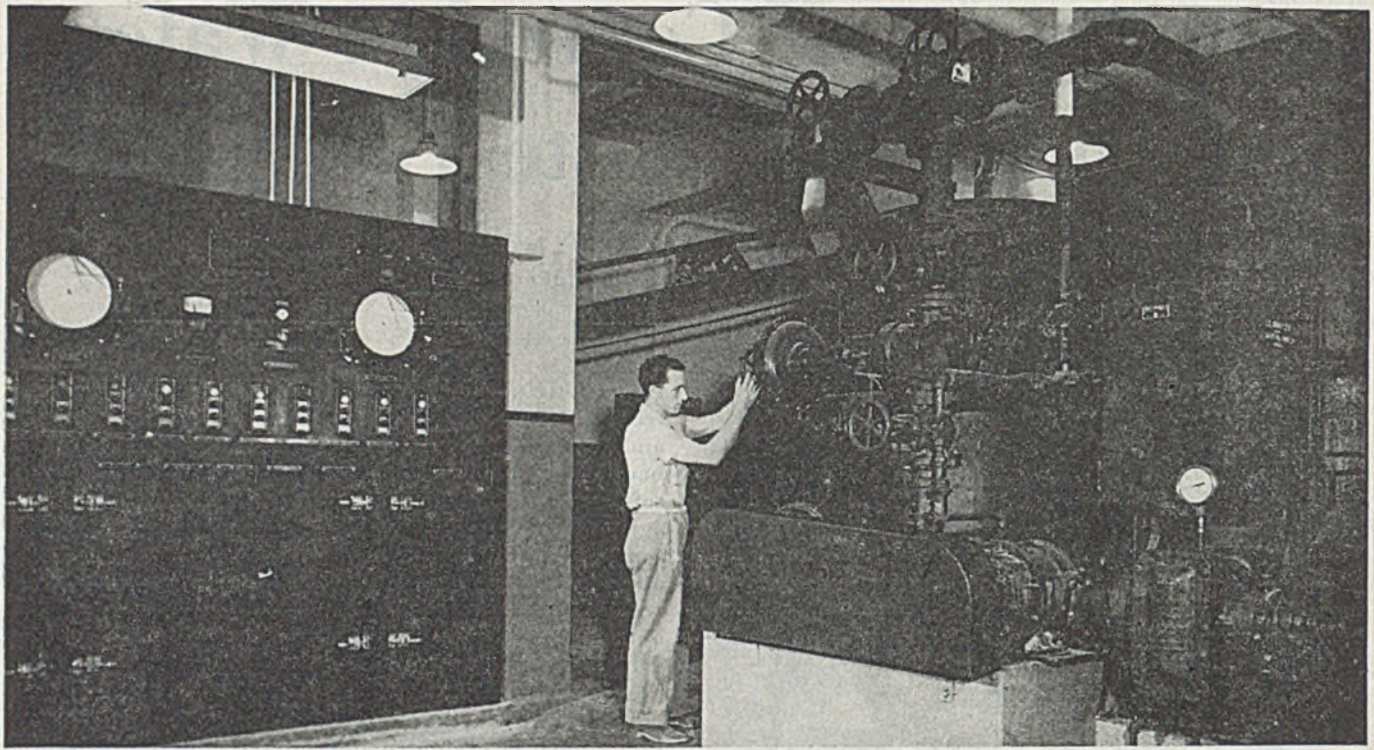
Figure 2. pH Meter and Controller for Boiler Feed Water



COURTESY, WRIGHT AERONAUTICAL CORPORATION

Figure 3. Flue Gas Scrubber, Compressor, and Automatic pH Controlled Gas Flow Valve for Recarbonation of Lime-Soda Softened Water

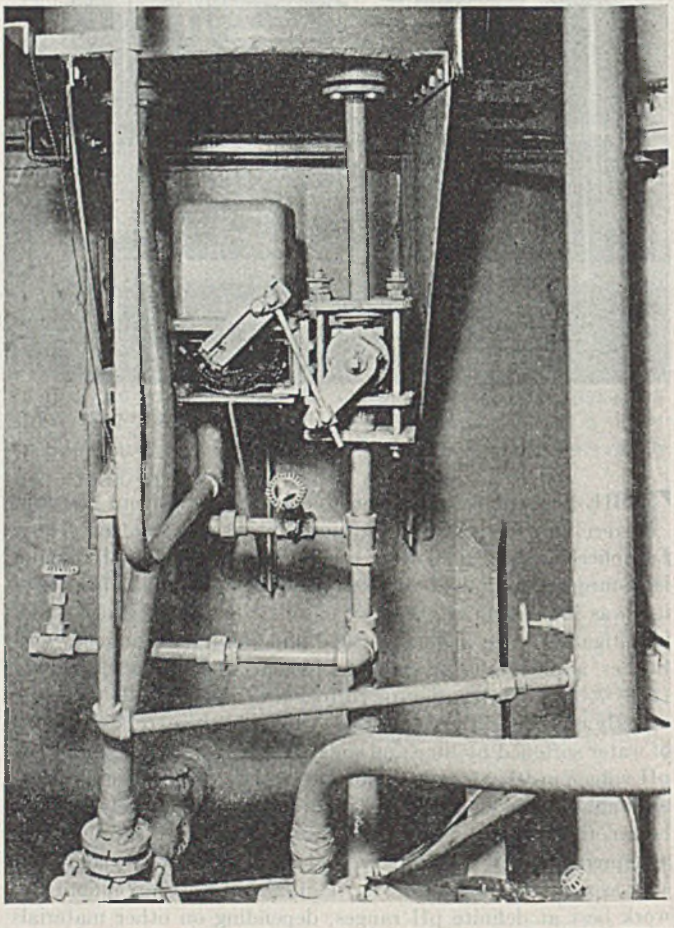
Waters to be treated by the zeolite process must, as a rule, be neutralized before softening in certain forms of zeolite and can be neither too alkaline nor too acid. Automatic pH control is frequently employed to assure proper preparation of water for this process.

Automatic pH control is increasingly important in industrial waste disposal. Many industrial wastes are strongly acid or strongly alkaline and must be properly neutralized before they are discharged or in order that they be fit for other treatment processes. Again the optimum pH for good coagulation with the various coagulants is important.

ELEMENTS OF DESIGN

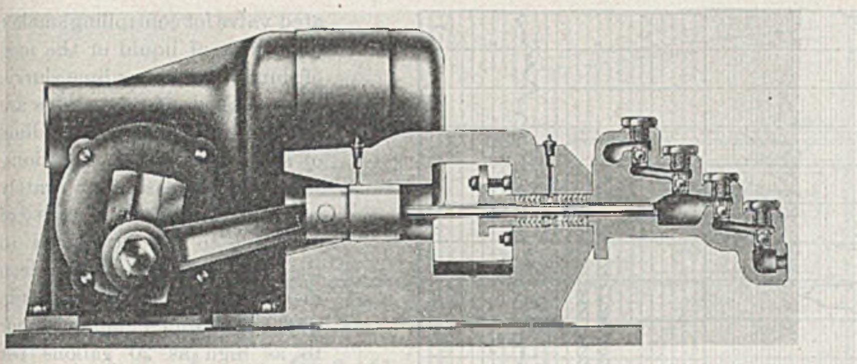
Some buffer action in an automatic pH control system is highly desirable. It would prove difficult, for example, to neutralize a solution of strong acid such as sulfuric with a strong base such as caustic soda directly and in dilute solution, holding as a control point a neutral pH of 7.0. The neutralization curve is so steep that control on this portion of the curve would be erratic. For such systems where little buffer action is present, an increased retention time in the reaction chamber is advisable so that relatively small amounts of either liquid to be treated or chemical corrective are added at one time, compared to the total volume in the reaction chamber. Where phosphate, borate, carbonate, or other inorganics or organics are present that will act as buffers, the problem of control at practically any desired pH is facilitated because of the lower slope of the neutralization curve, provided it is possible to reach the desired pH by the addition of corrective acid or alkali. The changes in the pH of the raw liquid, both the rate of change and degree of change, must be known and evaluated. It must be remembered that the term "pH" indicates the logarithm of the reciprocal of the hydrogen ion concentration, and that changes in pH are logarithmic and not straight-line.

The retention period for the chemical reaction may be as little as 5–10 seconds to as much as 15 minutes, depending on the system and these various factors. The less the slope of the neutral-



COURTESY, LEEDS & NORTHRUP COMPANY

Figure 4. Motor-Operated Valve for Sulfuric Acid Treatment of Boiler Feed Water



COURTESY, MILTON ROY COMPANY

Figure 5. Valve Design of a Controlled-Volume Pump

ization curve at the control point, the lower the retention time required for the individual system. A neutralization curve for a proposed system is of considerable value in making a recommendation for a possible application of automatic pH control.

Both the chemical reagent and the incoming raw liquid must be mixed intimately as rapidly as possible with all portions of the liquid in the reaction vessel and in a minimum of time. The sampling point from which a flow to the glass electrode is taken must be selected to give an average sample of the raw liquid with the chemical used for treatment. The electrode assembly can be arranged either for direct immersion in the mixing chamber or for placement immediately adjacent to the mixing chamber so that flow from the sampling point to the electrode involves a minimum possible lag. It is important to know the time required for neutralization to take place. With certain organics, or even with lime, some time is required for the neutralization reaction to be completed and to realize the full change in pH that will result from the addition of the treating chemical.

The true pH of a solution changes with temperature. An understanding of the magnitude of the pH difference between measured and true pH when the true pH is at an elevated temperature is necessary for a proper interpretation of the indicated and recorded data (*3*, *4*, *5*). With the glass electrode properly designed, it is possible to measure pH over a wide temperature range from as low as 5° to 100° C. When desired, a sample cooling coil can be installed prior to the electrode flow cell (Figure 1).

MECHANICS

In an automatic pH control system a variable is being measured that is the result of the reaction of the chemical whose flow is controlled by the meter with the raw liquid being treated. The establishment of equilibrium in such a system might be likened to a dog chasing its tail. There is a certain amount of lag in such a system; therefore provision must be made in the meter for operation of a controller that can be adjusted both for the percentage of full scale range (also known as throttling range) over which the controller is to operate and for the rate at which the increase or decrease of setting (also known as reset rate) of the chemical feed is to be effected.

This provision is necessary to allow for the factors discussed in the previous section—namely, buffer action and slope of the neutralization curve, retention time, reaction time, rate and degree of change in chemical characteristics of the raw liquid, control point, mixing, sampling, and temperature. Figure 2 shows typical pH meter and controller. When pH meters and controllers were first placed on the market, antimony-calomel electrode systems were popular. Since that time glass electrodes have been developed that are highly sensitive and more satisfactory, and have been employed in all installations described in this paper. The pH meter in reality measures the electromotive force between the glass electrode and the calomel, which is directly proportional to the hydrogen ion concentration of the solution. The pH controller, taking its impulse from the meter, must function to actuate the chemical feed or regulating device. This regulating device may be an air-actuated valve, a motor-operated valve, or the recently introduced controlled-volume pump. An air-actuated valve, for example, may be used to regulate the flow of flue gas used for recarbonation of a lime-soda softened water (Figure 3). It may also be used for regulating larger liquid flows by actuation

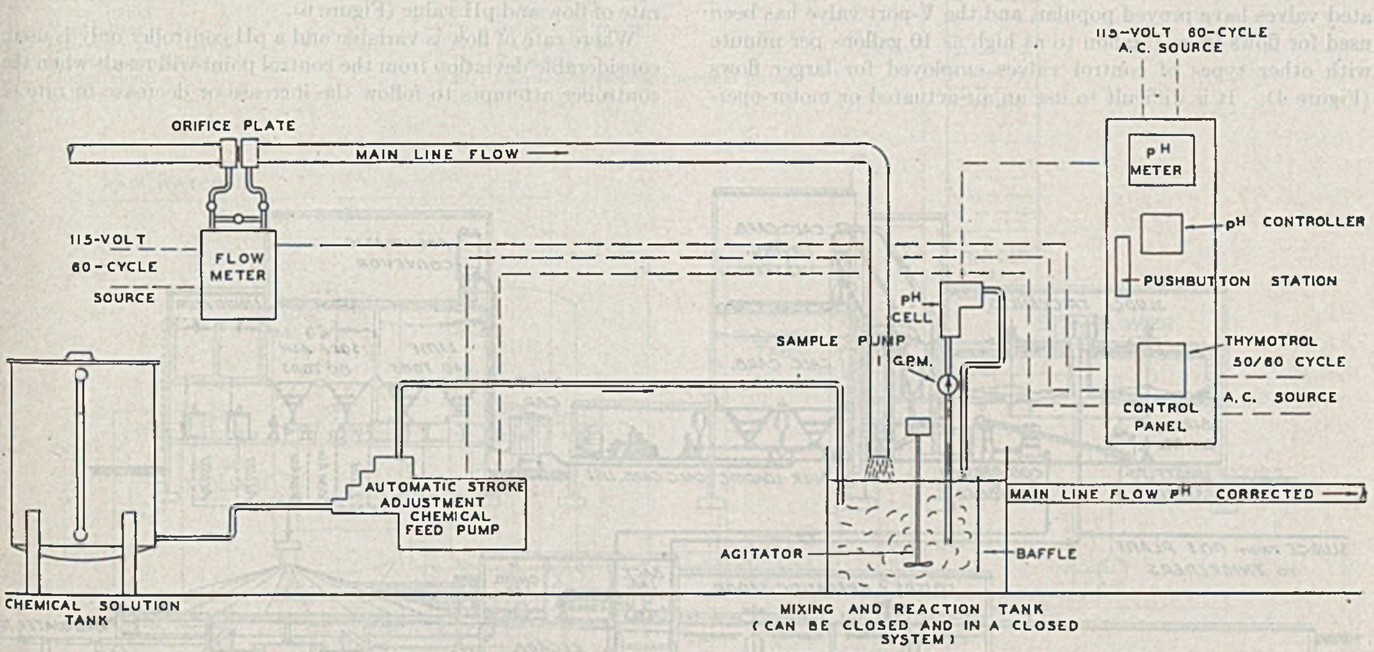


Figure 6. Automatic pH Control System with Controlled Volume Pumps

For Constant Main Line Flow. pH controller sets length of pump stroke through motorized adjustment (one control variable on pump capacity).

For Varying Main Line Flow. Speed of pump is directly proportional to main line flow through flowmeter by electronic control of motor speed. pH controller sets length of pump stroke through motorized adjustment, and thus gives full and independent correction of pump capacity for two metered variables.

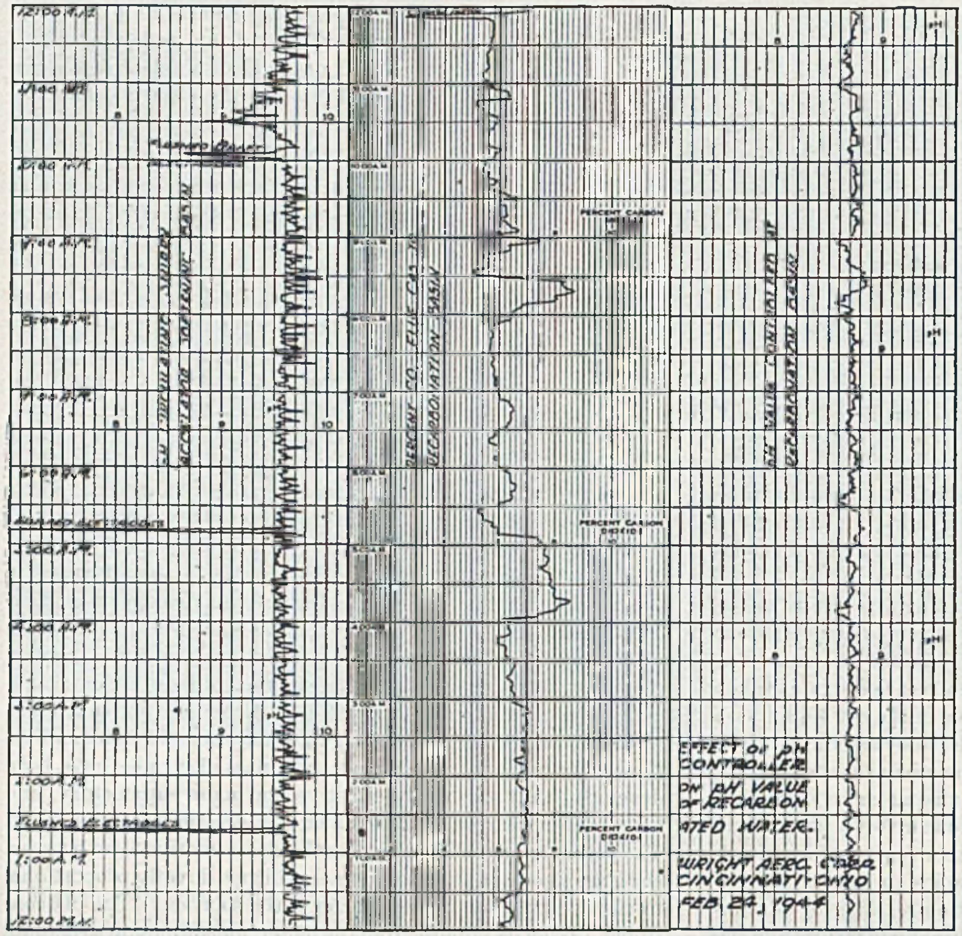


Figure 7. Typical Operation Curves for Automatic pH Control at Wright's Plant 2, with Variable Carbon Dioxide Content in Flue Gas, Variable pH on Influent, and Variable Flow

of an orifice-type or butterfly-type control valve. Motor-operated valves have proved popular, and the V-port valve has been used for flows from 1 gallon to as high as 10 gallons per minute with other types of control valves employed for larger flows (Figure 4). It is difficult to use an air-actuated or motor-operated valve for controlling smaller quantities of liquid or the feed of slurries, such as a lime slurry.

Controlled-volume pumps are admirably suited to the handling of slurries as well as solutions, since they measure accurately by displacement the quantity of chemical to be introduced to the system. These pumps can measure and inject chemicals in quantities from 1 pint per hour to as high as 20 gallons per minute per cylinder, and in the smaller capacities can pump chemicals against pressures as high as 20,000 pounds per square inch. Therefore these pumps make possible automatic pH control in a broad new field of application. They measure and pump in one operation, and as a result of the pump valve design the volume delivered is practically a constant, regardless of variation in discharge pressure (Figure 5). The delivery may be automatically regulated either through motor speed by electronic control (*9*) or through automatic adjustment of the length of stroke of the pump. Through the medium of stroke adjustment, it is possible to obtain full range automatic control from zero to maximum capacity of the chemical feed by the pump (Figure 6). It is also possible to superimpose two variables on one controlled-volume pump—that is, rate of flow and pH value (Figure 6).

Where rate of flow is variable and a pH controller only is used, considerable deviation from the control point will result when the controller attempts to follow the increase or decrease in rate of

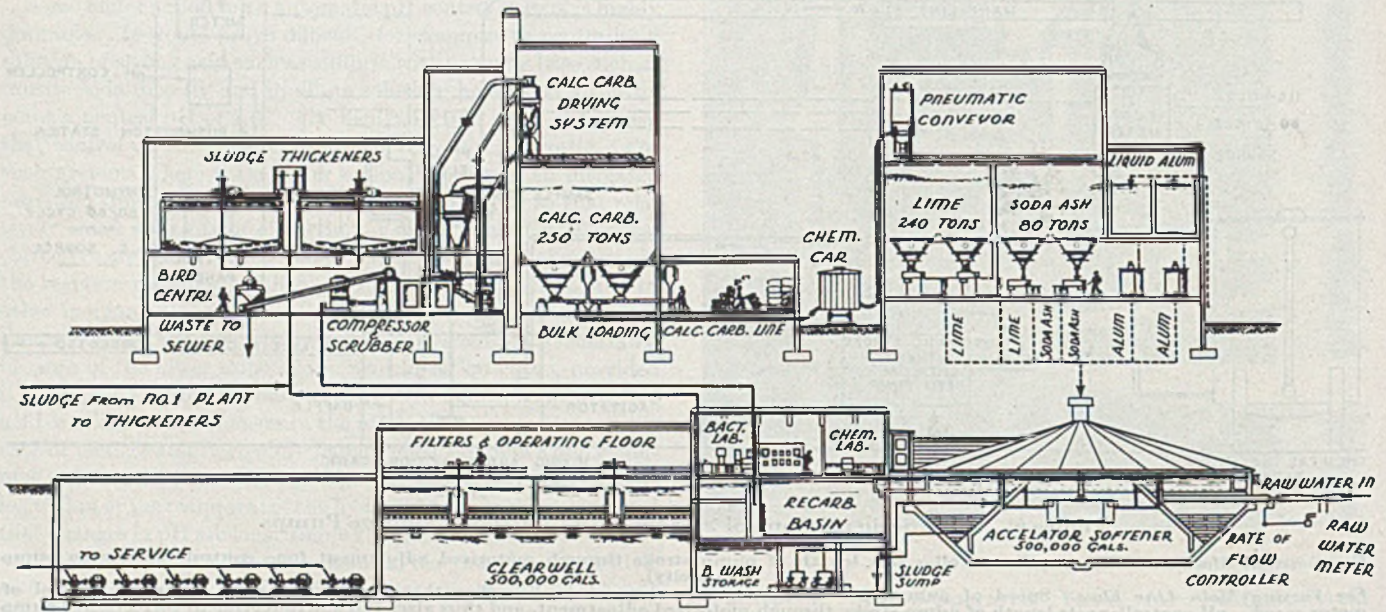


Figure 8. Flow Sheet of Water Treatment System for Wright's Plant 2

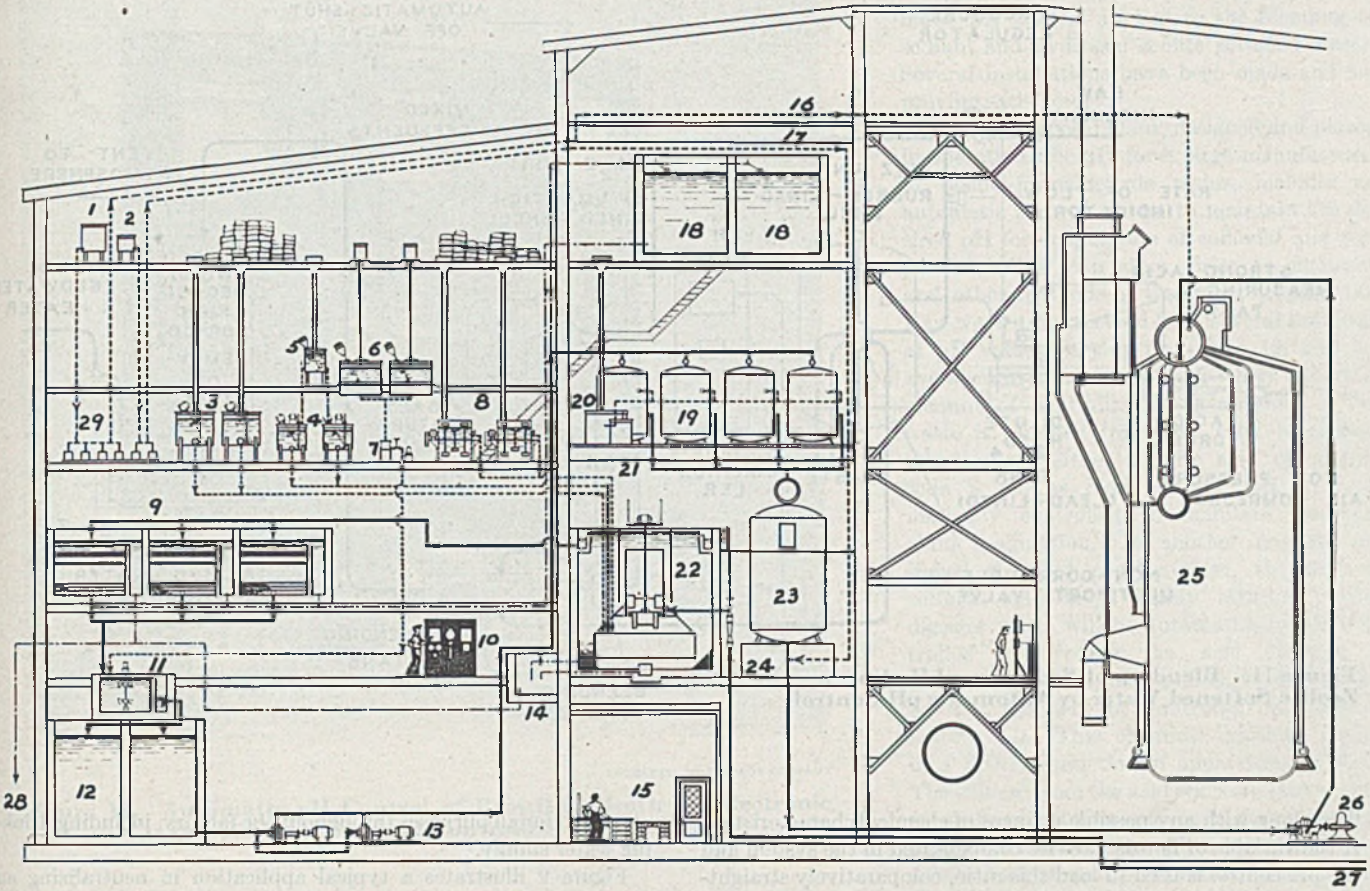


Figure 9. Flow Sheet of Boiler Feed Water Treatment of Republic Steel Corporation, with Automatic pH Control by Sulfuric Acid Following Lime Treatment and Prior to Zeolite

1. Phosphate
2. Sulfite
3. Soda ash feeders (2)
4. Ferric sulfate feeders (2)
5. Ferric sulfate dissolving tank
6. Sulfuric acid dilution tanks (2)
7. pH control acid feed
8. Lime feeders (2)
9. Gravity filters (3)
10. Meter panel
11. Neutralizer
12. Filtered water storage
13. Booster pumps (2)
14. Sludge sump
15. Laboratory
16. Chemical line to boiler drum
17. Sulfite line to feed water
18. Backwash water storage tanks
19. Carbonaceous zeolites (4)
20. Salt tank
21. Brine tank
22. Clarifier
23. Deaerating feed water heater
24. Raw water Venturi
25. Boiler
26. Boiler feed pump
27. Raw water in
28. To waste
29. Controlled-volume chemical pumps

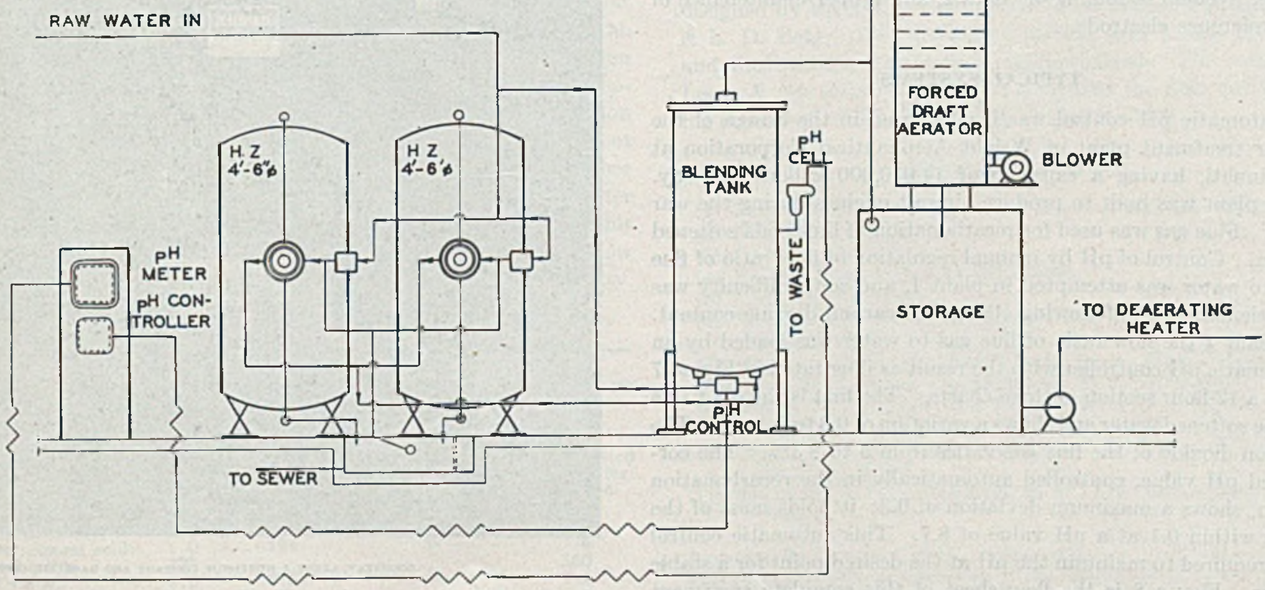


Figure 10. Blending of Raw and Hydrogen Zeolite Softened Water by Automatic pH Control (General Tire and Rubber Company)

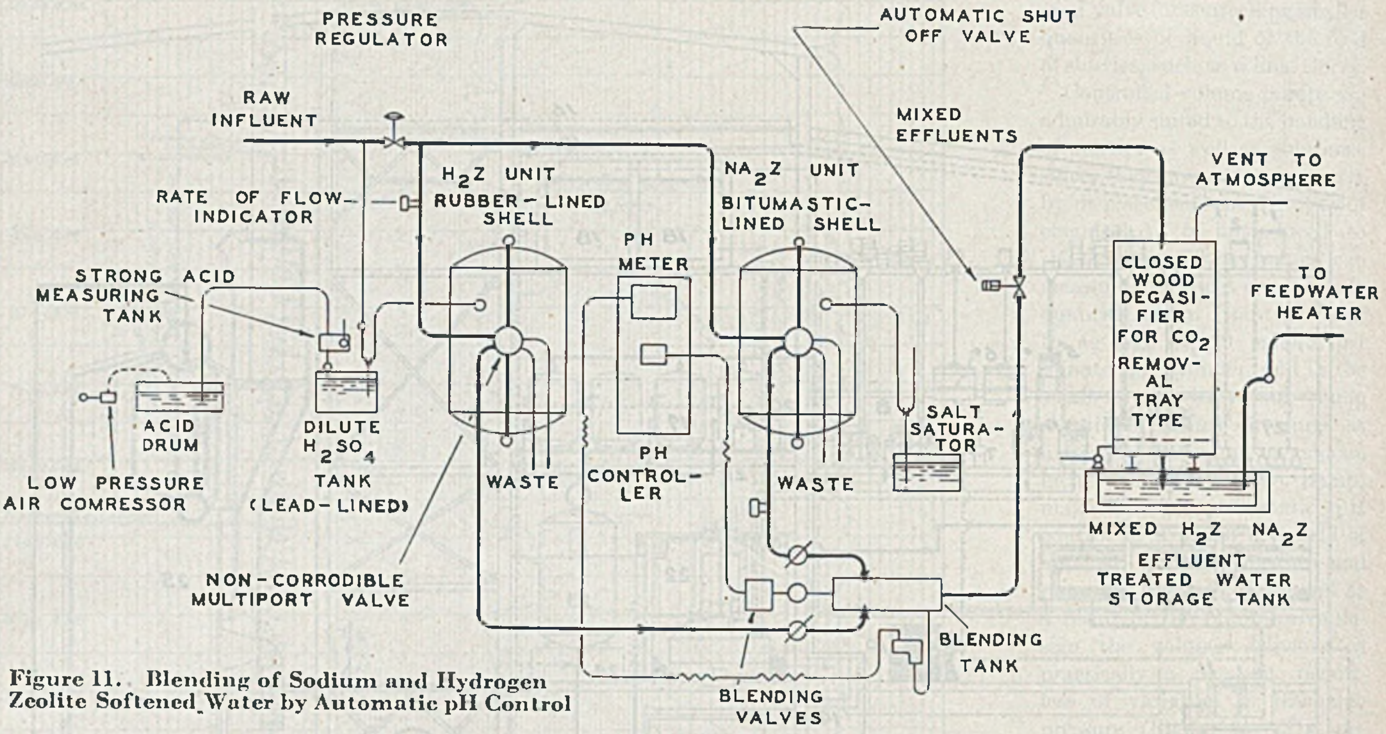


Figure 11. Blending of Sodium and Hydrogen Zeolite Softened Water by Automatic pH Control

flow along with any possible changes of chemical characteristics. If the variable of flow is likewise compensated in the system and the pH control is used to load this ratio, comparatively straight-line control can be obtained. On a controlled-volume pump this is done by operating the pump at a speed through an electronic control directly proportional to rate of flow and having the stroke length automatically regulated by the pH controller.

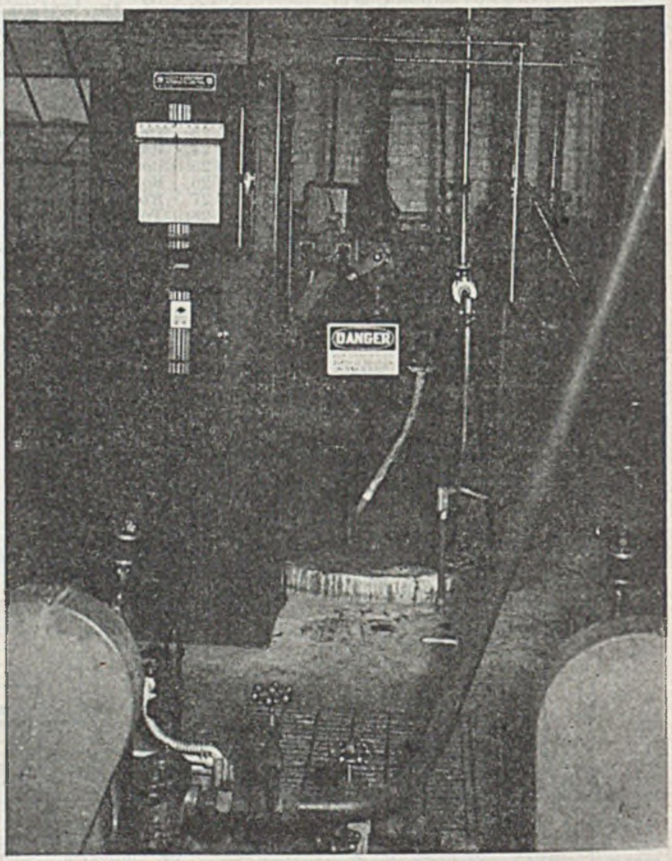
By various forms of interlocks it is also possible to impose the two variables (rate of flow and pH control) on both air-actuated and motor-operated valves; this practice is to be recommended where the variation in rate of flow of the raw liquid is appreciable.

The pH meters and controllers require some regular scheduled standardization and maintenance. Some models are available that include automatic standardization, others should be checked no less than once weekly. The pH cell with the glass electrode requires regular checking to ensure proper immersion of the electrode, freedom of fouling or coating, and proper maintenance of the reference electrode.

TYPICAL SYSTEMS

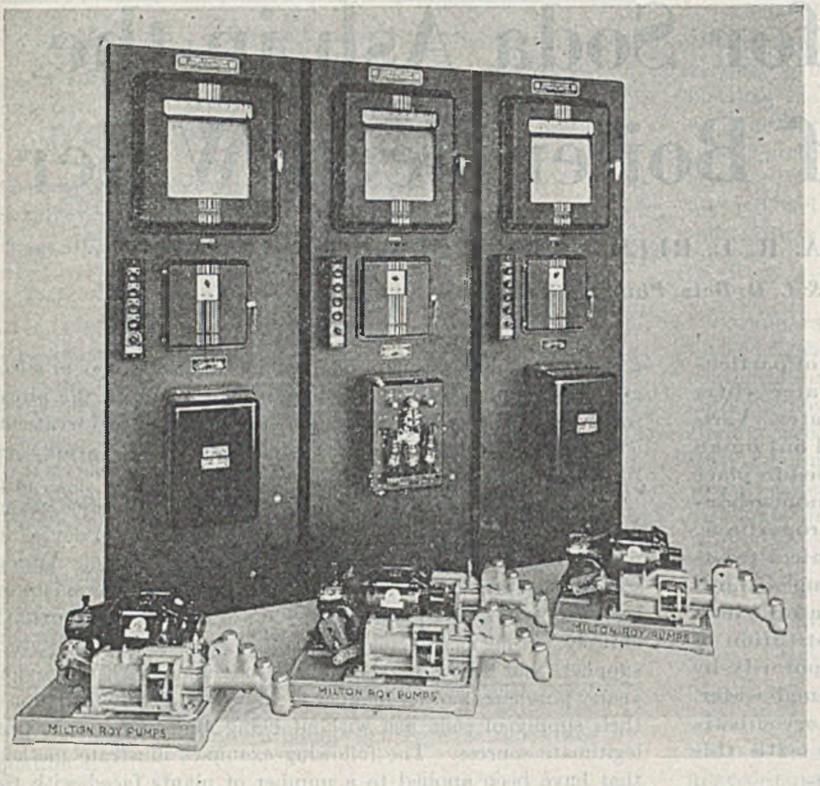
Automatic pH control was incorporated in the design of the water treatment plant of Wright Aeronautical Corporation at Cincinnati, having a capacity of 14,000,000 gallons per day. This plant was built to produce aircraft engines during the war (*10*). Flue gas was used for recarbonation of lime-soda softened water. Control of pH by manual regulation of flow ratio of flue gas to water was attempted in plant 1, and some difficulty was experienced in the following changes of carbon dioxide content. In plant 2 the flow ratio of flue gas to water was loaded by an automatic pH controller with the result as illustrated in Figure 7 with a 12-hour section of three charts. The first is the pH value of the softened water and shows a variation of 0.3 to 0.4 pH. The carbon dioxide of the flue gas varies from 5 to 8.3%. The corrected pH value, controlled automatically in the recarbonation basin, shows a maximum deviation of 0.3; it holds most of the time within 0.1 at a pH value of 8.7. This automatic control was required to maintain the pH at the desired point for a stable water. Figure 8 is the flow sheet of this complete treatment plant. Water from this plant was used for cooling aircraft engines and for all purposes throughout the factory, including drinking water supply.

Figure 9 illustrates a typical application in neutralizing an alkaline water prior to zeolite softening at the plant of Republic



COURTESY, LEEDS & NORTHRUP COMPANY AND BAKELITE CORPORATION

Figure 12. Automatic pH Control in Treatment of Phenol-Formaldehyde Waste



COURTESY, MILTON ROY COMPANY

Figure 13. Automatic pH Control of Penicillin Broth by Electronic Control of Motor Speed of Controlled-Volume Pump

Steel Corporation at Alabama City, Ala. (*8*). This treatment plant has a capacity of 400 gallons per minute.

The process is as follows: clarification and silica reduction by coagulation with ferric sulfate, lime, and soda ash at a pH of approximately 9.6; gravity filtration; pH-controlled sulfuric acid feed for neutralizing excess alkalinity to pH 7.5–8.0; carbonaceous zeolite softening; continuous sodium sulfite feed to boiler feed line; continuous internal treatment direct to boiler drum. Dilute sulfuric acid feed is employed in this case, controlled by a motor-operated valve. Rate of water flow through the plant is held constant with on-off flow as required to surge tank 12 so that correction for the single variable of pH proves satisfactory in this installation.

Hydrogen zeolite softeners have become increasingly popular in a number of recent installations. The maintenance of the proper residual alkalinity following the blending of the hydrogen zeolite softened water, either with raw water or with sodium zeolite water, is important to avoid any possibility of corrosion through the system. Figure 10 is an illustration of a flow sheet for an installation at the plant of General Tire and Rubber Company at Waco, Texas, where hydrogen zeolite treated water is automatically blended with well water by pH control. This combination was desirable in this case because of the very low hardness of the raw water supply and the high natural alkalinity. Table I shows typical analytical results of this control.

TABLE I. TYPICAL ANALYSIS OF WATER AT TREATMENT PLANT OF GENERAL TIRE AND RUBBER COMPANY

(In parts per million)

	Raw Water	Hydrogen Zeolite Treated	Blended (pH Controlled Automatically)	Final Treated Water after Aeration
Total hardness	14	0	6	6
Total alkalinity	370	0	46	44
Free mineral acid	0	135	0	0
Total solids	725	...	...	330
pH value	9.0	2.8	5.7	7.2

Figure 11 is a typical flow sheet for automatic pH control applied to the blending of sodium and hydrogen zeolite softened water. Several installations have been made and are proving satisfactory.

A waste disposal plant, designed and placed in operation recently for a large manufacturer of phenol-formaldehyde resins, includes an automatic control system to maintain the desired pH for coagulation of colloidal and suspended solids with alum, prior to filtration and other methods of treatment (Figure 12). Raw wastes are received from several buildings at pH values varying from 2 to 12, and are averaged in a raw surge tank where a certain amount of neutralization is obtained. The waste is pumped from this tank to a flash mixer where either sulfuric acid or caustic soda is fed as required, and pH is automatically controlled to maintain optimum alum coagulation. In another recently designed waste disposal system, the feed of sulfuric acid to a highly alkaline rubber digester waste will be automatically pH controlled by feeding the acid through a controlled-volume pump as illustrated by Figure 6. The pH will be controlled at approximately 3.0. This chemical cracking results in a B.O.D. reduction of approximately 40%. The effluent from the acid cracking tank will be neutralized with lime prior to further treatment.

Another installation (Figure 13) of three automatic pH controlled units, followed later by a fourth, has been made at a pharmaceutical laboratory for controlling the pH of penicillin broths. Two of these units control the feed of sulfuric acid to reduce pH to approximately 3.0; two others raise pH by regulating the feed of sodium carbonate, to maintain a control point of approximately 7.0. The speed of a controlled-volume pump is regulated through electronic control actuated by the pH controller.

The same principles of operation of automatic pH control now used successfully for treatment of water and waste can be and are being applied in many chemical processing operations.

ACKNOWLEDGMENT

The water treatment and waste disposal plants described were designed by the author at the time of his connection with W. H. & L. D. Betz. The permission of that firm to use these data and illustrations is gratefully acknowledged. The courtesy of Leeds & Northrup Company in reviewing the data and furnishing a number of the illustrations is appreciated.

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RECEIVED September 9, 1946. Presented before the Division of Water Sewage, and Sanitation Chemistry at the 110th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

Substitutes for Soda Ash in the Treatment of Boiler Feed Water

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The current shortage of soda ash is a matter of particular concern in the treatment of boiler feed water where lime-soda softening is used to treat make-up water. Various substitutes for soda ash have been worked out on an individual plant basis. Caustic soda can be used in place of lime and soda ash where the carbonate and noncarbonate hardness of the raw water are in the proper proportions. In some cases alteration of the internal chemical treatment of the boiler water permits lime softening without soda ash, and in others recirculation of boiler water to hot-process lime-soda softeners is effective. Substitution of zeolite mineral in a filter bed can serve temporarily by blending the zeolite effluent with lime-softened water. Barium carbonate has been used as a satisfactory substitute for soda ash although the higher cost with this chemical restricts its use to emergency periods.

THE nationwide chemical shortage, particularly of caustic soda and soda ash, has resulted in production difficulties in many industries. Soda ash is one of the most important chemicals used in the treatment of boiler feed water, and the production of power and steam is dependent on the properly controlled treatment of this feed water. Without properly treated boiler water, unscheduled boiler outages from scale and corrosion cause interruptions in plant operation and shutdowns.

One of the most commonly used methods for the external softening of boiler feed water is the lime-soda process, operated both hot and cold. Hydrated lime and soda ash are employed to precipitate the scale-forming calcium and magnesium ions from the raw water; these form insoluble precipitates of calcium carbonate and magnesium hydroxide which are separated from the softened water by sedimentation and filtration.

Lime is required for the precipitation of magnesium and the removal of the calcium bicarbonate hardness as follows:

$$MgSO_4 + Ca(OH)_2 = CaSO_4 + Mg(OH)_2 \quad (1)$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2CaCO_3 + Mg(OH)_2 + 2H_2O \quad (2)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O \quad (3)$$

Soda ash is needed to remove calcium noncarbonate hardness present in the raw water and also to precipitate the calcium chloride, calcium sulfate, etc., produced in the precipitation of magnesium salts by lime:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \quad (4)$$

When soda ash is unavailable for lime-soda softening, the effluent from the treatment process may be quite high in hardness. Use of unsoftened or partially softened make-up water would be disastrous in many cases of boiler operation under high pressure, despite increased application of internal treatment of boiler water. To maintain boilers on line during temporary interruptions in soda ash supply or under continuously curtailed supply conditions constitutes a problem often capable of solution by altering chemical balances throughout the system or by substituting treatment chemicals not usually considered feasible from an economic viewpoint. Where the continued operation of a complete industrial plant is dependent on the power or steam generation which, in turn, is directly dependent on the proper softening of the boiler feed water, increased chemical treatment costs of ten, fifty, or a hundred dollars per day are readily justified if continued plant operation can be assured.

During the past few years different systems of altered chemical balances and altered chemical treatment have been devised to permit continued and uninterrupted plant operation. Various substitution products and methods have been given consideration either to reduce the quantity of soda ash used or to eliminate it entirely. Some of the plants involved were advised by their suppliers that they would be allotted only about 70% of previous yearly purchases; other plants were faced with early depletion of their supply of soda ash without being able to renew it from legitimate sources. The following examples illustrate methods that have been applied to a number of plants faced with this shortage.

CAUSTIC SODA

While most of the sodium salts were scarce, some plants had available caustic soda which was utilized in place of soda ash (*4*). Actually, caustic soda is utilized in place of lime and as a result of this substitution, soda ash is formed; Equations 5, 6, and 7 illustrate the softening reactions using caustic soda.

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O \quad (5)$$

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4 \quad (6)$$

$$Mg(HCO_3)_2 + 4NaOH = Mg(OH)_2 + 2Na_2CO_3 + 2H_2O \quad (7)$$

Equations 5 and 7 show that soda ash is produced when caustic soda reacts with calcium or magnesium bicarbonate hardness. The soda ash thus becomes available for softening calcium sulfate hardness (Equation 4). Depending on the characteristics of the raw water, complete softening may be brought about by caustic soda alone or by a combination of lime and caustic soda. However, on waters that consist predominantly of noncarbonate hardness caustic soda can accomplish only partial softening. In general, caustic soda alone can be utilized for softening waters that possess a methyl orange alkalinity that exceeds half of the calcium content by 15 to 30 p.p.m. (Table I). Where methyl orange alkalinity exceeds half the calcium content of the water by more than 30 p.p.m., a combination of lime and caustic soda should be utilized to avoid an excessive alkalinity of the softened water. Waters that possess a methyl orange alkalinity less than half the calcium content can be only partially softened by caustic soda alone.

BOILER WATER RECIRCULATION

In many cases soda ash requirements have been partially reduced by recirculating boiler water blowdown to the softener, and thus making use of the caustic soda and soda ash content of the boiler water to replace a portion of the lime and soda ash normally used in the softening operation (*1, 2, 3, 7, 9, 10, 12*). Softening reactions follow Equations 4, 5, 6, and 7. Since the major portion of the boiler water alkalinity exists as caustic soda, the additional soda ash produced in Equations 5 and 7 is of bene-

Table I. Applicability of Caustic Soda

Raw Water Characteristics[a]	Treatment	Degree of Softening
$M < \frac{1}{2}Ca$	Caustic soda	Partial
$M = \frac{1}{2}Ca + (15\text{–}30 \text{ p.p.m.})$	Caustic soda	Complete
$M > \frac{1}{2}Ca + 30 \text{ p.p.m.}$	Caustic soda and lime	Complete

[a] M (methyl orange alkalinity) and Ca as $CaCO_3$.

Table II. Analyses with and without Boiler Water Recirculation

	Without Recirculation[a]			With Recirculation[b]		
	Raw	Lime-soda softened	Boiler	Raw	Lime-soda softened	Boiler
Hardness as $CaCO_3$, p.p.m.	180	20	0	180	20	0
Ca as $CaCO_3$, p.p.m.	120	16	...	120	16	...
Mg as $CaCO_3$, p.p.m.	60	4	...	60	4	...
Alkalinity as $CaCO_3$, p.p.m.						
Phenolphthalein	0	32	630	0	32	336
Methyl orange	120	60	700	120	60	374
Sulfate as SO_4	35	35	538	35	65.5	538
Chloride as Cl	10	10	154	10	19	154
Phosphate as PO_4	...	..	60	...	..	60
pH	7.3	10.1	11.7	7.3	10.1	11.5

[a] Lime requirement, 147 p.p.m. on raw water; soda ash, 106 p.p.m. on raw water. 6.5% boiler water blowdown (69,500 pounds per million pounds steam).

[b] Lime requirement, 132 p.p.m. on raw water; soda ash, 84 p.p.m. on raw water. 6.5% system blowdown (139,000 pounds per million pounds steam, of which 69,500 pounds are returned to softener).

lit in the removal of noncarbonate hardness as illustrated by Equation 4.

Table II shows the normal balances maintained on a hot process softener and the resulting boiler water characteristics, as well as the balances utilizing boiler water recirculation to the softener to bring about a reduction in soda ash requirements. As a result of recirculation, the reduction in lime requirements was approximately 10% and in soda ash requirements, 21%. A normal balance was maintained on the softener, and all factors of the boiler water balance remained the same with the exception of boiler water alkalinity. The reduction of boiler water alkalinity is a direct result of consuming it in the softening process. In many cases reduction in boiler water alkalinity is a desirable feature to minimize carry-over that may result from excessive boiler water alkalinity; boiler water is often recirculated solely for this purpose. In general, the application of boiler water recirculation to waters that consist predominantly of carbonate hardness brings about a greater percentage saving in soda ash than is covered by the case cited. Noncarbonate hardness waters involve only a minor percentage savings in the soda ash requirements.

ZEOLITE SOFTENING

A few of the plants faced with the need for reducing soda ash requirements had enough filters and filtering capacity to permit conversion of one of the filters to a zeolite softening unit, operated on the sodium cycle. In the zeolite softening process calcium and magnesium hardness is removed in exchange reactions with sodium ions substituted for the calcium and magnesium:

$$Ca(HCO_3)_2 + Na_2Z = CaZ + 2NaHCO_3 \quad (8)$$

$$MgSO_4 + Na_2Z = MgZ + Na_2SO_4 \quad (9)$$

Reaction 8 shows that the bicarbonate hardness is converted to sodium bicarbonate. When the zeolite softened water is blended with the raw water, the resulting characteristics are such that the hardness becomes totally carbonate. Table III shows the make-up of the blended water and the resulting softened water, which brought about a saving of 8% in lime and 60% in soda ash. At the same time the external chemical treatment cost was slightly lower with this treatment than was obtained by the normal procedure. By softening increased percentages of the raw water by the zeolite process, the use of soda ash could be totally eliminated.

In some of the plants employing batch cold-process lime-soda softeners with gravity filters, consideration was given to converting one of the gravity filters to a gravity zeolite softener and blending the effluents of both softening processes to produce a water as illustrated in Table IV. The quantity of soda ash saved by this procedure was in proportion to the amount of water softened by the zeolite unit. Since only 75% of the make-up water was softened by the lime-soda process, a direct saving of 25% in soda ash was achieved.

BARIUM CARBONATE

Barium carbonate was considered an emergency substitute for soda ash. Lime-barium softening for reducing the sulfate concentration is a process of historical interest but is in use, to the authors' knowledge, at only one plant in this country (*5, 6, 8, 11*). Barium carbonate was applied during the soda ash shortage, not with the primary intention of reducing the sulfate content of the treated water, but rather to obtain the advantage of the sodium carbonate produced as a by-product of sulfate removal:

$$Na_2SO_4 + BaCO_3 = BaSO_4 + Na_2CO_3 \quad (10)$$

$$CaSO_4 + BaCO_3 = BaSO_4 + CaCO_3 \quad (11)$$

$$MgSO_4 + BaCO_3 = BaSO_4 + CaSO_4 \quad (12)$$

$$MgCO_3 + Ca(OH)_2 = CaCO_3 + Mg(OH)_2 \quad (13)$$

As reaction 10 shows, sodium carbonate is formed by the reaction between barium carbonate and sodium sulfate present in the raw water. The sodium carbonate is then available for use in accordance with reaction 4. In addition, as reactions 11, 12, and 13 show, calcium sulfate and magnesium sulfate can be removed without the use of soda ash.

Table III. Blending of Zeolite Softened Water Prior to Lime-Soda Softening (in Parts per Million)

	Raw[a]	Zeolite-Softened	Blended[b]	Lime-Soda Softened
Hardness as $CaCO_3$	160	4	121	20
Ca as $CaCO_3$	110	...	84	16
Mg as $CaCO_3$	50	...	37	4
Alkalinity as $CaCO_3$				
Phenolphthalein	0	0	0	32
Methyl orange	130	130	130	60
Sulfate as SO_4	30	30	30	30
Chloride as Cl	12	12	12	12

[a] Chemical requirements: lime, 149 p.p.m.; soda ash, 68 p.p.m.

[b] 75% raw water, 25% zeolite-softened. Chemical requirements: lime, 137 p.p.m.; soda ash, 27 p.p.m.; salt, 140 p.p.m.

Table IV. Blending of Zeolite Softened Water with Lime-Soda Effluent (in Parts per Million)

	Raw	Lime-Soda Softened	Zeolite Softened	Blended[a]
Hardness as $CaCO_3$	220	35	4	28
Ca as $CaCO_3$	160	25	...	..
Mg as $CaCO_3$	60	10	...	..
Alkalinity as $CaCO_3$				
Phenolphthalein	0	45	0	35
Methyl orange	100	80	100	85
Sulfate as SO_4	80	80	80	80
Chloride as Cl	30	30	30	30

[a] 75% cold lime-soda softened, 25% zeolite-softened.

In some cases where the natural sodium sulfate content of the raw water was insufficient to produce the desired sodium carbonate excess required in the softener effluent, it was necessary to feed sodium sulfate to the softener and thereby produce soda ash directly in accordance with reaction 10.

Theoretical efficiency in the use of barium carbonate to produce soda ash has not been obtained in either laboratory test or full scale plant operation. Barium carbonate can be used in both hot and cold softening, but its action is more efficient in the hot (Table V).

Table V illustrates hot process tests in which normal softening action is obtained with theoretical quantities of lime and soda

TABLE V. RESULTS OF LABORATORY TESTS ON HOT AND COLD PROCESSES WITH BARIUM CARBONATE

	Hot Process[a]						Cold Process[b]								
	Raw water	Treated waters					Raw water	Treated waters							
% of theoretical requirements															
Lime	...	100	100	100	100	100	...	100	100	100	100	100	100	100	100
Soda ash	...	...	100	...	...	...	...	...	100	...	...	...	...	...	...
Barium carbonate	...	...	...	100	100	150	...	...	...	100	100	150	200	250	300
Sodium sulfate	...	...	...	100	150	150	...	...	...	100	150	150	200	250	300
Amounts used, p.p.m.															
Lime	...	172	172	172	172	172	...	172	172	172	172	172	172	172	172
Soda ash	...	...	200	...	...	...	...	...	200	...	...	...	...	...	...
Barium carbonate	...	...	...	370	370	555	...	...	...	370	370	555	740	925	1110
Sodium sulfate	...	...	...	223	334	334	...	...	...	223	334	334	466	558	670
Analysis, p.p.m.															
Hardness as $CaCO_3$	248	176	16	68	52	38	248	176	24	112	118	96	66	60	56
Ca as $CaCO_3$	168	174	14	55	30	23	168	172	21	105	101	77	42	33	31
Mg as $CaCO_3$, p.p.m.	80	2	2	13	22	15	80	4	3	7	17	19	24	27	25
Alkalinity as $CaCO_3$															
Phenolphthalein	0	6	16	6	12	12	0	26	46	26	26	26	36	48	54
Methylorange	100	16	40	24	38	44	100	34	64	38	40	36	52	74	92
Sulfate as SO_4	30	30	30	80	128	96	30	30	30	112	176	152	192	248	296
Chloride as Cl	164	164	164	164	164	164	164	164	164	164	164	164	164	164	164

[a] Conditions of test: 1-hour retention, 200° F., 1.0-liter samples.

[b] Conditions of test: 4-hour retention, 80° F., 1.0-liter samples.

ash. Lime alone is effective in precipitation of magnesium, but obviously additional softening power is required to reduce the calcium content. Using theoretical quantities of barium carbonate and sodium sulfate as substitutes for soda ash yields reasonably satisfactory results, with reduction in calcium to 55 p.p.m. as calcium carbonate. Further improvement in lowering the hardness of the treated water is obtained with additional barium carbonate and sodium sulfate.

Table V also shows the results of cold process tests with the same raw water. Application of theoretical quantities of barium carbonate and sodium sulfate does not achieve the same degree of hardness removal as secured at higher temperatures. Increased quantities of barium carbonate and sodium sulfate show steadily decreased calcium contents of the softened water, but these data indicate that this process is considerably less efficient at lower temperatures, possibly as a result of lower barium carbonate solubility at lower temperatures.

The insoluble barium sulfate precipitate formed in these reactions is removed along with the calcium carbonate and magnesium hydroxide through sedimentation and filtration as in normal lime-soda softener operation. Inasmuch as barium salts are toxic, qualitative barium determinations were conducted on the softener effluent, and the efficiency of filtration was also checked closely to make certain of the removal of the finely divided barium sulfate precipitate. Only small traces of barium were observed.

During initial application of barium carbonate to plant operation, the raw make-up water to the softener was depended upon to supply the amount of sulfate required for barium precipitation. Sulfate removal taking place during this process decreases the dissolved solids of the softener effluent, which is beneficial in numerous applications. Further analyses revealed that 100% of the natural sulfate content of the raw water did not react with the barium carbonate, but rather a sulfate residual of 20–40 p.p.m. as SO_4 remained in the softener effluent. Consequently, not enough carbonate was produced to yield as complete noncarbonate hardness removal as desired. Barium carbonate fed considerably in excess of theoretical requirements failed to produce further sulfate or hardness reduction. Excess barium carbonate feed without the sulfate available for precipitation was simply wasted, since this material remained in an insoluble, inert form.

Table VI illustrates the results obtained in field tests with barium carbonate in conjunction with a hot process lime-soda softener, having a capacity of 10,000 gallons per hour and operating at 218° F. Somewhat greater than theoretical quantities of barium carbonate were required, varying from 25–40%. The reason for this condition has not been closely investigated but was possibly due to an insoluble barium sulfate coating on the barium carbonate particles. In addition, slightly larger lime charges were required, of the order of approximately 10%. In general, reasonably good agreement is observed between laboratory and field tests on the hot process use of barium carbonate.

The use of barium carbonate in place of soda ash does not require alteration of normal softener control procedures, so no disadvantage has been encountered in this phase of operation. Lime control can be established on the basis of maintaining certain residual hydrate alkalinity values, and barium carbonate can be regulated to develop optimum excess carbonate alkalinity concentrations. Determinations for excess sodium sulfate would not be imperative since experience proved that the feed of this material, if required, could be adjusted in direct ratio to the barium carbonate charges.

Some state health authorities consider the barium-containing sludge to be a health hazard and will not permit it to be dumped in waterways. Potential users of barium carbonate process who must discharge sludge to streams and rivers should seek information concerning the attitude of their state health authorities before installing the process.

TABLE VI. RESULTS OF FIELD TESTS WITH THE HOT PROCESS (IN PARTS PER MILLION)

	Raw Water	Softener Effluents No. 1[a]	No. 2[b]	No. 3[c]	No. 4[d]	No. 5[d]
Hardness as $CaCO_3$	188	50	38	22	16	14
Ca as $CaCO_3$	122	40	28	..	14	12
Mg as $CaCO_3$	66	10	10	..	2	2
Alkalinity as $CaCO_3$						
Phenolphthalein	0	26	16	26	30	30
Methyl orange	48	40	34	40	50	52
Sulfate as SO_4	152	24	32	28	24	36
Chloride as Cl	8	8	8	8	8	8

[a] Theoretical lime and barium carbonate; no sodium sulfate.

[b] Theoretical lime; 50% excess barium carbonate; no sodium sulfate.

[c] 10% excess lime; 25% excess barium carbonate and sodium sulfate.

[d] 10% excess lime; 40% excess barium carbonate and sodium sulfate.

Assuming reaction 10 to proceed at 100% theoretical efficiency, the cost of the soda ash thus produced is 6.2 cents per pound. This cost is based on 3.25 cents per pound for barium carbonate of 98% purity and sufficient natural sulfate content of the raw water to complete the reaction. Where sodium sulfate must be supplied for the reaction, based on a cost of 2.1 cents per pound for this chemical, the cost of thus producing soda ash is 9.0 cents per pound. Where higher than theoretical quantities of barium carbonate and sodium sulfate are necessary, the cost of producing soda ash is correspondingly increased.

All applications proved that barium carbonate gave as great a hardness reduction as possible with the conventional use of soda ash. Obviously, operating chemical costs increased as a result of the cost of barium carbonate in comparison with soda ash and also the necessity of employing sodium sulfate in a large number of cases. However, the use of barium carbonate enables normal softening operations to be maintained during emergency periods when the soda ash supply may be inadequate, and thereby permits continuous operation without fear of interrupted production.

ACKNOWLEDGMENT

The authors wish to thank J. W. Polsky, who conducted the majority of the laboratory tests, and also express appreciation to W. H. & L. D. Betz for permission to present these data.

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RECEIVED September 6, 1947. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 112th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y.

Butanol-Acetone Fermentation of Wood Sugar

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Wood hydrolyzates were fermented with *Clostridium butylicum* No. 39 to butanol and acetone. The wood species and method of hydrolysis affect the fermentability of the liquors. Very mild or very vigorous conditions of hydrolysis do not produce an easily fermentable solution. Complete utilization of sugar could be obtained up to 3% concentrations. Solvent yields ranged from 24 to 38% of the sugar fermented.

THE fermentation of wood hydrolyzates by butanol-acetone bacteria is difficult. Sjolander, Langlykke, and Peterson (*10*) conducted butanol-acetone fermentations on hydrolyzates prepared by a method similar to the Scholler process and obtained a fermentable medium after precipitation of metals at pH 10, neutralization, and clarification with Norite decolorizing carbon. In the present paper other types of hydrolyzates have been studied, and attempts have been made to simplify the pretreatments for fermentation.

Two cultures had previously been selected for wood sugar fermentations: *Cl. felsineum* Carbone No. 41 by Sjolander *et al.* (*10*) for hydrolyzates and *Cl. butylicum* (Fitz strain) No. 39 by Wiley *et al.* (*11*) for sulfite waste liquor fermentation. These two cultures, as well as *Cl. butylicum* No. 37, *Cl. beijerinckii* No. 67, and *Cl. butylicum* No. 69, were compared on wood hydrolyzate, and No. 39 was selected as the most suitable organism. Fermentations were conducted with cultures transferred three to five times from the spore stock. Nutrients were supplied by 1% malt sprouts and 0.1% $(NH_4)_2HPO_4$. A trace of reduced iron was added to the media before autoclaving. From 0.1 to 0.3% calcium carbonate was added to the media after inoculation. Inoculum was produced on glucose–malt sprouts medium and used after 12 to 20 hours at 8% of the fermentation volume.

Determination of reducing sugars was made by the method of Shaffer and Somogyi (*9*); furfural by a colorimetric method (*1*); ethanol and butanol by Johnson's procedure (*6*); and acetone by Goodwin's method (*3*). Volatile acids were determined by titration of 11 volumes of distillate from 1 volume of sample.

Hydrolyzates of maple and spruce were prepared in a rotary digester similar to that described by Plow *et al.* (*8*). Maple sawdust was hydrolyzed by 3% sulfuric acid with an acid-wood ratio of 1:1 at 181° C. for 30 minutes. A milder hydrolysis of maple and of spruce was made with 1.8% acid, ratio 1:1 at 173° C. for 5 minutes. Oak and Douglas fir were hydrolyzed by the Madison wood sugar process as described by Harris and Beglinger (*4*). These samples were neutralized to pH 4.2 with lime at 138° C. (*4*, *7*). The oak sample represented the first 25% of the hydrolyzate received from the digester, and the Douglas fir liquor was from a normal run.

FACTORS AFFECTING FERMENTATION

It was first desirable to repeat the results of Sjolander *et al.* In their work the amount of decolorizing carbon was not stated, and it was found that with maple hydrolyzate, following their procedure, 10 to 20 grams of Norite decolorizing carbon per 100 ml. were required to duplicate their fermentation results. Fermentation of high temperature maple hydrolyzate prepared in this manner showed that 92% of the sugar in a 4.04 grams per 100 ml. solution was fermented in 5 days. The quantity of decolorizing carbon was found to be important; the use of 1 gram per 100 ml. resulted in the fermentation of 25% of the sugar, 5 grams gave 64%, 10 grams gave 72%, and 20 grams gave 93%. After the furfural was removed from the sample, the quantity of carbon required was decreased to less than 5 grams per 100 ml. The pH was found to be important, since 1 gram of carbon at pH 2.0 gave 17% fermentation, while 1 gram at pH 6.8 gave 51%.

The difficulty found with maple wood hydrolyzates was also found with spruce, Douglas fir, and oak. The fermentations were characterized by a long induction period and a slow sugar utilization. In some samples much of the inhibition could be accounted for by the presence of furfural—for example, the maple hydrolyzate made at 181° C. contained from 0.5 to 0.8 gram of furfural per 100 ml. On synthetic medium 0.1% furfural decreased the fermentation by 15%. Hydrolyzates containing more than 0.1% furfural stopped the development of the bacteria completely. Furfural was removed easily by distillation or by passing the liquor through a steam stripping column. When furfural was added back to the stripped liquor, the fermentations were not inhibited to the same extent as initially. This indicated that substances other than furfural were removed by the distillations.

When the concentration of the inhibitory substances was decreased by dilution of the liquor, the extent of fermentation was improved. Complete fermentation of sugars in wood hydrolyzates was usually obtained at about 3% concentration. With glucose–malt sprouts medium 5% concentration was about the maximum quantity which could be completely fermented with

Table I. Effect of Dilution on Fermentation

Source of Sugar	Fermentation Period, Hr.	Initial Sugar, G./100 Ml.	Amount Fermented[a], %
Glucose	90	6.50	81
	90	4.95	99
	65	4.00	98
Xylose	65	4.00	49
Glucose and xylose, 1:1	65	4.00	95
Spruce, 173° C.	120	6.40	37[b]
	120	4.85	62[b]
Maple, 173° C.	120	4.65	44[c]
	120	3.90	83[c]
Maple, 181° C.	90	4.65	71
	90	3.45	86
Oak	65	5.45	59
	65	4.16	86
	65	3.12	91
Douglas fir	65	3.95	40

[a] Media contained less than 0.02% furfural except for cases noted below.
[b] Media contained 0.03% furfural.
[c] Media contained 0.09% furfural.

the organism used. Xylose did not ferment so well as glucose and usually gave acids rather than neutral products. Wood sugars were more difficult to ferment, and frequently a quantity of sugar corresponding to the hexose fraction, as determined by yeast fermentation, was utilized, and the remainder was left untouched. Data are shown in Table I.

Since furfural was a minor constituent of these liquors, most of the inhibition results from the action of other substances. The data are too diverse to permit definite conclusions. The softwoods could contain wood oils, but spruce was found to ferment more easily than maple or oak, and Douglas fir was more difficult than either oak or maple. A partial explanation may be found in the fact that, under comparable conditions of hydrolysis, maple produces more pentose, furfural, and furfural degradation products than does spruce. In the vertical hydrolyzer the sugars are subjected to somewhat more vigorous conditions than in the single stage hydrolysis.

Alkaline precipitation was first applied as a means of removing metals (*10*). It may also produce reducing substances from sugars (*7*). If reduction were a prime factor for induction of the butanol fermentation, then the addition of a reducing agent other than reduced iron would be favorable. Some results are shown in Table II. The reduced iron can be replaced with sodium sulfite. Alkaline precipitation usually improved fermentations containing reduced iron. Metals were not present at inhibitory concentrations in the liquors used. The action of the alkaline precipitation in improving the fermentation is difficult to explain; it may result from the removal of some type of solid indicator acid coming from degradation products of furfural as described by Dunlop, Stout, and Swadesh (*2*).

Table II. Effect of Alkaline Precipitation and Reducing Agents on Fermentation

Treatment[a]	Source of Liquor	Initial Sugar, G./100 Ml.	Amount Fermented, %
None	Maple, 173° C.	6.16	2
Alkaline pptn.		6.16	35
None	Spruce, 173° C.	5.04	39
Alkaline pptn.		5.04	55
Alkaline pptn., iron omitted		5.04	62
None	Douglas fir	3.95	40
Added 0.1% Na_2SO_3		3.95	59
Alkaline pptn.		3.95	87
None	Oak	5.45	58
None		5.20	78
Added 0.1% Na_2SO_3		5.45	60
Added 0.1% Na_2SO_3, iron omitted		5.45	61
Alkaline pptn.		5.45	52

[a] Furfural-free medium containing reduced iron unless otherwise indicated.

Various other methods have been tried for improvement of the liquors for fermentation purposes. Precipitation with zinc, lead, barium, and iron salts were of no use. Clarification procedures employing carbons, lignin, sawdust, and proteins were useful only when the agents were applied at 1 to 20% concentrations.

The inhibitory substances are not present in maple wood before hydrolysis, since up to 10 grams of sawdust per 100 ml. did not harm the fermentations. The inhibitory materials originate during hydrolysis and, since they are not metals, must come from the wood.

In nearly every case yeast fermented the hydrolyzates more easily than did bacteria. For example, yeast fermented 60% of the sugars in maple liquor and No. 39 only 23%. However, it is necessary to employ large amounts of yeast for inoculum in the alcohol fermentation; this is not a feasible procedure in a bacterial fermentation.

EFFECT OF HYDROLYSIS

In order to obtain information on why the hydrolyzates were so difficult to ferment, the effect of the method of hydrolysis was studied for a simple case. Previous demonstrations of the effect of hydrolysis on fermentation have not been clearly made. Russian workers, Zubkova, Kochukova, and Zats (*12*), have summarized the difficulties of relating the fermentation data with the method of hydrolysis and suggest that the optimum fermentation conditions should be determined for each type of hydrolysis procedure. Harris *et al.* (*5*) published fermentation data for various hydrolysis procedures. However, the drastic conditions required to hydrolyze wood produce so much inhibitory material in the liquors that any hydrolysis variables that might affect the fermentation are not evident. For the most part the only known fermentation differences are dependent upon the total yield in quantity of sugar and the relative composition of fermentable hexose and pentose.

Table III. Effect of Period of Hydrolysis on Extent of Fermentation

Period of hydrolysis, min.	0	10	30	90
Products, % of dry wood[a]				
Insol. residue	71.9	66.1	58.0	64.6
Reducing sugar as glucose	15.3	18.8	15.0	11.5
Furfural	0.0	2.5	4.4	4.0
Volatile acid as acetic	3.6	4.5	5.0	4.9
Other sol. substance, difference	9.2	8.1	17.6	15.0
Moisture in press cake, %	41.5	47.4	49.6	50.4
Hydrolyzate liquor, lb.	14.0	21.6	21.2	25.6
Compn. of hydrolyzate, g./100 ml.				
Reducing sugar as glucose	10.9	8.7	7.1	4.5
Furfural	0.02	0.28	0.42	0.35
Volatile acid as acetic	2.3	1.7	1.8	1.4
Extent of fermentation as % of sugar at initial concn. of				
1 g./100 ml.	94	95	96	96
2 g./100 ml.	75	95	96	96
3 g./100 ml.	64	92	89	86
4 g./100 ml.	57	81	79	76
5 g./100 ml.	50	72	70	67
6 g./100 ml.	45	63	63	..
Yield of neutral solvents, % of fermented sugar	30	25	28	28

[a] Maple sawdust, 3% acid on wood, 1:1 water-wood ratio, 181° C.

After preliminary work four hydrolyses were carried out on bark-free air-dry maple sawdust. Hydrolysis of 10 pounds of sawdust was accomplished with 3% sulfuric acid (on weight of wood), a ratio of acid solution to wood of 1:1 at 181° C. The hydrolysis period was varied from 0 to 90 minutes; the 0-minute period was obtained by heating the charge to 181° and then blowing immediately. With a preheated digester about 1 minute was needed to reach the required temperature with occasional venting of gases during this period. The temperature was maintained by manual control. The digester was relieved through a condenser capable of permitting a pressure drop to atmospheric in about 2 minutes without loss of vapors other than noncondensable gases. The contents were removed quantitatively.

When the pressure within the digester was lowered rapidly, many of the wood particles were ruptured by expansion of steam inside the wood, and considerable mechanical disintegration and mixing occurred.

The wet residue was pressed in a lever-action screw press until all possible liquor was removed. Comparison of free-draining hydrolyzate with the press liquor showed that, with rapid blowdown of the digester, the two liquors were nearly identical. Analytical values per 100 ml. of drainings and press liquor were, respectively, 7.08 and 6.93 grams of sugar, 1.05 and 1.05 grams of sulfuric acid, 1.46 and 1.46 grams of volatile acid as acetic, and 0.56 and 0.36 gram of furfural. Since agreement was good, the two liquors were mixed together. It was assumed, therefore, that the residual water in the press cake contained the same concentrations of sugar and other substances that were found in the press liquor. It was possible to calculate from the data the percentage composition of the hydrolysis products formed from the wood. Results are shown in Table III.

The hydrolyzates were steam-stripped to less than 0.05% furfural, neutralized with lime to pH 6.8 and filtered. Dilutions to various initial sugar concentrations were made, and then the samples were fermented for 5 days. The amount of sugar fermented in duplicates was expressed as per cent of the initial sugar content. The results are shown in Table III.

The four hydrolyzates all fermented to the same extent with 1% initial sugar concentration. No appreciable quantity of polysaccharides could have been present. Maximum yield of sugar and fermentability were obtained with the 10-minute period. Hydrolysis for periods longer than 10 minutes decreased the fermentability, the yield of sugar, and the insoluble residue. As the period of hydrolysis was increased, the moisture content of the press cake, the per cent of furfural, and the per cent of unidentified soluble products increased.

Explanation of the poor fermentability of the 0-minute cook is based on the degradation products from the wood. Since the furfural formation was small, the substance causing this early inhibition must have been derived from degradation of noncarbohydrate material. It was found that the residue after hydrolysis had no detrimental effect when added to the fermentation medium; in fact, in some cases the addition improved the fermentation. The improved fermentability at 10 minutes would indicate that these first-formed substances were destroyed with extended hydrolysis. As the hydrolysis period was lengthened further, the carbohydrate degradation to furfural proceeds, and the furfural is apparently decomposed gradually with the formation of a second class of inhibitory materials.

SOLVENT YIELD

The yield of solvents from fermentation of wood hydrolyzates was low, since it was difficult to obtain complete fermentation of reasonably high sugar concentrations. Frequently the fermentations become acid and stop. Some typical results are shown in Table IV for fermentations of furfural-free liquor neutralized to pH 6.8. Neutral solvents varied from 24.5 to 38.5% of the sugar fermented, or from 5.6 to 14.1 grams per liter. Apparently it was more difficult to obtain a high yield of solvents from the hydrolyzates made at higher temperatures or acid concentrations than from those made under milder conditions of hydrolysis.

PRODUCTS CALCULATED PER TON OF WOOD

Utilization of maple wood by fermentation of single-stage hydrolyzates would require, per ton of dry wood, 60 pounds of sulfuric acid, 100 pounds of hydrated lime, 40 pounds of malt sprouts, 4 pounds of dibasic ammonium phosphate, and 12 pounds of calcium carbonate. The yield of neutral solvents varied between 75 and 100 pounds per ton. In addition about 50 pounds of furfural and 120 pounds of calcium acetate are present in the neutralized hydrolyzates from which the furfural must be removed before fermentation. Utilization of Douglas fir hydrolyzate from the Madison process (*4*) yielded, on the basis of 50% conversion of wood to sugar, about 200 pounds of neutral solvents per ton of wood. The method of hydrolysis is a most important factor in determining the final yield of solvents from wood sugars.

Table IV. Yield of Solvents from Wood Sugar Fermentations

Source of Sugar[a]	Initial Sugar, G./L.	Sugar Fermented, %	Neutral Solvents, G./L.			Yield[b], %	Acid as Acetic, G./L.
			Butanol	Ethanol	Acetone		
Maple, 181° C.	51.0	85	9.5	0.3	4.3	33	...
Maple, 181° C.	43.5	68	6.07	0.05	3.45	32	...
Maple, 173° C.	36.7	88	9.0	0.1	3.4	38	...
Spruce, 173° C.	53.8	64	..	..	..	35	...
Oak	52.0	79	6.78	0.15	3.41	25	0.6
Oak	54.5	60	6.19	0.39	2.92	29	0.9
Oak	31.2	91	4.04	0.22	1.17	19	3.7
Douglas fir	39.5	40	3.21	0.22	1.59	32	0.5
Douglas fir	31.6	83	4.34	0.28	1.86	25	2.6

[a] Liquor stripped free of furfural (less than 0.03%), neutralized with lime to pH 6.5.

[b] As per cent of sugar fermented.

SUMMARY

Wood hydrolyzates have been fermented to butanol and acetone with *Cl. butylicum* No. 39. Several suitable methods have been used to prepare the hydrolyzates for fermentation; the simplest was to remove the furfural by distillation and neutralize the liquors to pH 6.5 with lime.

The effect of hydrolysis on fermentation has been demonstrated for the temperature variable in a single-stage hydrolysis procedure. At 1% concentrations of sugar all samples fermented to the same extent. The most poorly fermented hydrolyzate was obtained at 0-minute hydrolysis. Above 3% sugar the extent of fermentation decreased with increasing period of hydrolysis.

Yields of neutral solvents ranging from 24 to 38% of the sugar fermented have been obtained.

ACKNOWLEDGMENT

The authors are indebted to Elizabeth McCoy of the Department of Agricultural Bacteriology for transfers of the cultures. Part of the maple hydrolyzates were kindly supplied by C. O. Guss and the oak and Douglas fir samples by E. E. Harris of the United States Forest Products Laboratory.

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Received November 4, 1946. Published with the approval of the Director of the Wisconsin Experiment Station.

Synthetic Elastomers as Plasticizers for Polyvinyl Resins

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Addition of Perbunan 26 or Perbunan 35 to a vinyl chloride resin decreases the amount of ester type plasticizers necessary to obtain equivalent or better physical properties. The fugitive tendency of ester type plasticizers is reduced by addition of small amounts of rubberlike 1-3 butadiene-acrylonitrile copolymers. The Perbunan 35NS VYNW–dioctyl phthalate blends have good oil resistance. The blends show only slight change in volume when tested in the A.S.T.M. standard hydrocarbon liquids. Other advantages which Perbunan 26NS or Perbunan 35NS impart to a VYNW plastic compound are improved elongation and low temperature properties as evaluated by brittle tests. Blends of Vinylite VYNW–Perbunan 35NS–dioctyl phthalate exhibit higher tensile strengths than dioctyl phthalate–VYNW systems, particularly if the concentration of total plasticizer is above 32% by weight. Tensile tests indicate that the high acrylonitrile type copolymers are more compatible in dioctyl phthalate–plasticized VYNW than are the low acrylonitrile copolymers. The Perbunan-VYNW and Perbunan-VYNW–dioctyl phthalate blends show better aging properties than VYNW–dioctyl phthalate blends when held 6 to 14 days in an air oven at 250° F. Perbunan-VYNW blends show improved light aging properties when the Perbunan is held at about 12.5 to 50 parts on the Vinylite. The processing properties of Perbunan-VYNW blends are improved by the addition of S-polymers. The blends can be extruded to form a smooth tube at 220° F. The aging property of Perbunan-VYNW and Perbunan-VYNW–dioctyl phthalate blends may be improved by adding S-polymers to the blends.

THE importance of a plasticizer in polyvinyl chloride and its copolymers is second only to that of the resin itself. The kind and amount of plasticizer determine to a large degree the properties of the final composition. In 1941 Fuoss (*1*) stated that plasticization is the addition of a substance of relatively low molecular weight to a high polymer. In the last few years, however, a number of workers have concentrated on the use of high-molecular-weight materials as plasticizers for rubbers and resins. A few investigators have reported on the physical properties of polyvinyl chloride plasticized with rubberlike copolymers of 1-3 butadiene and acrylonitrile. Henderson (*2*), Winkelmann (*7*), Moulton (*4*), and Kenney (*3*) have published data on rubber-resin blends. In this paper the authors present results of the plasticization of Vinylite (VYNW), a copolymer containing 95 % of vinyl chloride and 5% of vinyl acetate, by the use of several synthetic elastomers such as Perbunan and S-polymers (*5, 6*).

The main object of the work is to report recent results with Perbunan NS–VYNW blends as well as Perbunan NS–dioctyl phthalate–VYNW blends. The Perbunan NS polymers are a commercial class of butadiene-acrylonitrile copolymers stabilized with an improved nonstaining and nontoxic antioxidant (stabilizer 8567). The term "NS" indicates nonstaining. In this study the total plasticizer concentration was varied over a wide range. The increments were small enough so that any deviations from expected normal behavior would be disclosed. Coupled with this study, control investigations were carried out on the conventional VYNW–dioctyl phthalate system. The ester type plasticizers, etc., are required to obtain processing properties in the rubber-resin type blends.

Another phase of the present investigation covers the use of S-polymers (styrene copolymers) in Perbunan-VYNW blends as well as the use of S-polymers in Perbunan–VYNW–dioctyl phthalate blends. The S-polymers were evaluated in the Perbunan-Vinylite system, as they showed excellent aging properties and good compatibility in the system.

The resin copolymer (Vinylite, VYNW) chosen for the work was obtained from the Bakelite Corporation. It contained 95% vinyl chloride and 5% vinyl acetate. The dioctyl phthalate made from 2-ethyl hexyl alcohol was supplied by Ohio Apex, Inc. The basic formulation in parts by weight was as follows:

Copolymer (VYNW)	100
Vinylite stabilizer	3
Stearic acid	1.5
Plasticizer	Variable

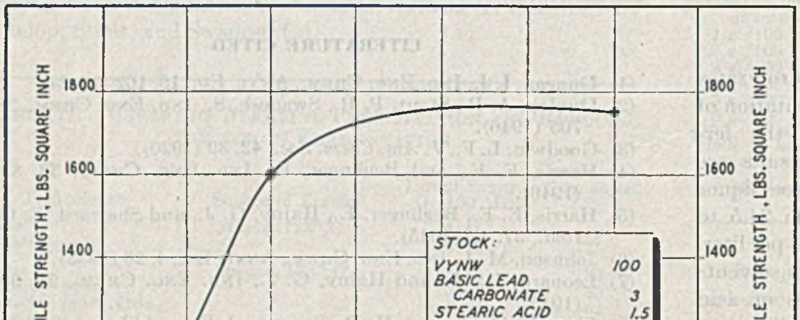

Figure 1. Effect of Mill Mixing Time on Tensile Strength of Perbunan 35NS 90–VYNW Blends

Table I. Effect of Mill Mixing Time on Physical Properties of Perbunan 35NS 90–VYNW Blends

(Formula: VYNW 100; basic lead carbonate, 3; stearic acid, 1.5; Perbunan 35NS 90, 50; dioctyl phthalate, 50)

Stock No.	1	2	3	4	5	6	7	8
Mill mixing procedures								
Dioctyl phthalate–VYNW milled at 280–285° F., min.	5	5	5	5	5	5	5	5
Perbunan 35NS 90–VYNW milled at 270° F., min.	3	3	5	5	10	10	30	30
Perbunan 35NS 90–VYNW milled at 140° F., min.	0	15	0	15	0	15	0	15
Physical properties								
Tensile, lb./sq. in.	1080	1050	1200	1110	1600	1610	1710	1750
Ultimate elongation, %	250	220	270	320	320	260	370	210
Shore durometer hardness	73	70	70	72	72	75	75	72
Crescent tear at room temp., lb./in.	190	175	225	190	255	215	245	190
Soly. at room temp. in 5% concd. cyclohexane	Sol.	Sol.	Sol.	Sol.	Not sol.	Part sol.	Not sol.	Not sol.

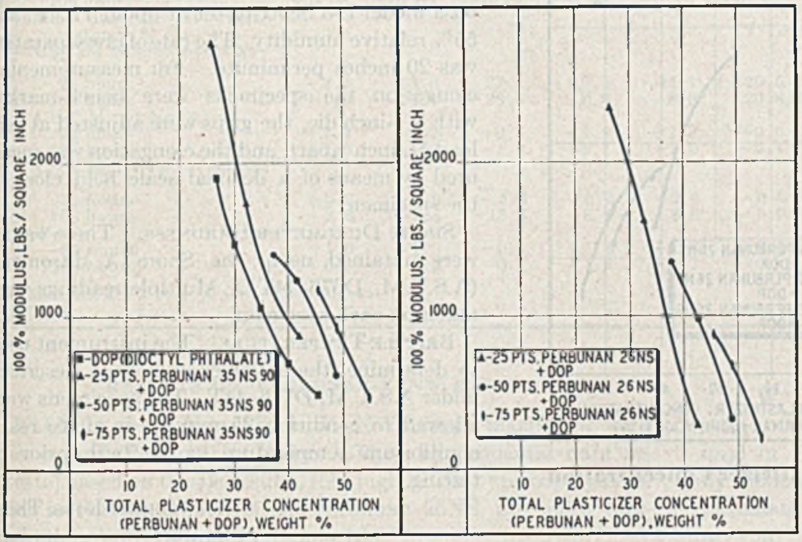

Figure 2. 100% Modulus Plotted against Plasticizer Concentration in VYNW

The synthetic rubber plasticizer, such as Perbunan, was varied from 12.5 to 150 parts, based on 100 parts VYNW. However, when the rubber plasticizer was used with dioctyl phthalate, it was varied from 25 to 75 parts, based on 100 parts VYNW, and dioctyl phthalate was varied from 12.5 to 50 parts by weight. Fillers were omitted from the formulation so that properties of the compound would be a function only of the kind and amount of plasticizer used. In most of the work basic lead carbonate was used as a stabilizer for the VYNW and the stearic acid as a parting agent; this facilitated easy release of the stock from the hot mill. The amounts of these two latter materials were kept constant. The synthetic elastomers studied were: Perbunan 35NS 90, Perbunan 26NS, Perbunan 18, S-40, S-50, and S-60. In this work the Perbunan polymers used had a 2-minute Mooney viscosity of 90. As the Perbunan number increases the acrylonitrile in the copolymer increases, and, likewise, as the S number increases the amount of styrene in the resin increases. The S-polymers are copolymers that contain styrene. (The S-polymers are high-molecular-weight aliphatic olefin-styrene copolymers. The products are now being made by the Standard Oil Company of New Jersey.) The tests carried out on a number of the plasticized compounds were as follows: 100% modulus, tensile strength, ultimate elongation, Shore durometer hardness, brittle temperature, specific gravity, weight loss, heat aging at 250° F., light aging, and volume increase in A.S.T.M. reference fuels No. 1, No. 2, No. 3, and water.

PREPARATION OF SAMPLES

Milling Procedure. A number of qualitative experiments were performed with the rubber-resin mixtures in order to determine the best mixing time and temperature. In this preliminary mixing work a number of blends were made on a 6 × 12 inch mill at 260–280° F. Time of milling varied from 3 to 30 minutes. Coupled with this part of the investigation it seemed desirable to determine the effect of cold milling. Half of the hot-mill blends were, therefore, given an additional mill mixing at 140° F. for 15 minutes. Results of this work, as well as results on a Perbunan type blend, are found in Table I. Some of the data are presented in Figure 1.

Results show that at about 280° F. higher tensiles were obtained when the mill mixing was continued from 12 to 30 minutes. Additional mill mixing at 140° F. for 15 minutes did not alter the tensile strength of the test blends; however, tear resistance was reduced.

A comparison of tensile and tear tests with the solubility data show that the best tensile and tear data were obtained on the blends which were not completely soluble in cyclohexanone. This work indicated that, as the time of heating was increased, the Perbunan NS cross-linked to form a gellike structure. It was apparent that this gel or improved dispersion was responsible for an improvement in the physical properties as judged by tensile, tear, and lack of discoloration on light aging.

Several attempts were made to formulate blends of the synthetic elastomers and Vinylite VYNW at lower temperatures—that is, 140° or 200° F.; however, good uniform blends were not possible at the low temperatures. All data indicate that for the best results the resin must be fluxed with the rubberlike plasticizer.

The final milling procedure as developed from the study of mixing conditions is given. The ingredients, with the exception of the synthetic rubbers, were weighed out and dry-blended by hand. After blending, the dry mixture was treated, in a number of the experiments, with dioctyl phthalate; and the blend was then charged to a 6 × 12 inch laboratory rubber mill heated with

Table II. Comparison of Physical Properties of Blends of VYNW with Various Types of Perbunan

Stock No.	1	2	3	4	5	6	
Formula, parts by wt.							
VYNW	100	100	100	100	100	100	100
Basic lead carbonate	3	3	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Perbunan	12.5	25	37.5	50	75	100	150
Perbunan in blend, %	10.7	19.4	26.4	32.4	41.7	48.8	58.8
Physical properties							
Tensile, lb./sq. in.							
Perbunan 18	4470	3080	1410	750	490	60	50
26NS	6460	4710	3130	2540	1710	1380	890
35NS 90	7610	7080	3900	2910	2650	2120	1800
Ultimate elongation, %							
Perbunan 18	15	30	..	35	110	160	305
26NS	70	60	120	165	160	200	230
35NS 90	15	40	225	295	235	210	270
Shore durometer hardness							
Perbunan 18	96	95	94	91	79	76	69
26NS	97	97	93	93	89	86	70
35NS 90	96	97	94	94	90	77	70

Table III. Physical Properties of Perbunan 18–VYNW Blends Containing Dioctyl Phthalate

Stock No.	1	2	3	4	5
Formula, parts by wt.					
VYNW	100	100	100	100	100
Basic lead carbonate	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5
Perbunan 18	12.5	25	50	75	100
Dioctyl phthalate	50	50	50	50	50
Physical properties					
Tensile, lb./sq. in.	2450	2030	1380	1050	320
Ultimate elongation, %	310	360	330	375	155
Shore durometer hardness	83	83	79	73	69

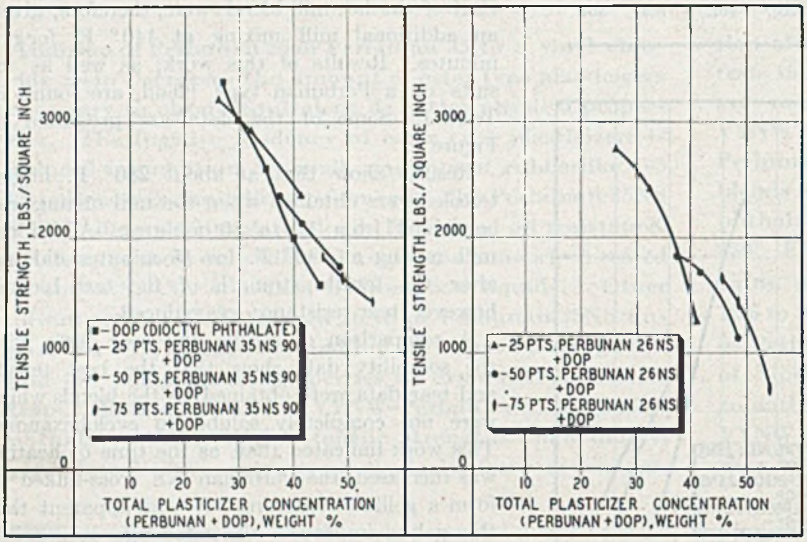

Figure 3. Tensile Strength Plotted against Plasticizer Concentration in VYNW

Table IV. Physical Properties of Perbunan 35NS 90–VYNW Blends

Stock No.	1	2	3	4	5	6	7	8	9
Formula, parts by wt.									
VYNW	100	100	100	100	100	100	100	100	100
Basic lead carbonate	3	3	3	3	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Perbunan 35NS 90.	25	25	25	50	50	50	75	75	75
Dioctyl phthalate	12.5	25	50	12.5	25	50	12.5	25	50
Perbunan 35NS 90 in blend, %	17.6	16.2	13.9	30.0	27.9	24.4	39.0	36.7	32.7
Dioctyl phthalate in blend, %	8.8	16.2	27.9	7.5	13.9	24.4	6.5	12.2	21.8
Total plasticizer in blend, %	26.4	32.4	41.8	37.5	41.8	48.8	45.5	48.9	54.5
Physical properties									
Tensile, lb./sq. in.	3200	2920	2380	2380	2120	1750	1850	1670	1440
Modulus at 100%, lb./sq. in.	2790	1750	880	1400	1230	610	1160	930	460
Ultimate elongation, %	220	310	380	320	350	380	280	310	420
Shore durometer hardness	93	87	72	87	80	65	84	80	60
Specific gravity	1.290	1.250	1.218	1.217	1.200	1.181	1.181	1.180	1.154
Brittle temperature, ° F.	−30	−40	−40	−40	−40	−50	−40	−40	−50
Weight loss at 180° F.[a], %									
Air oven method									
72 hours	−0.19	−0.38	−0.41	−0.24	−0.50	−0.55	−0.40	−0.50	−0.50
168 hours	−0.37	−0.89	−0.90	−0.30	−0.95	−0.99	−0.70	−0.80	−0.90
Uncorked A.S.T.M. tube method									
72 hours	−0.06	−0.15	−0.14	−0.07	−0.15	−0.14	−0.16	−0.21	−0.13
168 hours	−0.10	−0.16	−0.25	+0.05	−0.17	−0.21	−0.19	−0.29	−0.20
Volume increase at room temp.[a], %									
A.S.T.M. reference fuel No. 2									
24 hours	+9.1	+9.5	−2.8	+10.4	+7.0	−3.9	+8.8	+7.8	+6.7
168 hours	+15.8	+4.0	−15.4	+10.5	+2.5	−12.6	+6.5	+3.6	−3.0
A.S.T.M. oil No. 3									
24 hours	−0.3	−0.6	+0.3	−0.6	−0.4	+0.2	−0.2	−0.2	+0.5
168 hours	−0.3	−0.4	+0.5	−0.1	−0.2	+0.5	+0.2	−0.1	+0.6
A.S.T.M. reference fuel No. 1									
24 hours	−0.7	−0.4	+0.6	−0.6	−0.5	+0.4	−0.5	−0.6	+0.1
168 hours	−0.5	+0.3	+3.1	−0.3	+0.1	+2.7	+0.1	−0.2	+2.2
Water									
24 hours	−0.6	−0.6	+0.1	−0.8	−0.8	+0.1	−0.8	−1.5	0.0
168 hours	−0.5	−0.6	+0.1	−0.9	−0.9	+0.1	−0.7	−0.7	+0.2

[a] Samples are 2 × 1 × 0.075 inch blocks.

steam to about 280-300° F. The resin was then fluxed about 2 minutes and allowed to mill with a rolling bank for 5 minutes with occasional cutting. To this plastic at about 280° F. was added the rubber. Mill mixing was continued for about 12 minutes at 280° F. The batch was then sheeted off the mill at 0.075- to 0.15-inch thickness.

Molding Method. This operation was carried out in a standard A.S.T.M. four-cavity mold (D15–41) yielding slabs 6 × 6 × 0.075 inch. The molding cycle was 10 minutes at minimum ram pressure at 280° F., then 10 minutes at 900 pounds per square inch at 280° F. The stock was cooled under pressure in the mold.

TEST METHODS

Tensile Strength, 100% Modulus, and Ultimate Elongation. These tests were made on a model L-3 Scott tester at about 77° F. and 55% relative humidity. The rate of jaw separation was 20 inches per minute. For measurement of elongation the specimens were bench-marked with a 1-inch die, the grips were adjusted at zero load $^3/_4$ inch apart, and the elongation was measured by means of a decimal scale held close to the specimen.

Shore Durometer Hardness. These values were obtained using the Shore A durometer (A.S.T.M. D676–44T). Multiple readings were taken on each specimen.

Brittle Temperature. The instrument used to determine these values was that described under A.S.T.M. D746–44T. The specimens were allowed to condition 25 minutes in air to reach equilibrium temperature in the bath prior to testing.

Weight Loss. These values were obtained at 180° F. Method A: The test samples were held on a polished steel plate in an air oven; method B: the test samples were held in an uncorked A.S.T.M. tube heated externally by the use of an oil bath. The tube was 300 mm. long and 38 mm. in outside diameter.

Volume Increase. These values were obtained in standard laboratory fluids at room temperature. SR-6 or A.S.T.M. D471–46T reference fuel No. 2 was formulated from 60% diisobutylene, 20% toluene, 5% benzene, and 15% xylene. SR-10 or A.S.T.M. reference fuel No. 1 is pure diisobutylene. A.S.T.M. oil No. 3 is a low V.I. mineral oil with an aniline point at 70° C.

Table V. Physical Properties of Perbunan 26NS–VYNW Blends

Stock No.	1	2	3	4	5	6	7	8	9
Formula, parts by wt.									
VYNW	100	100	100	100	100	100	100	100	100
Basic lead carbonate	3	3	3	3	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Perbunan 26NS	25	25	25	50	50	50	75	75	75
Dioctyl phthalate	12.5	25	50	12.5	25	50	12.5	25	50
Perbunan 26NS in blend, %	17.6	16.2	13.9	30.0	27.9	24.4	39.0	36.7	32.7
Dioctyl phthalate in blend, %	8.8	16.2	27.9	7.5	13.9	24.4	6.5	12.2	21.8
Total plasticizer in blend, %	26.4	32.4	41.8	37.5	41.8	48.8	45.5	48.9	54.5
Physical properties									
Tensile, lb./sq. in.	2770	2410	1290	1850	1700	1140	1630	1430	670
Modulus at 100%, lb./sq. in.	2350	1630	280	1340	980	330	880	680	200
Ultimate elongation, %	260	300	320	275	300	340	350	350	350
Shore durometer hardness	90	84	68	88	80	67	81	74	65
Specific gravity	1.276	1.242	1.166	1.220	1.198	1.160	1.177	1.167	1.135
Brittle temperature, ° F.	−40	−40	−50	−60	−60	−60	−60	−60	−50
Weight loss at 180° F.[a], %									
Air oven method									
72 hours	−0.56	−0.95	−0.98	−0.66	−1.08	−1.09	−0.26	−0.46	....
168 hours	−1.06	−2.25	−2.28	−0.96	−1.38	−1.14	−0.41	−0.63	....
Uncorked A.S.T.M. tube method									
72 hours	−0.11	−0.10	−0.24	−0.10	−0.02	−0.09	−0.08	−0.12	−0.08
168 hours	+0.08	−0.06	−0.26	−0.08	−0.06	−0.14	−0.08	−0.11	−0.12
Volume increase at room temp.[a], %									
A.S.T.M. reference fuel No. 2									
24 hours	−2.4	−13.0	−27.4	−3.5	−11.1	−20.5	+5.5	−3.0	−17.3
168 hours	+1.3	−11.2	−28.3	−0.8	−8.9	−20.8	+9.4	−0.4	−15.7
A.S.T.M. oil No. 3									
24 hours	+1.4	+2.2	−0.6	+1.9	+1.3	−0.6	+1.5	+1.4	−0.6
168 hours	+1.5	+1.6	−1.9	+3.7	+1.0	−2.1	+2.5	+1.5	−1.1
A.S.T.M. reference fuel No. 1									
24 hours	+0.2	−0.9	−4.5	−0.2	−2.6	−0.6	−0.3	−0.2	−2.7
168 hours	+3.6	−1.3	−18.3	−3.5	−8.6	−9.9	+3.8	+2.8	−7.8
Water									
24 hours	+1.6	+1.2	−0.3	+1.8	+1.4	−0.6	+1.3	+1.7	−0.3
168 hours	+0.5	+0.2	−0.3	+1.8	+0.7	−0.4	+0.6	+0.6	0.0

[a] Samples are 2 × 1 × 0.075 inch blocks.

RESULTS ON PERBUNAN-VYNW BLENDS

Table II presents results on VYNW blends plasticized with the several Perbunan polymers. These experimental data indicate, based on tensile results, that high nitrile type copolymers, such as Perbunan 35NS 90 and Perbunan 26NS, are more compatible in VYNW than Perbunan 18.

RESULTS ON PERBUNAN NS-VYNW-DIOCTYL PHTHALATE BLENDS

100% Modulus. This family of curves indicated that all the plasticizers tested behaved similarly in VYNW (Figure 2), the only difference being in their relative plasticizing efficiencies. The Perbunan 35NS 90-dioctyl phthalate-VYNW systems give higher moduli, for the same total weight per cent plasticizer, than do Perbunan 26NS-dioctyl phthalate-VYNW systems. This result is rather confusing as it may indicate that Perbunan 26NS is a better plasticizer for VYNW than Perbunan 35NS 90. However, this lower modulus for Perbunan 26NS may be due only to the fact that this type of rubber is less compatible in the system. Tensile data tend to show this to be true.

Tensile Strength. Except for the possible existence of slight plateaus in the curves (Figure 3), it can be said that, within the limits studied, tensile strength is inversely proportional to concentration of plasticizer. However, Perbunan 35NS 90 + dioctyl phthalate-formulated blends with VYNW had higher tensiles than VYNW-dioctyl phthalate blends, provided concentrations of total plasticizer were above 34% by weight. Where tensile strengths are significant, it seems desirable to use Perbunan 35 in preference to Perbunan 26 or Perbunan 18. This observation is apparent from the results shown in Figure 3 and Table III. (Perbunan 18 results are not presented in the figures, as a complete study on a wide range of plasticizer concentrations was not made with this polymer.)

Shore Durometer Hardness. Curves are given (Figure 4) for the several plasticizers; they show that, for all practical purposes, a straight-line relation exists over the range studied.

Brittle Temperature. Results (Figure 5) show that, for an equal weight of plasticizer, the Perbunan NS-dioctyl phthalate-VYNW system has a brittle temperature below that of the dioctyl phthalate-VYNW system. At a plasticizer concentration of 30% by weight the rubber type-vinyl blends give a brittle test about 35 ° F. below that obtained with dioctyl phthalate-VYNW. These results are worthy of note, as dioctyl phthalate is one of the better low temperature type ester plasticizers now used in VYNW. Twenty-six per cent plasticizer (formulated by compounding 17.6% Perbunan 35NS 90 and 8.8% dioctyl phthalate in the blends) gave a stock with a brittle temperature of −40° F. This result is remarkable considering the low amount of plasticizer employed.

Volatility Tests. Results in Tables IV, V, and VI show that when the amount of plasticizer is held constant in VYNW the Perbunan-dioctyl phthalate-VYNW blends (2 × 1 × 0.075-inch test blocks) have less weight loss at 180° F. than do dioctyl phthalate-VYNW blends. For example, stock 3 (Table I), plasticized with 13.9% Perbunan 35NS 90 and 27.9% dioctyl

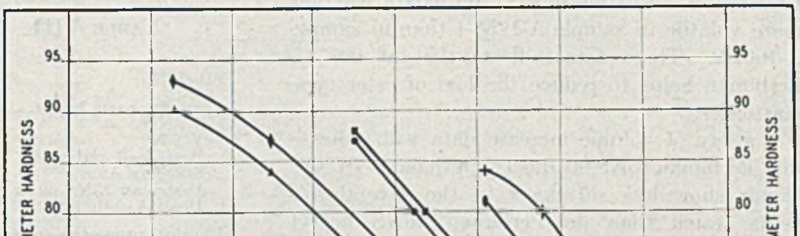

Figure 4. Durometer Hardness Plotted against Plasticizer Concentration in VYNW

TABLE VI. PHYSICAL PROPERTIES OF VYNW–DIOCTYL PHTHALATE MIXTURE *vs.* PERBUNAN-VYNW–DIOCTYL PHTHALATE MIXTURE

Stock No.	1	2	3
Formula, parts by wt.			
VYNW	100	100	100
Basic lead carbonate	3	3	3
Stearic acid	1.5	1.5	1.5
Perbunan 35NS 90	....	25	....
Perbunan 26NS	....	....	25
Dioctyl phthalate	50	25	25
Perbunan in blend, %	0	16.2	16.2
Dioctyl phthalate in blend, %	32.4	16.2	16.2
Total plasticizer in blend, %	32.4	32.4	32.4
Physical properties (unaged)			
Tensile, lb./sq. in.	3000	2920	2610
Ultimate elongation, %	280	310	300
Shore durometer hardness	85	87	84
Specific gravity	1.250	1.250	1.242
Brittle temperature, ° F.	−20	−40	−40
Crescent tear at room temp., lb./in.	420	380	355
Wt. loss at 180° F. by uncorked A.S.T.M. tube method, %			
72 hours	−0.16	−0.15	−0.10
168 hours	−0.23	−0.16	−0.06
Volume increase at room temp.[a], %			
A.S.T.M. reference fuel No. 2			
24 hours	−6.0	+9.5	−13.0
168 hours	−8.6	+4.0	−11.2
A.S.T.M. oil No. 3			
24 hours	0.0	−0.6	+2.2
168 hours	−0.4	−0.4	+1.6
A.S.T.M. reference fuel No. 1			
24 hours	−4.0	−0.4	−0.9
168 hours	+1.2	+0.3	−1.3
Water			
24 hours	−0.4	−0.6	+1.2
168 hours	−0.2	−0.6	+0.2
Physical properties (oven-aged for 3 days at 250° F.)			
Tensile, lb./sq. in.	2910	2900	2520
Ultimate elongation, %	150	140	150
Shore durometer hardness	89	87	89

[a] Samples are 2 inch × 1 inch × 0.075 inch blocks.

TABLE VII. AGING STUDY ON PERBUNAN 35NS 90–VYNW BLENDS

Stock No.	1	2	3	4	5
Formula, parts by wt.					
VYNW	100	100	100	100	100
Basic lead carbonate	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5
Perbunan 35NS 90	..	25	50	75	100
Dioctyl phthalate	50	50	50	50	50
Physical properties (unaged)					
Tensile, lb./sq. in.	2940	2380	1750	1440	1240
Ultimate elongation, %	270	380	380	420	420
Shore durometer hardness	80	72	65	60	55
Crescent tear at room temp., lb./in.	420	315	275	235	170
Physical properties (oven-aged for 3 days at 250° F.)					
Tensile, lb./sq. in.	2920	2260	1450	880	750
Ultimate elongation, %	160	140	60	45	15
Shore durometer hardness	85	70	75	70	90
Physical properties (oven-aged for 7 days at 250° F.)					
Tensile, lb./sq. in.	4280	3190	2230	1310	670
Ultimate elongation, %	35	60	20	20	0
Physical properties (oven-aged for 14 days at 250° F.)					
Tensile, lb./sq. in.	630	370	1880	4720	5520
Ultimate elongation, %	0	0	0	0	30

phthalate, lost 0.25% in weight; and stock 5, plasticized with 27.9% Perbunan 35NS 90 and 13.9% dioctyl phthalate, lost only 0.17% in weight. To obtain a better picture of heat volatility some tests were made on a 0.5-mm. thick film in an air oven at 90° C. for 11 days. Results are as follows:

	Sample A-1755-1	Sample A-1907-2
VYNW, grams	100	100
Basic lead carbonate, grams	3	3
Stearic acid, grams	1.5	1.5
Perbunan 35NS 90, grams	...	25
Dioctyl phthalate	50	25
Heat volatility, %	9.9	2.5

Under this test the dioctyl phthalate was far more volatile in sample A-1755-1 than in sample A-1907-2. These data indicate that at 90° C. Perbunan helps to reduce the loss of ester type plasticizer.

A study of volume increase data will indicate that Perbunan 35NS 90-dioctyl phthalate–VYNW blends show less shrinkage in the several solvents tested than do Perbunan 26NS–dioctyl phthalate–VYNW blends. The solvent resistance of the Perbunan 35NS 90 type blends is very good.

HEAT AGING. Tables VI, VII, and VIII give data on the aging property of blends. The results indicate that when the amount of plasticizer is held constant the aging properties at 250° F. for the Perbunan–dioctyl phthalate–VYNW blends are as good as those of the dioctyl phthalate–VYNW blends. The data of the preceding paragraph indicate that less plasticizer is lost when Perbunan is present. The Perbunan–dioctyl phthalate–VYNW blends show good aging properties when held for 7 days at 212° F. For improved heat stability, the rubber portion should be protected with 2 parts of an antioxidant such as Deenax (Enjay Co.), PDA (Bensen Engineering Co.), or Stabelite (C. P. Hall).

LIGHT AGING. In the light aging study 6 × 6 × 0.075 inch pressed slabs were placed in the Fadeometer (ultraviolet light) at 125° F. Results are recorded in Table IX. Observations indicate that the blends treated with Stabelan A (Stabelan Chemical Company) show less color change than the Vinylite type compounds stabilized with lead carbonate and V-1-N (Advance Solvents and Chemical Corp.). In fact, stock 6 shows no change in color after 175 hours in the Fadeometer, and stock 3 shows only slight change in color. After the 175-hour test stocks 3 and 6 were stiff, like all the other Perbunan-Vinylite aged compounds. However, the Fadeometer-aged blends that contained Stabelan A could be bent 180° at room temperature without cracking.

A number of light aging studies indicated that the best compounds are formed when the mill mixing time is greater than 4 minutes at 280° F. and the amount of Perbunan is held at about 12.5 to 50 parts on the VYNW.

TABLE VIII. PHYSICAL PROPERTIES OF STABILIZED PERBUNAN 35NS 90–VYNW BLENDS

Stock No.	1	2	3	4	5	6	7	8
Formula, parts by wt.								
VYNW	100	100	100	100	100	100	100	100
V-1-N[a]	3	..	..	3	..	..	..	..
Basic lead carbonate	..	3	..	..	3	..	3	..
Stabelan A[b]	..	..	3	..	..	3	..	3
Perbunan 35NS 90	..	..	..	50	50	50	50	50
Dioctyl phthalate	50	50	50	..	..	..	50	50
Physical properties (unaged)								
Tensile, lb./sq. in.	3070	3190	3240	3130	2990	3260	1930	1880
Modulus at 100%, lb./sq. in.	1670	1870	2180	3130	2990	3120	650	740
Ultimate elongation, %	280	290	250	240	180	150	370	380
Shore durometer hardness	85	84	87	96	95	94	68	71
Physical properties (oven-aged for 3 days at 250° F.)								
Tensile, lb./sq. in.	1790	1870	1780	2400	2280	2580	1100	900
Modulus at 100%, lb./sq. in.	1680	1760	1710	..	..	..	..	..
Ultimate elongation, %	140	160	110	50	70	70	80	90
Shore durometer hardness	80	62	78	59	89	83	82	75
Physical properties (oven-aged for 6 days at 250° F.)								
Tensile, lb./sq. in.	4080	4060	4210	4530	4320	3950	2380	3160
Modulus at 100%, lb./sq. in.	..	..	4210	..	..	..	..	..
Ultimate elongation, %	45	20	100	20	40	10	60	60
Shore durometer hardness	81	84	89	92	97	92	90	91

[a] Product of Advance Solvents and Chemical Corporation.
[b] Product of Stabelan Chemical Company.

Table IX. Light Aging Study on VYNW Blends

Stock No.	1	2	3	4	5	6	7	8
Formula, parts by wt.								
VYNW	100	100	100	100	100	100	100	100
V-1-N	3	.....	.....	3	....	.....	....	...
Basic lead carbonate	...	3	.....	...	3	.....	3	...
Stabelan A	...	.....	3	...	....	3	....	3
Perbunan 35NS 90	...	.....	.....	50	50	50	50	50
Dioctyl phthalate	50	50	50	...	....	.....	50	50
Fadeometer exposure								
100 hours	Light	Brown	No change in color	Brown	Brown	No change in color	Brown	Light yellow
175 hours	Brown	Dark brown & spotted	Slight change in color	Dark brown	Brown to black	No change in color	Brown	Yellow

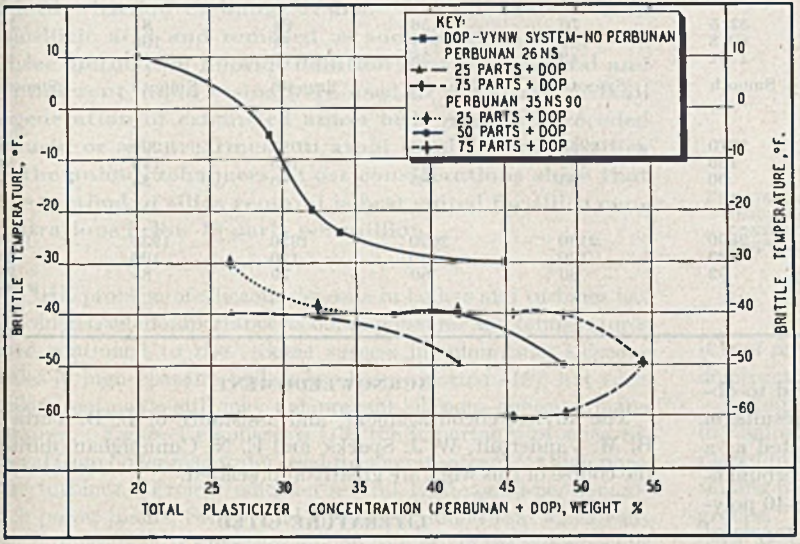

Figure 5. Brittle Temperature Plotted against Plasticizer Concentration in VYNW

RESULTS ON S-POLYMER–PERBUNAN–VYNW BLENDS

In many experiments it was observed that mixtures of S-polymer and VYNW were extremely difficult to obtain. In fact, in a number of cases incompatibility was recorded unless special techniques were employed. These involved high temperatures and extremes in mastication, and even then complete homogeneity was not achieved.

It was found that Perbunan acted as an efficient plasticizer for VYNW. In other previous experiments it was also observed that Perbunan was completely compatible with the S-polymers. These investigations revealed that blends of Perbunan–S-polymer could be calendered at 225° F. to produce self-supported films or extruded to give satisfactory tubing and insulation. The concentration of S-polymer could vary over the range 25 to 75%. This mutual compatibility suggested a means of securing homogeneous blends of VYNW and S-polymers. Therefore, a resin composition having unique properties might be expected, since the good qualities of VYNW and S-polymers might complement each other.

For this work the S-polymer was compounded in the Perbunan at 220° F. on a rubber mill. The mixture had good processing properties on the mill. The S-polymer–Perbunan mixture was added to VYNW on a mill at 280–290° F. Total mixing time for the S-polymer–Perbunan-VYNW mixture was 15 minutes.

Table X lists results on S-polymer–Perbunan 35NS–VYNW blends. The concentration of Perbunan 35NS was held at 50 parts based on the VYNW, while the S-polymer concentration was held at 50 parts on the VYNW. With an S-polymer concentration of 50 parts on the VYNW the tensile strength was increased as the S number, or styrene content, of the resin was raised. For example, the S-40 blend had a tensile of 1760 pounds per square inch, whereas the S-60 blend (stock 4) had a tensile of 1960 pounds per square inch. Also, as the S number of the polymer was decreased the low temperature brittle point was lowered. The per cent elongation to break was increased as the styrene content of the copolymer was decreased. These data were expected, as the low styrene copolymers are more rubberlike, while the high S-polymers are more resinlike. All of the blends listed in Table X had good crescent tear values at room temperature. This test indicated that the S-polymer–Perbunan-VYNW mixtures were compatible.

Some of the advantages obtained by using S-polymers in the Perbunan 35NS–VYNW blends are improved processing properties and improved oven aging properties.

To improve the low temperature brittle point for the S-40 polymer–Perbunan 35NS–VYNW blends, some dioctyl phthalate was compounded into the system on a rubber mill at 280°F. Results are recorded in Table XI. These data show that a substantial reduction in brittle point was obtained when dioctyl phthalate was used. However, the results on stock 1 showed that, if the amount of S-40 polymer was held low—that is, 10

Table X. S-Polymers in Perbunan 35NS 90–VYNW Blends

Stock No.	1	2	3	4
Formula, parts by wt.				
S-40	....	50	...	...
S-50	....	...	50	...
S-60	....	...	...	50
VYNW	100	100	100	100
Perbunan 35NS 90	50	50	50	50
Basic lead carbonate	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5
S-resin in blend, %	0	24.4	24.4	24.4
Perbunan 35NS 90 in blend, %	32.4	24.4	24.4	24.4
Total plasticizer in blend, %	32.4	48.8	48.8	48.8
Physical properties (unaged)				
Tensile, lb./sq. in.	2910	1760	1950	1960
Ultimate elongation, %	290	190	170	80
Shore durometer hardness	94	93	95	96
Brittle temperature, ° F.	−40	+40	+70	+80
Crescent tear at room temp., lb./in.	480	420	495	460
Extrusion at 220° F.*				
Inches/min. (*a*)	Couldn't extrude	70	68.5	67.0
Grams/min. (*b*)		100	93.6	98.8
Swell index (*b*)/(*a*)		1.43	1.37	1.48
Appearance		Smooth	Smooth	Smooth
Physical properties (oven-aged for 3 days at 250° F.)				
Tensile, lb./sq. in.	1870	2240	2480	2950
Ultimate elongation, %	160	140	120	60
Shore durometer hardness	62	85	80	85
Physical properties (oven-aged for 6 days at 250° F.)				
Tensile, lb./sq. in.	4060	2160	2520	28
Ultimate elongation, %	20	120	110	4
Shore durometer hardness	84	80	95	[illegible]

* 80 r.p.m., 0.4-inch die by 0.3-inch pin.

Table XI. Perbunan–VYNW S-40 Blends

Stock No.	1	2	3	4	5	6	7
Formula, parts by wt.							
S-40	10	25	50	25	25	50	50
VYNW	100	100	100	100	100	100	100
Perbunan 35NS 90	50	50	50	50	50	50	50
Basic lead carbonate	3	3	3	3	3	3	3
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Dioctyl phthalate	.....	.....	.....	25	50	25	50
Observations	No odor, no surface tack	No odor, no surface tack	No odor, no surface tack	No odor, no surface tack	Slight odor, slight tack	Slight odor, slight tack	Slight odor, slight tack
Physical properties (unaged)							
Tensile, lb./sq. in.	2490	2010	1760	1710	1330	1250	800
Ultimate elongation, %	140	190	190	310	400	320	50
Shore durometer hardness	95	94	93	88	71	87	71
Specific gravity	1.222	1.222	.....	1.171	1.142	1.139	1.125
Brittle temperature, ° F.	−30	+20	+40	−20	−30	−10	−20
Crescent tear at room temp., lb./in.	560	505	420	280	170	220	110
Extrusion at 220° F.*							
Inches/min. (*a*)	62	52.5	70	56	61	84	72
Grams/min. (*b*)	123	80.8	100	77.4	81	100	84
Swell index (*b*)/(*a*)	1.98	1.54	1.43	1.38	1.33	1.19	1.17
Appearance	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth
Physical properties (oven-aged for 3 days at 250° F.)							
Tensile, lb./sq. in.	2960	2370	2240	1520	1080	1290	860
Ultimate elongation, %	50	130	140	130	140	140	30
Shore durometer hardness	80	90	85	85	80	85	75
Physical properties (oven-aged for 6 days at 250° F.)							
Tensile, lb./sq. in.	3360	2890	2160	2090	1320	1930	1490
Ultimate elongation, %	20	120	120	110	120	100	30
Shore durometer hardness	81	92	80	80	79	84	76

* 80 r.p.m., 0.4-inch die by 0.3-inch pin.

parts on the VYNW—no dioctyl phthalate was required to obtain good low temperature properties. Once again the results on extrusion at 220° F. showed that the S-40 polymer acted as a processing aid for the Perbunan-VYNW blends or the Perbunan-VYNW–dioctyl phthalate blends. As the amount of S-40 polymer was increased in the blend, the extrusion rate was improved and the swelling index was reduced. The S-40 polymer–Perbunan-VYNW–dioctyl phthalate blends exhibited interesting aging properties when held at 250° F. in an air oven. For example, in the 6-day aging test the Perbunan-VYNW blend showed a short elongation to break, whereas the S-polymer–Perbunan 35NS–VYNW type blends retained to a great extent their original elongation.

ACKNOWLEDGMENT

The advice, encouragement, and assistance of L. B. Turner, B. M. Vanderbilt, W. J. Sparks, and E. N. Cunningham during the course of this work are greatly appreciated.

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Received May 9, 1947.

EXPRESSED PEACH KERNEL OIL

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Until a little over two decades ago the so-called peach kernel oil of commerce (sometimes also called "oil almonds P.K.") was obtained from apricot kernels. In 1923, at the request of agents of the United States Department of Agriculture, the oil expressed from domestic apricot kernels was correctly named "apricot kernel oil" and is commercially known as such today.

Peach pits are more difficult to dry and to crack than apricot pits. The percentage of dry kernels obtained from peach pits is, in most cultural varieties, only 9 to 11 of the whole dried pits. Frequently the percentage is even lower. This is less than half the yield from apricot pits, which is 20 to 33% of the kernels, according to variety. For these reasons true peach kernel oil had seldom, if ever, been manufactured in commercial quantities.

Scarcity of edible and pharmaceutical oils and an improved commercial outlet for the by-product shells have resulted in the possibility of an oil pressing operation on a commercial scale. In this operation 21,400 kg. of peach kernels (containing 42.3% of oil) were pressed to produce peach kernel oil and oil-cake meal.

The crude oil has a yellow color and a strong flavor and odor of benzaldehydecyanhydrin. It was easily improved in flavor and lightened in color by simple treatment with an activated montmorillonite. The characteristics of the treated oil are:

Specific gravity, 15° C.	0.9224
Refractive index, 25.5° C.	1.46990
Saponification value	191.4
Unsaponifiable matter, %	0.65
Iodine number (Wijs)	98.1
Acid value	0.67
Titer, ° C.	11
Color (Lovibond)	25 yellow, 3 red
Flavor	Bland, mildly almondlike

The titer is 2° lower than the lowest of the range given by Jamieson (*2*). However, it is within the 5–13° C. range given by Hilditch (*1*).

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Received October 4, 1946.

Silica-Free Boiler Feed Water by Ion Exchange

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The complete removal of silica from water has been attained with ion exchange resins. Silica is converted to fluosilicic acid and removed as such by an anion resin. Three methods of fluoride addition for silica removal and six different anion resins were used in the study. Alkali regeneration of exhausted anion beds must be preceded by acid or salt treatment to avoid precipitation of silica in the anion exchangers. Cost considerations show that this method of silica removal is best suited for silica concentrations below 10 parts per million.

THE problem of siliceous deposits in boilers and turbines has increased in importance as boiler pressures and temperatures have continued to rise. Some success in minimizing siliceous scales in high pressure boilers has been reported (*12*), but such boiler treatments still may not prevent siliceous deposits in the turbines. Figure 1 emphasizes (*13*) the importance of silica removal from boiler feed water used to generate steam for high pressure turbines. From studies on several 1200-pound-per-square-inch power plants, Straub and Grabowski found that silica concentrations above 0.1 part per million (p.p.m.) in the steam would cause deposits in the low pressure portion of turbines. They reported that addition of sodium and potassium chlorides to the boiler water reduced the amount of silica in the steam. Increasing the pH of the water, however, was much more effective.

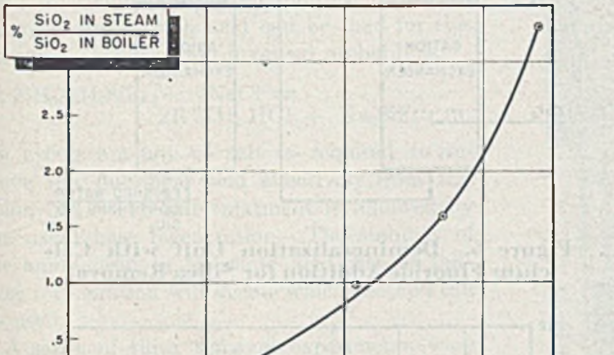

Figure 1

The most desirable method of reducing siliceous scale would be to eliminate the silica entirely. Several methods for reducing the silica concentration in boiler feed water with metallic oxides and hydroxides in various forms have been suggested and used (*8*). At standard demineralization temperatures of less than 100° F. none of these methods reduces the silica below about 2 p.p.m. When a demineralizing unit is being used with such silica removal methods, 2 p.p.m. silica constitutes an appreciable amount of the total solids in the make-up water. More silica is also present in the steam because of the low boiler salt content. Consequently, it is of prime importance to remove the last traces of silica in the demineralized boiler feed water.

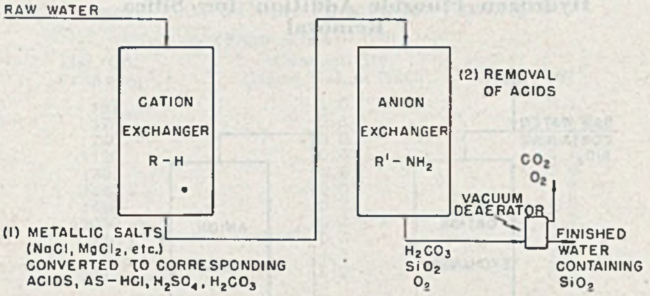

Figure 2. Typical Demineralization Unit

A simplified diagram of a typical demineralizing unit is shown in Figure 2. Such a unit consists of cation and anion exchangers placed in series. These cation resins are synthetic materials containing replaceable hydrogens as in carboxy, hydroxy, or sulfonic groups. Anion resins contain amine groups which form salts with acids. The cation exchangers are regenerated with acid, whereas basic solutions are used for anion regeneration. In passing through a demineralizing unit, the mineral salts in the incoming water are converted to the corresponding acids in the cation resin bed. These acids are then absorbed by the anion resin. Typical equations for such a demineralizing unit are:

$$2RH + CaCl_2 \longrightarrow CaR_2 + 2HCl \quad (1)$$

$$2R'NH_2 + 2HCl \longrightarrow 2R'NH_2.HCl \quad (2)$$

where R = cation resin
R' = anion resin

In a mixture of strong acids such as hydrochloric and sulfuric, carbonic acid when present is not effectively removed in the anion bed. It can be removed from the effluent, however, by an open gravity degasifier. If oxygen-free water is desired, this degasifier may be replaced by a vacuum deaerator. With present anion resins silica also is not removed efficiently by the standard demineralizing process (*5*). Partial silica removal is obtained with the

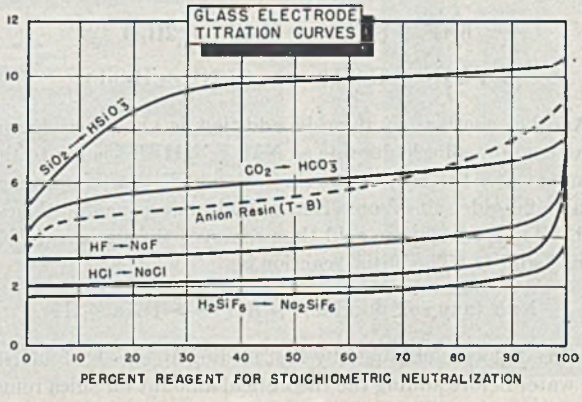

Figure 3

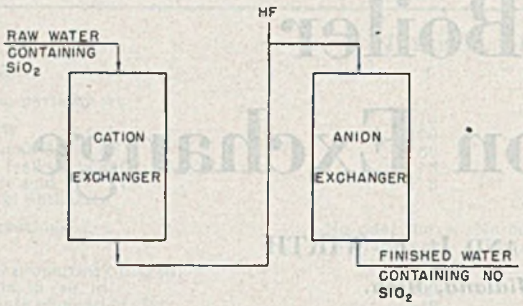

Figure 4. Demineralization Unit with Hydrogen Fluoride Addition for Silica Removal

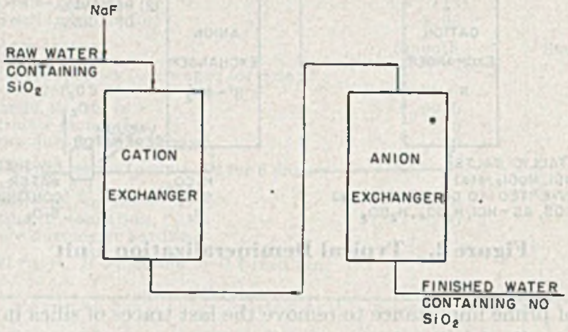

Figure 5. Demineralization Unit with Soluble Fluoride Addition for Silica Removal

more basic anion exchange resins in multibed operation, but for only a portion of the run (*10*).

The Dow Chemical Company has been doing laboratory work on a process which converts silica to fluosilicic acid and removes it in the standard demineralizing process (*3*). The titration curves in Figure 3 show (*6, 9*) that those acids below the curve for the anion exchange resin, as fluosilicic, readily form stable salts of the anion exchange resin and are removed from solution. Silicic and other weak acids above the anion curve do not form stable salts of the resin and are incompletely removed from the water. In demineralizing a natural water treated with fluoride for silica removal, the cation effluent contains carbonic, hydrofluoric, hydrochloric, sulfuric, and fluosilicic acids. In general the anion exchanger will absorb strong acids in preference to weak acids. Hence carbonic acid appears first in the anion effluent, followed by hydrofluoric, hydrochloric, sulfuric, and fluosilicic acids as the run continues. Therefore silica as fluosilicic acid continues to be removed from the water after the conductivity of the anion effluent rises.

Several methods can be used to react the fluoride with the silica. Figure 4 shows a scheme in which hydrofluoric acid is used. The reactions involved are:

$$6HF + SiO_2 \longrightarrow H_2SiF_6 + 2H_2O \qquad (3)$$

$$2R'NH_2 + H_2SiF_6 \longrightarrow (R'NH_2)_2.H_2SiF_6 \qquad (4)$$

Another method of fluoride addition is shown in Figure 5. Here a water-soluble fluoride as NaF or NH_4HF_2 is fed to the incoming water before it enters the cation bed. In this process the soluble fluoride salt is converted to hydrofluoric acid in the cation bed. The hydrofluoric acid then removes the silica as in Equations 3 and 4. The initial reaction is:

$$NaF \text{ (any sol. fluoride)} + RH \longrightarrow RNa + HF \qquad (5)$$

Best results were obtained by first feeding an excess of fluoride to the water before adding the theoretical amount for silica removal. In this way some hydrofluoric acid is loaded on the anion resin before the major portion of the run starts. A third method which has been utilized is given in Figure 6. Here a relatively insoluble fluoride as CaF_2 is intimately mixed with the cation resin bed. The solubility of calcium fluoride in water is so low that recirculation of acid cation exchange water through a calcium fluoride bed and back into the raw water would require 100% recycle to remove a few p.p.m. silica. By mixing the calcium fluoride with the cation bed, however, a much greater fluoride concentration is obtained for silica removal. The high fluoride concentration produced initially in this method is absorbed by the anion resin and removes silica later in the run.

The initial reaction is:

$$CaF_2 \text{ (any relatively insol. fluoride)} + 2RH \longrightarrow R_2Ca + 2\,HF \qquad (6)$$

The hydrogen fluoride removes the silica as shown in Equation 3. The excess hydrogen fluoride reactions are:

$$R'NH_2 + HF \longrightarrow R'NH_2.HF \qquad (7)$$

$$6R'NH_2\,HF + SiO_2 \longrightarrow (R'NH_2)_2\,H_2SiF_6 + 4R'NH_2 + H_2O \qquad (8)$$

The removal of silica by the fluoride method seems to be an equilibrium phenomenon. Excess fluoride is required to remove the silica effectively from water. Six different anion resins were used. Four of these are commercially available—Amberlite IR-4 (Resinous Products and Chemical Company), Deacidite (The Permutit Company), Duolite A-2 (Chemical Process Company), Ionac A-293 (American Cyanamid and Chemical Corporation)—while the other two are experimental preparations. One of the experimental resins is a condensation product of phenol, formaldehyde, and tetraethylene pentamine prepared according to the method of Cheetham and Myers (*4*). The other laboratory resin is a condensation product of phenol, formaldehyde, and ammonium sulfate. All six anion exchangers removed silica from water by the fluoride method. The optimum operating conditions for the resins, however, differed. Extensive work was done with the pentamine laboratory preparation (designated as

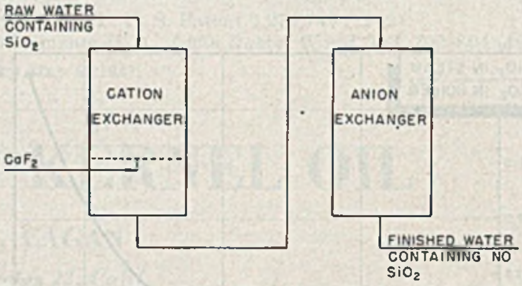

Figure 6. Demineralization Unit with Calcium Fluoride Addition for Silica Removal

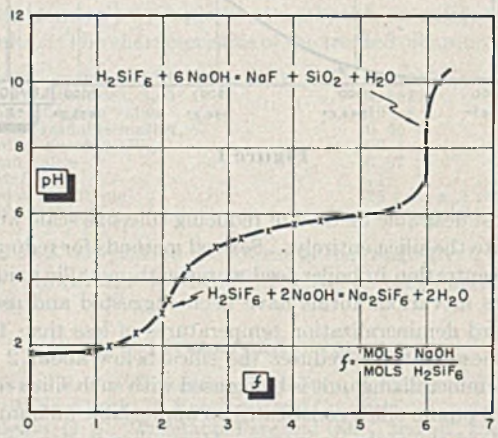

Figure 7. Glass Electrode Titration of Fluosilicic Acid

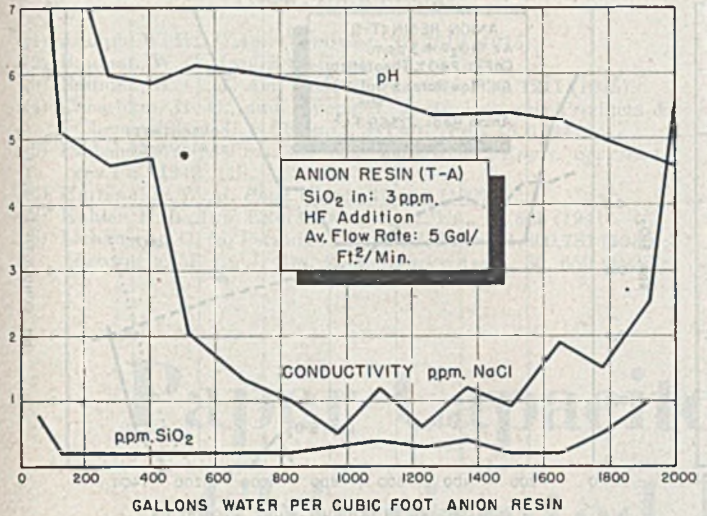

Figure 8

T-A in this paper), Duolite A-2 (T-B), and the ammonium sulfate resin (T-C).

Regeneration of a silica-removal demineralizing unit differs from that for the standard units. The cation bed is still regenerated with acid, but the anion resin cannot be directly treated with a basic solution. Figure 7 shows (*9*) the complete titration curve for fluosilicic acid, which is stable only in the low pH portion of the curve. For pH values higher than about 4, fluosilicic acid decomposes to silica. Hence, if the anion exchanger were treated directly with a base, silica would be deposited in the bed. To avoid this difficulty, the anion bed is first treated with a 5–10% solution of a strong acid. This acid treatment displaces the fluosilicic acid from the anion exchanger. The anion bed is then regenerated with a base as in the standard demineralizing units. Strong salt solutions will also remove the fluosilicic acid from the anion bed. The effluent from a cation exchanger being regenerated with acid can be used for this purpose. The reaction involved probably is:

$$(R'NH_2)_2.H_2SiF_6 + 2NaCl \rightleftarrows 2R'NH_2.HCl + Na_2SiF_6 \quad (9)$$

An excess amount of salt is required to remove the fluosilicic acid effectively from the anion bed. The salt treatment is followed by the usual base regeneration. The stability of the anion resin in alternate acid-base or salt-base regeneration will decide which method can be used.

A series of silica removal experiments were carried out using the three fluoride addition methods already described. Figure 8 shows the results obtained from a run in which 15% of the anion bed was converted to the hydrofluoride form by HF addition directly to the bed. The raw water to the exchangers was Midland city tap water containing 3 p.p.m. silica. The exhausted anion exchanger was treated with 5% hydrochloric acid before regeneration. Silica removal from the anion bed was 98% complete. Anion resin T-A was used in a 1-inch-diameter Saran tower with a bed depth of 30 inches. The cation exchanger used in all the silica tests was Dowex-30 (*2*).

Runs were also made using a soluble fluoride, as NaF. Tower tests showed that with sodium fluoride 150–175% of the theoretical fluoride is required to remove silica completely, when the fluoride is proportioned directly to the raw water. Only 130% of the theoretical fluoride is required when the 30% excess fluoride is fed at the start of the run and theoretical fluoride is proportioned to the raw water for the remainder of the run. Table I shows the tower data from such a run using T-B anion exchanger. Initial silica was 3.5 p.p.m., and the anion bed flow rate was 2 gallons per square foot per minute on a bed depth of 30 inches.

Table I. Sodium Fluoride Addition for Silica Removal, with 0.00376 Cubic Foot Anion Resin T-B

(P.p.m. silica = 0.0)

Gal./Cu. Ft. Anion	Conductivity, Grains/Gal. as NaCl	pH
187	1.0	9.3
373	0.3	8.6
746	0.0	...
1120	0.0	6.7
1305	0.0	5.6
1493	0.0	5.3
1680	0.3	5.0
2050	0.3	4.7
2240	0.5	4.6
2425	1.5	4.1
2610	3.0	3.8

This method of fluoride addition was also used with a 6-inch-diameter glass column containing about one half cubic foot anion resin T-C in about a 36-inch bed depth. Figure 9 shows the laboratory setup for this unit. Pyrex columns were used frequently in the experimental work and showed no detectable silica loss. The data from a run of this unit is shown in Figure 10.

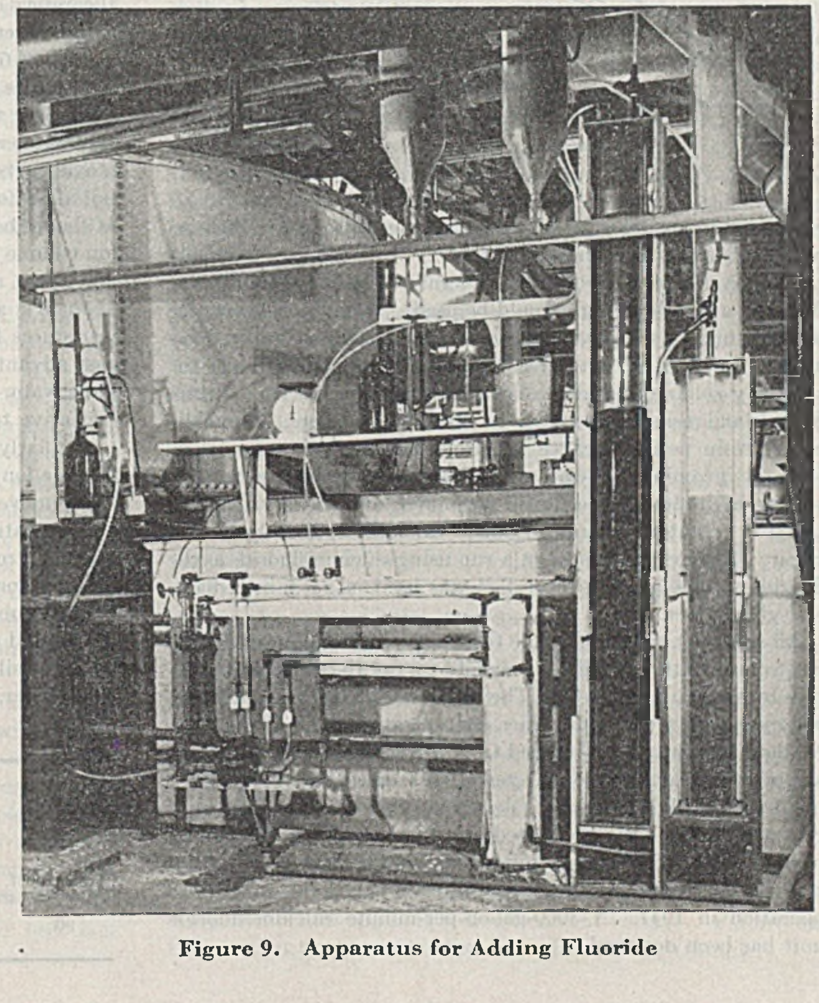

Figure 9. Apparatus for Adding Fluoride

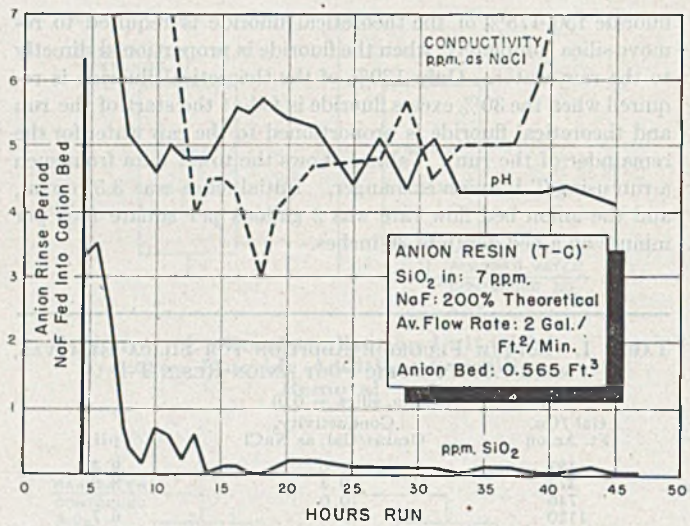

Figure 10

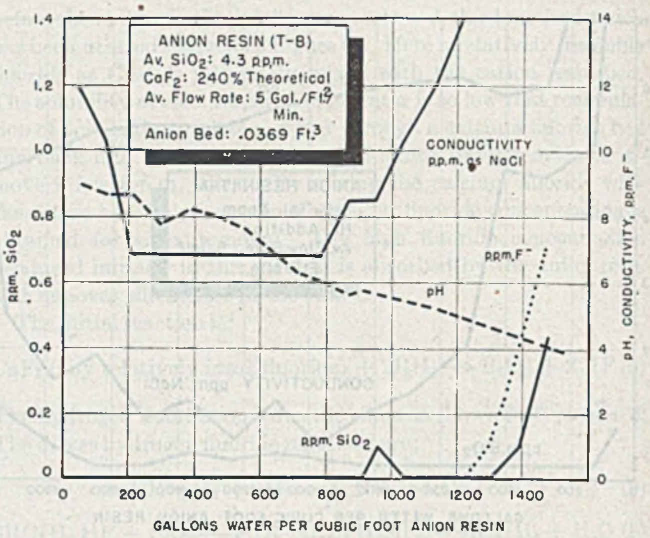

Figure 11

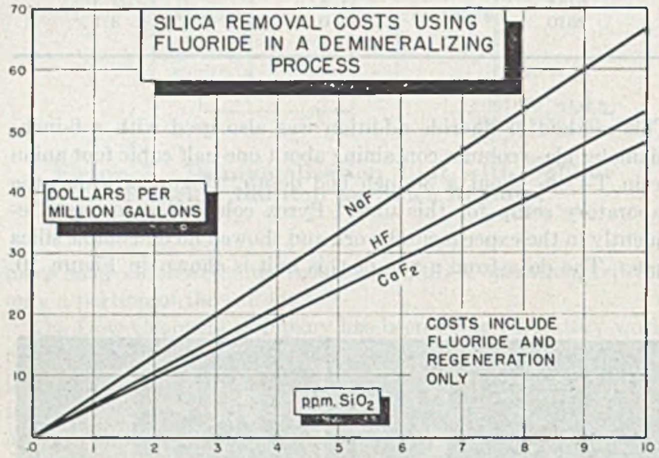

Figure 12

Somewhat more fluoride was required for equivalent silica removal using this resin than resin T-B.

Work was also carried out to determine if relatively insoluble fluorides as CaF_2 or MgF_2 could be used. Such fluorides can be used by mixing them with the cation exchanger. Proper operation leaves the bottom portion of the bed relatively free of the sparingly soluble fluoride while intimate mixing of the calcium fluoride and resin occurs above the slurry feed header. The acidic cation resin performs three functions: (*a*) removes metal ions from the incoming feed water, (*b*) reacts with the calcium fluoride to form hydrofluoric acid for silica removal, and (*c*) acts as a filter bed for retention of unconsumed calcium fluoride particles. Figure 11 shows the results of a run using calcium fluoride as the fluoride source. Anion resin T-B was used in a 1.5-inch-diameter glass tower.

All silica (*7*) and fluoride (*1*) tests were made colorimetrically. Salt concentrations were determined by a Sol U-Bridge and hardness by standard soap test. The experimental work was done on waters having a maximum silica concentration of about 7 p.p.m. Midland city water is obtained from a river source. The average tap water analysis for the year 1942 is given in Table II.

Further work is planned to determine the optimum silica concentrations which can be treated by this method. A 200-gallon-per-minute demineralizing unit using sodium fluoride for silica removal in boiler feed make-up water is scheduled to go into operation in 1947. A 3000-gallon-per-minute calcium fluoride unit has been designed.

In applications of this method for silica removal it should be remembered that the fluoride ion is one of the first to break through. Great care must be taken in the operation of such units if fluoride is harmful in the effluent. Water used for drinking which contains over a few p.p.m. fluoride causes mottled teeth. The effect of fluorides in boilers has not as yet been definitely established.

Of interest to prospective users is the cost of the fluoride silica removal method. Figure 12 shows cost curves for the removal of various silica concentrations with sodium fluoride, hydrogen fluoride (both 175% theoretical), and calcium fluoride (250% theoretical). For these calculations efficiencies for sulfuric acid cation regeneration of 35% and a sodium carbonate anion regeneration of 67% were used.

All costs are as of July 1946 (*11*). An additional charge of two dollars per ton was added to the calcium fluoride cost for grinding the commercial material through 300 Tyler mesh. The silica removal costs include only fluoride and regeneration costs, and do not allow for the additional wash water and equipment required. It should be noted that with hydrogen fluoride no additional cation volume is required. With fluoride salts, however, a water of 200 p.p.m. as calcium carbonate and 1 p.p.m. silica would require about 5% additional cation bed. The use of hydrogen fluoride introduces handling and maintenance problems which offset its cost advantage. The calcium fluoride method is well suited to large water-treating units. Sodium fluoride, although the most expensive treatment, is easily handled and proportioned. It is particularly well suited for small scale water treatment. The fluoride ion exchange treatment is the only one at present which will remove silica in the cold to concentrations below 2 p.p.m. Concentrations to 5 p.p.m. can be treated very economically. Fluoride treatment of silica higher than 10 p.p.m. is best preceded by an absorption method.

The problem of complete silica removal from water has long confronted the water profession. Now for the first time the last traces of silica can be removed efficiently and also economically from water.

TABLE II. MIDLAND, MICH. TAP WATER AVERAGE ANALYSIS FOR YEAR 1942

Cl as NaCl. P.P.M. Total	Parts per Million				Alkalinity as $CaCO_3$, P.P.M.		Palmitate Hardness as P.P.M.
	Ca	Mg	SO_4	SiO_2	CO_3	HCO_3	$CaCO_3$
90	20	9	55	5	26	29	73

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Received September 9, 1946. Presented at the 7th Annual Water Conference, Engineers' Society of Western Pennsylvania, Pittsburgh, Pa., January 1947.

Paper Capacitors Containing Chlorinated Impregnants

BENEFITS OF CONTROLLED OXIDATION OF THE PAPER[1]

D. A. McLEAN

Bell Telephone Laboratories, Inc., Murray Hill, N. J.

Contrary to the usual belief, properly controlled oxidation of kraft insulating paper can have marked beneficial effects on its electrical properties. The insulation resistance and power factor of kraft capacitor tissue at elevated temperatures are improved by oxidation. The effect of oxidation is permanent in the sense that it remains after the paper has been humidified and redried. These improvements persist when the paper is impregnated with anthraquinone-stabilized chlorinated diphenyl. In addition, oxidation of the paper brings about a substantial improvement in the accelerated life performance of capacitors. The benefits of controlled oxidation have been realized in the commercial production of capacitors.

OXIDATION is known to degrade the mechanical properties of paper. It has often been assumed that oxidation is also harmful to the electrical quality of insulating paper. The data presented here demonstrate that this is not always so; on the contrary, large benefits may be realized by subjecting insulating paper to controlled oxidation. These benefits have been demonstrated with respect to kraft capacitor tissue and to such tissue when impregnated with pentachlorodiphenyl subsequent to oxidation. Effects of oxidation on other types of paper are unknown, but improvements in the cases studied are large enough to suggest extension of the study to other types. Improvement of the electrical performance of capacitor tissue by controlled oxidation is probably related to the stabilizing action of oxidizing organic compounds previously described (*1*).

In these experiments the samples were capacitor windings comprising standard aluminum capacitor foil interleaved with 0.0004-inch kraft capacitor paper. In some windings two layers of paper were used between foils and in other cases three layers. These will be referred to as two-layer and three-layer samples. In all cases the units were of such size as to give a capacity of about 1 microfarad when impregnated with pentachlorodiphenyl. The paper used represented the product of several suppliers. For the impregnant, pentachlorodiphenyl (Aroclor 1254) stabilized with 1.5% anthraquinone was used.

In some instances the units were assembled in capacitor cans with phenol plastic terminals, as shown in Figure 1. Generally two units were assembled in a can and were connected in parallel to form a 2-microfarad test capacitor. A small filling hole in the top was soldered shut after processing. In other instances pairs of units were held in steel clamps during processing and were mounted in glass tubes for measuring, as shown in Figure 2. In this case three leads were brought out so that each 1-microfarad unit could be measured separately. These variations in the method of mounting samples did not appear to alter the nature of the results.

Many of the samples tested were vacuum-dried and impregnated in the capacitor shop in commercial equipment. The shop process was designed to attain moisture contents of less than 0.5% whether the samples had been prebaked or not. It involved 46 hours of vacuum treatment at 120° C., including periods of alternate vacuum during which the samples were momentarily vented to atmospheric pressure every 15 minutes.

Other samples were prepared by special methods adapted to particular experiments in connection with which they will be described. The oxidation treatments described apply to the paper and foil windings prior to impregnation and were carried out in the absence of the impregnant. The impregnant was not exposed to any oxidation treatment.

Insulation resistance values in megohms were calculated from the current flowing at the end of 1-minute application of direct current potential. These values were then multiplied by the capacity in microfarads to bring all values to a common basis and are reported as the product of megohms × microfarads.

Power factor measurements were made by standard methods at a frequency of 1000 cycles and about 5 volts applied to the sample. The significance of these testing conditions has been discussed previously (*3*).

Life tests were made by maintaining the samples at a constant temperature and applying a direct current voltage. Failure was indicated by the blowing of fuses in series with each sample.

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[1] The first three papers of this series appeared in January 1945, May 1946 (*1*), and November 1946 (*3*).

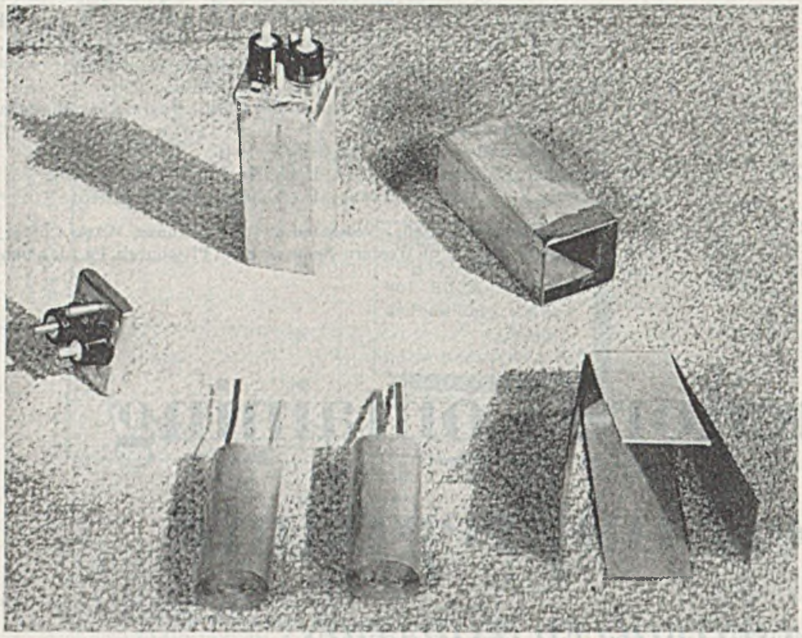

Figure 1. Parts and Assembly of Samples Used to Obtain Data for Figures 3, 4, and 5

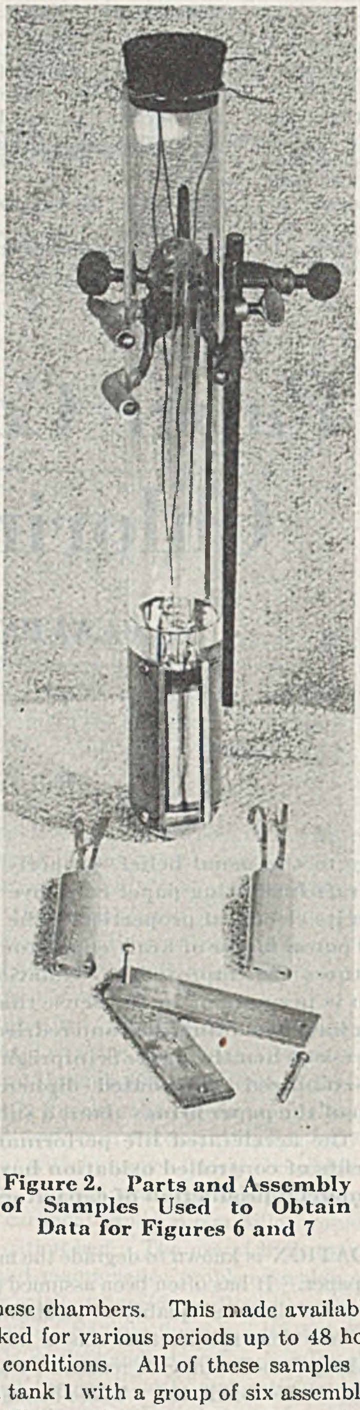

Figure 2. Parts and Assembly of Samples Used to Obtain Data for Figures 6 and 7

INSULATION RESISTANCE AND POWER FACTOR

Table I gives the results of some experiments made during one phase of the study of effects of oxidation. Three-layer windings were made from six different lots of paper representing the product of two paper manufacturers. From each of these six lots, two test capacitors were treated by the shop process without any preliminary treatment. Two others were first baked in a mechanical convection air oven for 40 hours at 135° C. and then put through the shop process. The air baking produces a large beneficial effect, the minimum factor of improvement being 2.14 and the average 3.31. In subsequent work several samples of paper have been encountered which showed factors of improvement less than 2.14, but none which showed a greater improvement than the factor of 4.96 for sample 6.

The following large scale experiment was performed: Prebaking of capacitor assemblies consisting of three-layer units in standard cans (Figure 1) was carried out in three different chambers, all adjusted to 135° C. Tank 1 was held under a vacuum of about 6 mm. and vented to atmospheric pressure momentarily every 15 minutes. Tank 2 contained stagnant air at atmospheric pressure. The third condition was obtained in a laboratory oven in which air was circulated rapidly. Every 8 hours for 48 hours, six 2-microfarad assemblies (two three-layer units in parallel) were placed in each of these chambers. This made available samples which had been baked for various periods up to 48 hours under the three different conditions. All of these samples were then brought together in tank 1 with a group of six assemblies having no pretreatment. All were then put through the shop process described. Insulation resistance measurements were made at 65° C. with 1050 volts applied.

TABLE I. EFFECT OF AIR BAKING ON INSULATION RESISTANCE AT 65° C.

(Assemblies processed by shop process; baking was 40 hours in air at 135° C.)

Paper Sample	Insulation Resistance, Megohms × Microfarads		Improvement Ratio, Av.
	Not baked	Baked	
1	178	685	3.92
	177	710	
2	187	711	3.76
	169	630	
3	162	362	2.14
	175	356	
4	150	356	2.35
	141	324	
5	190	510	2.76
	189	540	
6	96	456	4.96
	86	452	
			Average 3.31

Average insulation resistance values for each group of six are plotted in Figure 3. The results are consistent with Table I and amply confirm the benefits of baking in air upon the insulation resistance. The possiblity that baking in air simply results in removal of more moisture is eliminated by this experiment, since the samples baked in vacuum show no corresponding improvement in properties, although the conditions for water removal are better than for the other groups. The small progressive improvement in insulation resistance of the vacuum-treated samples may result from the removal of small additional amounts of moisture. However, it is more likely that even here the improvement reflects a small amount of air-baking since (*a*) the residual pressure during the vacuum treatment was about 6 mm. of mercury and (*b*) the tank was vented to atmospheric pressure momentarily every 15 minutes.

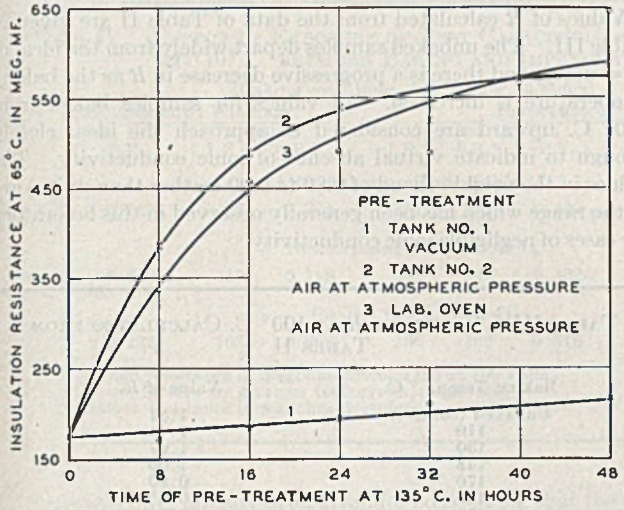

Figure 3. Comparison of Effects of Air Baking and Vacuum Baking on Insulation Resistance of Test Capacitors

Figure 4 illustrates further the effect of heating in air prior to treating by the shop process. The distribution of insulation resistance values for 971 capacitors processed without an air bake is compared with the distribution for a group of fifty-five similar capacitors which were heated in air for 48 hours at 135° C. prior to processing. The most probable value for the unbaked capacitors is about 175 megohm-microfarads; that for the baked is 525, an improvement ratio of 3.0. Furthermore, the lowest values observed for the air-baked samples are higher than the best values for the unbaked samples.

The beneficial effects of air baking on direct current life are shown in Figure 5, which gives results of accelerated life tests at 1500 volts on several groups of samples represented in Figure 3. The test temperature was 90° C. during the first 200 days of test and 85° C. for the remainder of the test. There is an indication of an optimum life at some baking time less than 48 hours. However, a sample of four is scarcely enough to give a reliable picture where small differences are involved, because of the wide spread of life values for any given condition. This wide spread is an unfortunate characteristic of virtually all capacitor life test data. The difference between the life test performance of baked and unbaked samples is great enough to be highly significant despite the small number tested.

It seemed reasonable to assume that the effects of baking depend upon a reaction between the paper and oxygen of the air and are not related to the electrode metal. However, some experiments to test this point appeared in order. Unbaked units using a particular paper gave an average insulation resistance value of 95 megohm-microfarads at 65° C. and 1050 volts. When rolls of this paper were baked prior to making the capacitor windings, and in the absence of the foil and all other components, six values ranging from 500 to 765 megohm-microfarads were observed. When the foil was baked and the paper not, three values ranging from 106 and 115 were observed.

Several experiments have been carried out to determine the relation between insulation resistance and the conditions of air baking. A group of two-layer windings all containing the same paper were divided into groups of four and one group air-baked for 16 hours at each of the following temperatures: 110°, 130°, 148°, 170°, 187°, and 210° C. For comparison with these, four unbaked windings were vacuum-dried.

The procedure was as follows: The windings were held in pairs between metal clamps with spacers to give a consistent thickness and pressure. The set of unbaked samples was placed in a laboratory vacuum tank at 135° C. and evacuated to less than 1.0 mm. of mercury for 20 hours. During the last four hours of this period air was admitted momentarily approximately every half hour to aid in flushing out residual moisture. After this drying treatment the units were transferred rapidly while still hot to a large test tube with a container of P_2O_5 in the bottom. Leads insulated with Pyrex tubing were brought out through a rubber stopper in the top of the tube. Measurements of insulation resistance at 100 volts and power factor at 1000 cycles, 5 volts, were made on these dried unimpregnated windings at 65° and 100° C. While still at 100° C. the windings were transferred rapidly to a windlass over impregnant at 135° C., evacuated for 5 minutes, lowered into the impregnant, and soaked in the impregnant at atmospheric pressure for 2 hours. Insulation resistance measurements at 100 and 533 volts as well as power factor measurements were then made on the impregnated units.

In preparing the baked samples, windings were assembled in clamps as described and heated for 16 hours in an air oven regulated at the desired temperature. The windings were then transferred to a vacuum tank at 135° C. and evacuated for 4 hours, air being admitted every half hour and immediately pumped out again. The dry windings were then transferred to a glass test tube for measurement, exactly as in the case of the unbaked samples. The subsequent measurements and treatments were the same as for the unbaked samples.

The average results for each group are given in Table II. Figures 6 and 7 present all of these average values except the 100-volt insulation resistance values for the impregnated samples.

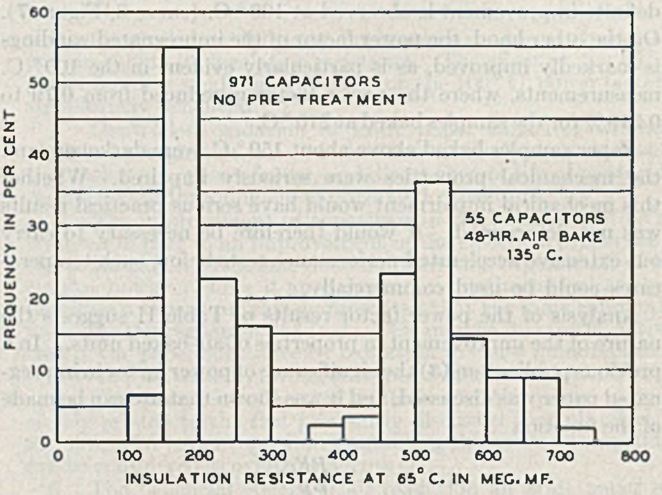

Figure 4. Effect of Air Baking on Distribution Curve of Insulation Resistance

TABLE II. EFFECT OF BAKING ON PROPERTIES OF DRY PAPER, BOTH UNIMPREGNATED AND IMPREGNATED

16-Hr. Pretreatment, °C.	Unimpregnated Windings				Impregnated Windings					
	65° C.		100° C.		65° C.			100° C.		
	I.R.[a]	P.F.[b]	I.R.[a]	P.F.	I.R.[a]	I.R.[c]	P.F.	I.R.[a]	I.R.	P.F.
Unbaked (control)	374	0.232	103	0.208	186	156	0.518	25.3	14.2	0.79
110	554	0.238	133	0.216	293	232	0.480	32.2	21.5	0.536
130	975	0.256	151	0.200	405	384	0.442	40.5	29.5	0.450
148	910	0.250	150	0.198	342	349	0.467	38.8	26.0	0.461
170	932	0.262	137	0.189	434	371	0.415	44.3	31.8	0.374
187	1020	0.254	152	0.190	366	283	0.430	42.3	29.4	0.360
210	1110	0.240	183	0.173	324	329	0.395	41.3	39.9	0.319

[a] Insulation resistance in megohm-microfarads at 100 volts.
[b] All power factors are given at 1000 cycles, in per cent.
[c] Insulation resistance in megohm-microfarads at 533 volts.

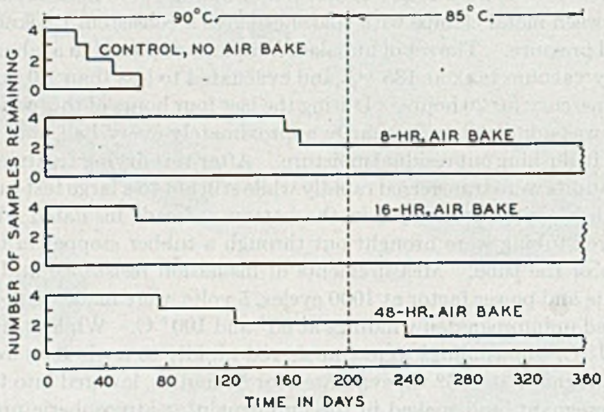

Figure 5. Effect of Air Baking on Life of Test Capacitors with Applied Direct Current Voltage of 1500

The particular paper used did not show the effect of air baking to so great a degree as most others, the improvement ratio being about 2.0. The irregularity of the curves is probably explained by sampling variations, since each group of four showed considerable spread.

The marked effect of baking on the insulation resistance of the unimpregnated windings is of interest, since it shows that the improvement is observed even in the absence of impregnant, and that much of the effect observed in impregnated units is an intrinsic improvement in the paper.

Air baking is seen to have only a small effect on the power factor of unimpregnated windings. In fact, no significant improvement is shown in the 65° C. values (curve 3, Figure 6). A small but definite improvement is observed at 100° C. (curve 3, Figure 7). On the other hand, the power factor of the impregnated windings is markedly improved, as is particularly evident in the 100° C. measurements, where the power factor is reduced from 0.79 to 0.319% for the samples baked at 210° C.

Paper samples baked above about 150° C. were darkened, and the mechanical properties were seriously impaired. Whether this mechanical impairment would have serious practical results was not determined. It would therefore be necessary to carry out extensive accelerated performance tests before such temperatures could be used commercially.

Analysis of the power factor results of Table II suggests the nature of the improvement in properties of air-baked units. In a previous publication (*3*) the significance of power factor in impregnated paper was discussed, and it was shown that use can be made of the function

$$R = \frac{\frac{PF_i}{PF_u}}{\frac{C_i}{C_u}}$$

where PF and C represent power factor and capacity, respectively, and the subscripts i and u refer to the impregnated and unimpregnated condition, respectively.

If regions of anomalous dispersion in the impregnant are avoided (as in the present work), all conductivity in the impregnant may be assumed to be ionic. For the case of negligible ionic conductance in the impregnant, R has a theoretical value of unity. Experimentally it has been found that, in instances where the conductivity of the impregnant is known to be negligible, R actually is a little less than unity, usually about 0.9. This small discrepancy with theory is attributed to minor inadequacies of certain assumptions made in the derivation.

If the conductivity of the impregnant is not negligible, then R is greater than unity, and a number of cases of R greater than 10 have been observed.

Values of R calculated from the data of Table II are given in Table III. The unbaked samples depart widely from the ideal of R = unity, and there is a progressive decrease in R as the baking temperature is increased. All values for samples baked from 130° C. upward are considered to approach the ideal closely enough to indicate virtual absence of ionic conductivity. The values in the neighborhood of 0.80 to 0.90 (rather than unity) are in the range which has been generally observed in this laboratory for cases of negligible ionic conductivity.

Table III. Values of R at 100° C. Calculated from Table II

Baking Temp., ° C.	Value of R
Unbaked (control)	1.81
110	1.14
130	1.07
148	1.06
170	0.90
187	0.85
210	0.84

The general significance of the relation shown by Table III can be stated in the following way: Table II shows that (*a*) the power factor of the paper alone is modestly improved by baking and (*b*) the power factor of the impregnated paper is greatly improved. Table III shows that *b* cannot be explained entirely by *a* but that there is an additional factor—namely, the decrease in ionic conductivity of the impregnant in the baked samples.

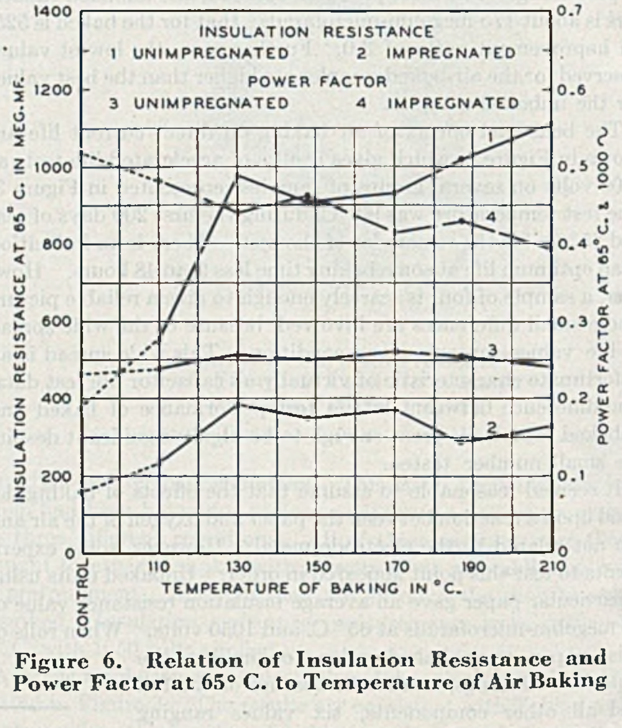

Figure 6. Relation of Insulation Resistance and Power Factor at 65° C. to Temperature of Air Baking

Another indication of variation in ionic conductivity is the following: As shown by Table II, the power factor of the impregnated controls increases substantially when the temperature is varied from 65° to 100° C., as is characteristic of ionic conductivity. The increase in power factor is progressively less for samples baked at 110° and 130° C. For samples baked above 130° C. there is a decrease in power factor as the temperature is raised, the decrease being greater the higher the temperature of baking. Undoubtedly in these cases the ionic conductivity in the impregnant is so low as to be insignificant compared to the alternating current losses in the paper, and the decreasing power factor reflects the decrease of power factor of paper with increasing temperature in the range under consideration (Table II).

Table IV. Effect of Exposure of Test Capacitors to 100% Humidity at 110° C. between Baking and Impregnation

(Baking conditions, 148° C. for 16 hours)

Unimpregnated Windings				Impregnated Windings					
65°C.		100°C.		65°C.			100°C.		
I.R.[a]	P.F.[b]	I.R.[a]	P.F.	I.R.[a]	I.R.[c]	P.F.	I.R.[a]	I.R.[b]	P.F.
After Exposure (from Table II)									
1010	0.227	128	0.201	357	352	0.430	44.5	28.8	0.495
Not Exposed (from Table II)									
910	0.250	150	0.198	342	349	0.467	38.8	26.0	0.461
Control (from Table II)									
374	0.232	103	0.208	186	156	0.518	25.3	14.2	0.79

[a] Insulation resistance in megohm-microfarads at 100 volts.
[b] All power factors are given at 1000 cycles, in per cent.
[c] Insulation resistance in megohm-microfarads at 533 volts.

Reasons have already been given for considering that the effect of the baking treatment is not associated with an especially effective elimination of moisture brought about by the baking treatment. One further experiment was carried out to test this point. A set of four units from the same group used to obtain the results in Table II was air-baked at 148° C. for 16 hours, then exposed to water in a closed tube at 110° C. for 14 hours (100% relative humidity). They were then vacuum-dried for 20 hours at 135° C., and electrical measurements made on the redried units at 65° and 100° C. After this they were impregnated with pentachlorodiphenyl-anthraquinone solution and remeasured. The data are given by the first row of data in Table IV. It is obvious that the properties correspond much more closely to those of the baked samples (148° C.) of Table II than to those of the unbaked samples. This experiment provides strong evidence (*a*) that the effect of baking does not result from better dehydration and (*b*) that the baking treatment produces an effect which is not destroyed by drastic humidifications.

The first conclusion should be qualified by stating that extensive heating of paper in vacuum decreases the equilibrium moisture content (*2*). Although no similar investigation has been made of the effect of heating paper in air on the equilibrium moisture content, presumably this also will result in an alteration of the adsorption isotherm. However, the fact that extensive heating in vacuum does not markedly improve the insulation resistance, despite its influence on the adsorption isotherm, indicates that this phenomenon has a negligible effect on the insulation resistance of well dried samples.

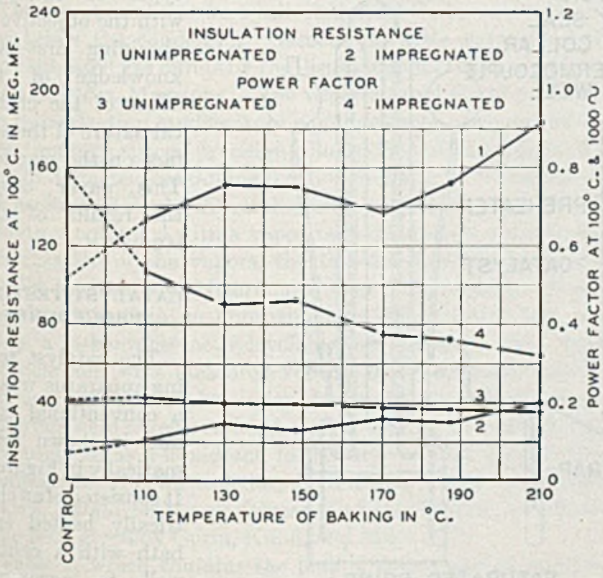

Figure 7. Relation of Insulation Resistance and Power Factor at 100° C. to Temperature of Air Baking

This investigation has dealt chiefly with the benefits of oxidation of the paper for capacitors containing anthraquinone-stabilized impregnant. However, air baking of windings prior to impregnation has also been found to improve the insulation resistance of capacitors containing unstablilized chlorinated diphenyl. The data of the following table, which gives the effect of air baking on insulation resistance, are typical. Assemblies were processed by shop process: baking was 16 hours at 130° C.; and the impregnant was unstabilized pentachlorodiphenyl. Units for insulation resistance are given in megohm-microfarads at 65° C. and 1050 volts:

Not baked	Baked
245	545
244	460

From the standpoint of life, air baking does not eliminate the need for stabilization, even though it is likely to result in an improvement in life of unstabilized samples. In baked samples the presence of anthraquinone results in roughly a tenfold increase in life. The best results are obtained by baking plus use of a stabilized impregnant.

THEORY AND CONCLUSIONS

Although work required to confirm a detailed theory of the effect of controlled oxidation still remains to be done, it is possible to draw the following general conclusions, which are of theoretical as well as practical importance:

1. Controlled oxidation of kraft paper produces marked improvements in its insulation resistance. The effect on the 65° C. power factor is small, but the effect on the 100° C. power factor is significantly beneficial.
2. Controlled oxidation of kraft paper capacitor windings prior to impregnation has a marked beneficial effect on the insulation resistance, power factor, and direct current life of pentachlorodiphenyl-anthraquinone–impregnated capacitors.
3. The improvement of capacitors in this manner can be attributed in part to an improvement in the electrical properties of the kraft paper. It seems doubtful that this explains all of the results, however, since it appears from a mathematical analysis based on a theory previously presented that the ionic conductivity of the impregnant is reduced. This may be due to the activation of the paper substance by oxidation to cause immobilization of the ionic material by strong adsorption or chemical reaction.
4. The beneficial effects of oxidation of the paper may be closely related to the fact previously discussed that all effective stabilizers for paper capacitors containing chlorinated compounds can be considered as oxidizing agents (*1*).
5. The beneficial effects of air oxidation on kraft paper are permanent in the sense that they are not erased by a subsequent exposure of the paper to high humidities.

COMMERCIAL APPLICATION

These findings have been reduced to practice by the Western Electric Company workers, who have used controlled oxidation for several years to aid in producing capacitors of improved electrical characteristics and life. This process was a factor in satisfactory performance of electrical equipment built for the armed forces during the war.

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Received October 7, 1946.

Isomerization of 1- and 2-Pentenes

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The vapor-phase isomerization of 1-pentene and 2-pentene was studied over the temperature range 177° to 427° C. and at liquid space velocities from 0.5 to 24 hour^{-1}. The catalysts employed were specially prepared aluminas of low sodium content and of acidic nature. Reactions varying from simple double bond shifting to skeletal isomerization were found to occur, depending on the chemical nature of the catalyst surface and the temperature of the reaction. Based on the apparent similarity between the nature of the solid catalysts studied and the acidic catalysts commonly used in liquid phase hydrocarbon reactions, a mechanism involving carbonium ions is proposed to explain the vapor phase isomerization of olefins.

RECENT workers in the field of catalytic vapor-phase olefin isomerization are in substantial agreement about the general type of catalyst required for double bond shifting and for skeletal isomerization. There is, however, wide variance in the activities of the catalysts employed. McCarthy and Turkevich (*7*), using Alorco grade A activated alumina, report that substantially equilibrium concentrations of 1-butene and 2-butene were rapidly attained at 450° C. and more slowly at 400° C. when the starting material was 2-butene. When the starting material was 1-butene about 30 seconds were required to reach equilibrium at 450° C., and at 400° C. equilibrium was not reached because of excessive decomposition at the necessarily long contact times. These workers avoided skeletal isomerization by use of a non-acidic catalyst and claim that polymerization took place only in the runs using long contact times.

Ewell and Hardy (*3*) studied the isomerization of the pentenes over a variety of catalysts including Alorco A and catalysts prepared by coprecipitating alumina and other oxides by use of ammonia. Equilibrium between 1-pentene and 2-pentene was attained at temperatures ranging from 265° to 365° C. and at very long contact times. Hay, Montgomery, and Coull (*5*) investigated the isomerization of 1-hexene over various acidic catalysts, such as acid-treated clay, acid-treated alumina, and the Universal Oil Products polymerization catalyst. These authors report extensive skeletal isomerization together with various amounts of cracking and polymerization, depending on the experimental conditions used. They employed a relatively limited range of space velocities and studied the reaction between 285° and 500° C.

For some time an extensive study of alumina has been pursued in this laboratory and effort has been made to correlate (*a*) the various changes in physical properties—for example, surface area, density, and crystal structure—which alumina undergoes on heat treatment and (*b*) the chemical nature of the surface with the catalytic activity. The isomerization of 1-pentene under mild conditions was chosen as one of the routine tests of catalytic activity since the composition of the product could be followed by its refractive index increase, provided no side reactions or skeletal isomerization took place.

This reaction proved to be clean cut and simple for most of the catalysts tested, since the temperatures employed were around 250° C. and only double bond shifting took place. Aluminas which had been acid-treated to reduce their sodium content showed activity for skeletal isomerization and could not be evaluated by using only the refractive index increase of the product. One catalyst was found to give measurable conversion at 105° C., while others were quite effective at liquid space velocities above 24 hour^{-1}.

In view of the high activity of pure alumina gel for simple double bond isomerization and of the acid-treated alumina for skeletal isomerization, it was decided to make a more complete study of these reactions using the aforementioned types of catalysts, with the objective of obtaining first-hand knowledge of the effect of the chemical nature of the surface on the reaction. This paper covers the results of this study.

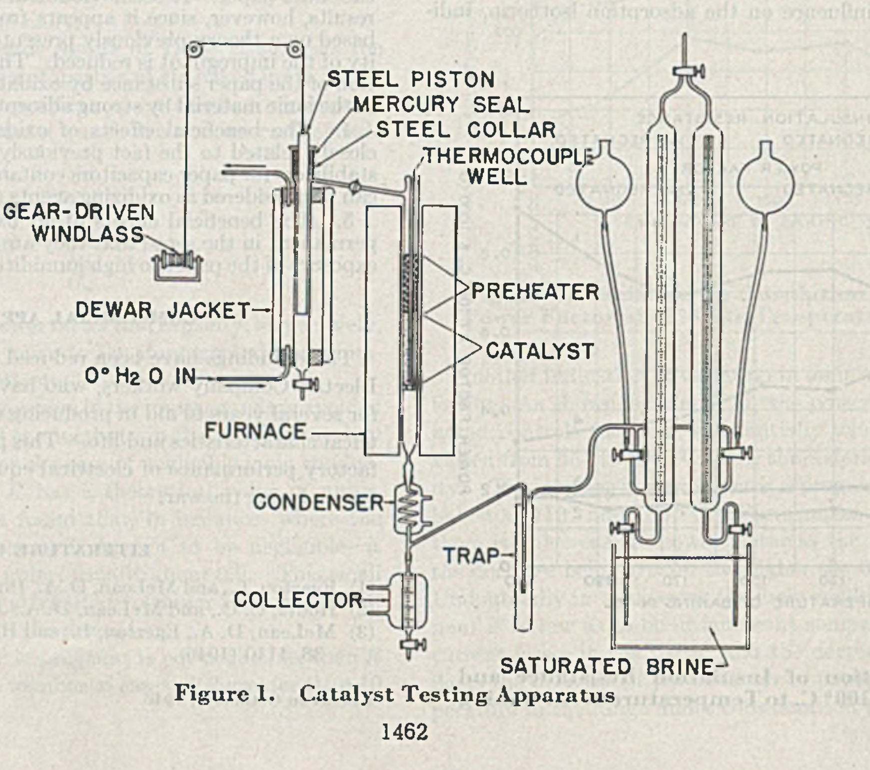

Figure 1. Catalyst Testing Apparatus

CATALYST TESTING PROCEDURES

The catalyst testing apparatus was of a conventional type and is shown schematically in Figure 1. It consisted of an electrically heated lead bath with a central well to accommodate a glass reactor.

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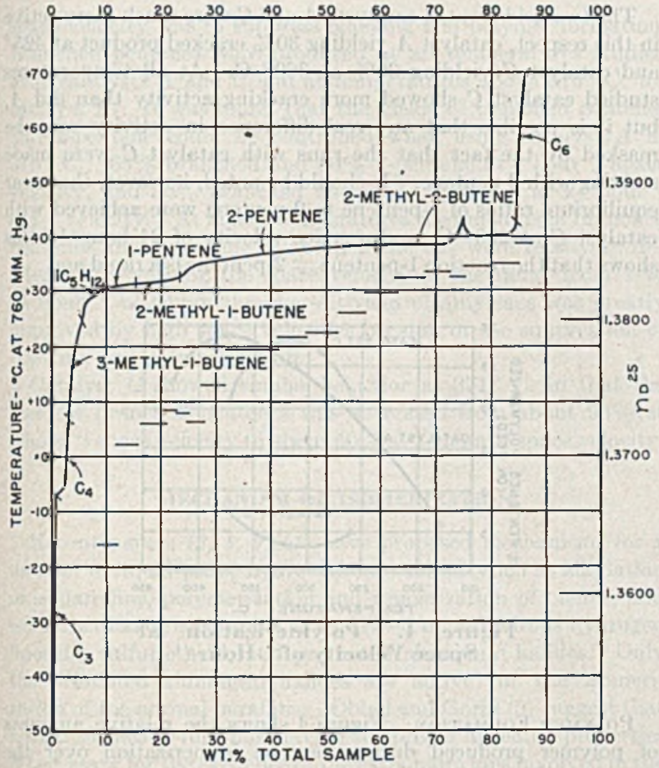

Figure 2. Typical Distillation Plot

The temperature was controlled manually, and the catalyst zone was maintained to within ±2° C. of the desired temperature. The catalyst bed was about 20 cm. long and was preceeded by a 10-cm. bed of crushed quartz which served to preheat the pentene feed. The catalyst was mixed with small glass beads during runs at high space velocity in order to keep the bed depth constant and to avoid using excessive amounts of feed. A fresh sample of catalyst was used in every run, and no attempt was made to study the active life of these catalysts.

Phillips' technical 2-pentene (n_D^{25} 1.3778) and Phillips' technical 1-pentene (n_D^{25} 1.3675–1.3682) were used in this study. The pentene at 0° C. was displaced from a thermostated reservoir by a steel plunger lowered at a constant rate by means of a motor-driven windlass. This feed device (*10*) was found to be satisfactory and could be made to deliver from 7 to 200 cc. per hour by changes in the driving gear.

The liquid products were collected at 0° C. in a vessel located just below the condenser. Gaseous products were collected in two calibrated gas burets by the displacement of saturated brine.

Analytical Methods. The vaporous and liquid products of the isomerization studies were combined and analyzed by fractionation on a special precision column (*8*), 4 feet long and 0.416 inch in diameter, containing 0.416-inch-diameter truncated conical packing of 50 × 70 mesh stainless steel wire gauze. This column is equipped with a vapor take-off, and, in order to avoid condensation of the vapors, the take-off lines are heated electrically by means of Nichrome ribbon. The column efficiency was determined to be approximately eighty theoretical plates using a *n*-heptane-methylcyclohexane mixture. Low boiling hydrocarbons were measured volumetrically as vapor and later condensed for refractive index determination. Higher boiling materials were taken overhead also as vapors, and condensed for measurement as a liquid and for refractive index determination. Components were identified by boiling points and by refractive indices. Data on the performance of this column on alkylates have been given by Gorin, Kuhn, and Miles (*4*).

Table I, which contains the boiling points and refractive indices of the various pentene isomers, shows that the analysis of these products was difficult. Complication was caused by the small concentrations of some components—that is, 3-methyl-1-butene and 1-pentene—the presence of which was not always apparent from the distillation curve. Figure 2 shows a sample distillation of the product from a high temperature run over a hydrofluoric acid-treated alumina catalyst.

In a few instances the break between 2-methyl-1-butene and 1-pentene was obscured by too rapid take-off in the operation of the column, and the resulting liquid cuts were too wide for more than a rough approximation of their composition from boiling point and refractive index. In these few instances, since the analysis for the more abundant component, 2-methyl-2-butene, was reliable, equilibrium ratios taken from Ewell and Hardy (*3*) were used to calculate the amount of 2-methyl-1-butene present in the 1-pentene cut. When this correction was applied it was found that the ratio of 1-pentene to 2-pentene in the product was brought into fair agreement with that determined by Ewell and Hardy.

It is recognized that the analytical procedure used to identify the products leaves much to be desired with respect to precision; nevertheless it is felt that the analyses justify the conclusions drawn from the work.

Cracking of the pentenes took place in the run, as shown by the presence of low boiling paraffins and isopentane in Figure 2 and by the presence of a small amount of carbonaceous residue on the catalyst. One of the branched pentenes probably acted as a hydrogen acceptor; this would account for the isopentane which was found.

CATALYSTS

The catalysts used in this study were specially prepared aluminas of low sodium content and of acidic or neutral character. Neutral alumina indicates that the alumina contained no added acid and was substantially pure alumina.

Catalyst *A* was prepared by leaching Alorco grade A alumina with 0.1 *N* acetic acid until the sodium content was reduced from about 0.49% to less than 0.08% by weight. The alumina was dried at 100° C., activated at 500° C. for 2 hours, impregnated with 5% hydrofluoric acid, and then reactivated at 500° C.

Table I. Data on Various Pentene Isomers (*1*)

Compound	B.P., ° C.	n_D^{25}
3-Methyl-1-butene	20.20	....
1-Pentene	30.1	1.3680
2-Methyl-1-butene	31.1	1.3745
trans-2-Pentene	36.0	1.3764
cis-2-Pentene	37.0	1.3789
2-Methyl-2-butene	38.45	1.3841

Catalyst *B* was a gel-type alumina prepared from pure aluminum metal by peptization with dilute acetic acid (*6*). The resulting sol was a thick sirupy liquid which was dried to give a granular alumina of high catalytic activity. Before use the catalyst was activated at 500° C. for 2 hours. This alumina was not treated with a mineral acid, but it did contain a small amount of acetic acid until the high temperature activation step destroyed the organic material.

Catalyst *C* was prepared by impregnating catalyst *B* with 5% aqueous hydrofluoric acid, drying at 100° C., and activating at 500° C. for 2 hours.

In catalysts *A* and *C* the fluorine content was reduced about 4% by the activation treatment given them. Prolonged heat treatment was found to remove most of the hydrogen fluoride from these catalysts.

EXPERIMENTAL RESULTS

Isomerization runs were made at various temperatures ranging from 177° to 427° C. and at liquid space velocities from 0.5 to 24 hour⁻¹. The results of these experiments are presented in Tables II and III.

Table II. Isomerization of 1-Pentene

Reaction Conditions		Compn. of Product, Wt. %				Compn. of Pentene Cut, Wt. %		
Temp., ° C.	L.H. S.V.^{a}	C_4 & lighter	Pentenes	Polymer	Material balance	1-pentene	2-pentene	Branched pentenes
Over Catalyst *A*								
177	1	0	93.8	6.2	101.0	46.2	53.8	0.0
177	6	0.7	95.3	4.0	95.0	42.9	57.1	0.0
177	24	0.3	97.7	1.9	96.0	82.0	18.0	0.0
260	0.5	0.7	77.1	22.2	100.0	15.1	54.5	30.4
260	3	0.4	85.7	13.9	99.0	11.1	67.0	21.9
260	12	0.2	94.6	5.2	99.0	4.9	78.2	16.9
316	1	0.4	78.4	21.2	90.6	5.6	30.8	63.6
316	6	1.5	74.4	24.1	99.8	3.9	47.5	48.6
316	24	0.8	91.4	7.8	96.1	12.0	55.4	32.6
371	1	7.3	63.6	29.1	101.6	9.5	36.9	53.6
371	6	5.9	74.7	19.4	97.5	10.7	38.6	50.7
371	24	2.4	92.9	4.7	91.3	11.0	44.0	45.0
427	6	25.8	52.6	21.6	100.0	0.0	35.7	64.3
427	24	8.5	81.0	10.5	99.7	5.2	31.2	63.6
Over Catalyst *B*								
260	0.5	0	95.7	4.3	102.0	10.8	89.2	0
260	1.0	0	95.1	4.9	99.1	14.8	85.2	0
260	1.0	0	92.2	7.8	96.8	11.0	83.9	5.1
260	6.0	0	93.0	7.0	97.2	30.8	64.4	4.8
316	0.5	0	96.0	4.0	100.4	13.0	87.0	0
316	3.0	0.4	97.8	1.8	98.3	14.2	81.6	4.2
316	6.0	0.4	97.9	1.7	98.9	10.7	89.3	0
371	0.5	3.9	87.1	9.0	100.8	4.6	62.7	32.7
371	1.0	1.9	89.7	8.4	98.7	8.7	55.5	35.8
371	3.0	0	95.4	4.6	101.4	9.8	70.3	19.9
371	6.0	0	96.4	3.6	100.0	12.7	59.1	28.2

^{a} Liquid hourly space velocity.

Table III. Isomerization of 2-Pentene over Catalyst *C*

Reaction Conditions		Compn. of Product, Wt. %				Compn. of Pentene Cut, Wt. %		
Temp., ° C.	L.H. S.V.^{a}	C_4 & lighter	Pentenes	Polymer	Material balance	1-pentene	2-pentene	Branched pentenes
260	1	10.5	68.3	21.2	106.0	11.0	67.0	22.0
260	12	0.7	94.3	5.0	98.3	13.0	80.4	6.6
260	24	0.0	96.2	3.8	104.0	7.3	84.0	8.7
316	1	19.6	51.8	28.6	105.0	0.0	28.6	71.4
316	12	2.7	84.7	12.6	102.0	19.0	52.3	28.7
316	24	2.2	90.5	7.3	105.0	14.2	69.5	16.3
371	6	23.3	57.6	19.1	101.0	0	13.7	86.3
371	12	12.6	71.9	15.5	...	0	22.7	77.3
371	24	7.3	77.3	15.4	98.8	8.0	46.2	45.8

^{a} Liquid hourly space velocity.

Fractionation analyses of the products showed the presence of material boiling outside of the pentene range—that is, butane and lighter and material boiling above 2-methyl-2-butene. These hydrocarbons are referred to as cracked product (C_4 and lighter) and polymer (C_6^+), respectively. In the few cases where isopentane was detected it was reported together with the butanes as cracked product.

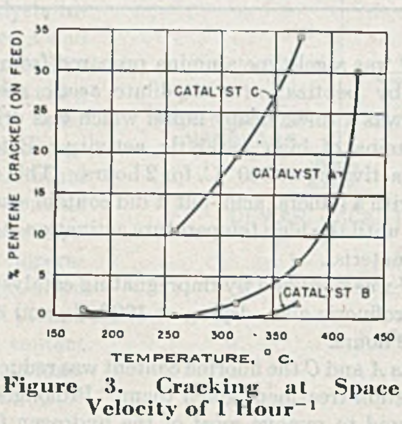

Figure 3. Cracking at Space Velocity of 1 Hour^{-1}

Cracking. The amounts of cracked product produced during the isomerization of 1-pentene over catalysts *A* and *B* and of 2-pentene over catalyst *C*, all at a liquid space velocity of 1 hour^{-1}, are shown in Figure 3. The pure alumina (catalyst *B*) showed little activity for cracking at temperatures up to 317° C. and and only slight cracking activity at 371° C.

The two acid-treated catalysts *A* and *C* were much more active in this respect, catalyst *A* yielding 30% cracked product at 425° and catalyst *C* yielding 30% at 360° C. At all temperatures studied catalyst *C* showed more cracking activity than did *A*, but it is possible that any real difference in activity may be masked by the fact that the runs with catalyst *C* were made starting with 2-pentene. It should be noted, however, that near equilibrium ratios of 1-pentene to 2-pentene were achieved with catalyst *C* at 260° C. and a space velocity of 24 hour^{-1}; this shows that the reaction 1-pentene $\rightleftharpoons$ 2-pentene is a rapid one.

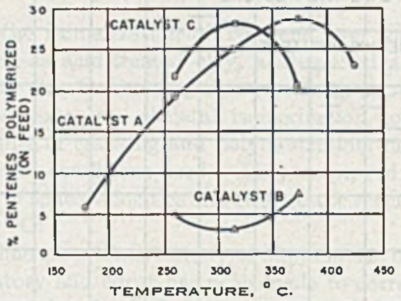

Figure 4. Polymerization at Space Velocity of 1 Hour^{-1}

Polymer Formation. Figure 4 shows the relative amounts of polymer produced during pentene isomerization over the three catalysts. Catalyst *B* yielded about 5% C_6^+ at temperatures from 260° to 371° C. Products from runs with catalysts *A* and *C* showed a maximum polymer concentration of about 28% at 371° and 316° C., respectively. It is interesting to note that 371° C. is the temperature above which extensive cracking takes place with catalyst *A*. Similarly, it may be said that cracking overbalances polymer formation on catalyst *C* at some temperature above 316° C. These data all refer to runs at 1 hour^{-1} space velocity; the curves will be different under other conditions.

Production of 2-Pentene. Of the three catalysts investigated, the pure alumina gel (catalyst *B*) gave the most clean-cut reaction. Figure 5 shows that between 260° and 316° C. and at 1 hour^{-1} space velocity, catalyst *B* gave a product containing about 85% 2-pentene in the pentene cut, the balance being 1-pentene. Catalyst *A* produced a pentene cut containing approximately 55% 2-pentene at 177° and 260° C. (1 hour^{-1} space velocity), the remainder being 1-pentene and branched-chain pentenes. Above 260° C. the concentration of 2-pentene dropped off sharply because of the formation of branched pentenes. Runs with catalyst *C* were made starting with 2-pentene, and the results were similar to those obtained with catalyst *B* in that the concentration of 2-pentene in the pentene cut dropped off sharply with increasing temperature. The highest concentration of 2-pentene in the pentene cut was obtained with catalyst *B*, which yielded about 90% at 316° C. and 6 hour^{-1} space velocity.

Branched Pentanes. The concentrations of the branched amylenes, 3-methyl-1-butene, 2-methyl-1-butene, and 2-methyl-2-butene, were combined and plotted as a function of temperature in Figure 6. These products resulted from runs with 1-pentene over catalysts *A* and *B* and with 2-pentene over *C*. The most active catalyst for skeletal isomerization was the acid-treated alumina gel (catalyst *C*), which yielded over 90% branched pentenes in the pentene cut at 360° C. and 1 hour^{-1} space velocity. Catalyst *A* appeared to show a linear function of activity with temperatures and yielded 70% branched pentenes at 427° C. The neutral alumina gel (catalyst *B*) produced practically no branching at 260° and 316° C. but did become active in this respect at 371° C.

Effect of Space Velocity. The chief effect of increasing space velocity was to suppress cracking and polymer formation. Branched pentenes were produced at all temperatures studied over catalysts *A* and *C* and at temperatures above 316° C. for catalyst *B*. It was found that the yields of branched pentenes and 2-pentene could be controlled when using catalyst *A* at 316° C.: 65% branched and 30% 2-pentene at 1 hour^{-1} space velocity, and 30% branched and 55% 2-pentene at 24 hour^{-1} space velocity. At higher temperatures the amounts of branched pentenes and 2-pentene in the pentene cut were relatively unaffected by varying the space velocity in the range from 1 to 24 hour^{-1}, although the over-all yield of amylenes was greatly improved by high space velocities because of the suppression of cracking and polymerization.

Catalyst *C* showed similar behavior at 371° C. in that the yield of branched pentenes was decreased from about 90% at 6 hour^{-1} space velocity to about 50% at 24 hour^{-1} space velocity.

MECHANISM OF ISOMERIZATION

Recent papers (*2, 4, 9, 11*) have proposed mechanisms for a number of liquid-phase hydrocarbon reactions such as alkylation of isoparaffins, polymerization and isomerization of olefins, and isomerization of *n*-paraffins as catalyzed by anhydrous hydrogen fluoride, sulfuric acid, and promoted aluminum halides. Only the promoted aluminum halides are active for the isomerization of the normal paraffins. Oblad and Gorin (*9*) suggest that a solid surface or interface having the proper dielectric properties is necessary for the existence of the carbonium ions involved in the mechanism of *n*-butane isomerization.

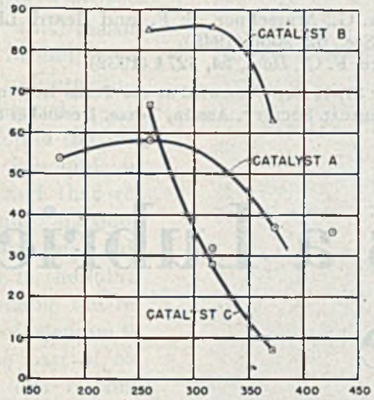

Figure 5. Amount of 2-Pentene in Pentene Cut at Various Temperatures for Space Velocity of 1 Hour^{-1}

The present authors believe that the mechanism of the isomerization of normal olefins by contact catalysts occurs in a manner quite similar to that of alkylation, isomerization, and similar reactions described previously, and that the necessary carbonium ions are readily formed under the conditions existing on the surface of the various aluminas employed in the present study.

The alumina surface is envisioned as being covered to some degree with protons attached to oxygen atoms in the alumina lattice or attached to fluoride ions chemisorbed on the alumina surface. The protons and the fluoride anions come from the acid used in preparing or treating the alumina. In the case of the neutral alumina the protons are present because of the slightly acidic nature of hydrated alumina, which persists to some extent even after calcination at 500° C. The bulk of the water remaining on the alumina after activation probably exists on the surface. Thus the surface alumina is hydrated to a large extent. The fluoride ions may be replaced by the negative ions in hydrochloric, sulfuric, phosphoric, and other acids. The acids are strongly adsorbed on the alumina, since long heating times and high temperatures are necessary to remove these substances from the alumina.

The mechanism of the isomerization of normal olefins is postulated, bearing in mind the statements made in previous paragraphs, as follows: Under conditions prevailing on a neutral or acid-treated alumina surface, carbonium ions are formed by the addition of a proton to the double bond of the olefin. The carbonium ion at its moment of formation is bound to the surface of the alumina by means of the interaction between the positive carbonium ion and the electronegative proton donor. The latter is either an oxygen atom or an acid anion. At temperatures below 250–300° C. the principal reaction occurring on the surface of the alumina is believed to be rearrangement of the adsorbed carbonium ion by a proton shift, which moves the positive charge to a more centrally located carbon atom. This arrangement is more stable thermodynamically than the original adsorbed carbonium ion. Loss of a proton from a neighboring carbon atom to the donor group at the instant of desorption leaves the double bond closer to the center of the molecule. At higher temperatures the more difficult skeletal rearrangements occur to an increasing extent. This reaction is much slower than a double bond shift and involves the migration of a methyl group. The latter is believed to occur in a manner similar to that which has been postulated for *n*-paraffin isomerization (*9*). The double bond shift is so rapid at the higher temperatures that it makes little difference whether 1-pentene or 2-pentene is the starting material when skeletal isomerization is predominant. Formation and adsorption of the carbonium ion from the olefin feed is followed by rearrangement to a secondary carbonium ion in the case of 1-pentene. The secondary carbonium ion in any case undergoes a methyl group–proton exchange to a more stable tertiary carbonium ion, and this is followed by loss of a proton to a donor group at the moment of desorption to yield a branched pentene. The composition of the product depends on the relative rates of formation and desorption of the various branched pentenes, and if sufficient reaction time is allowed an equilibrium amount of each possible product will be obtained at each temperature studied.

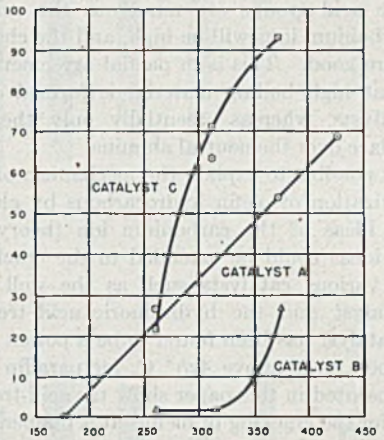

Figure 6. Amount of Branched Pentenes in Pentene Cut at Various Temperatures for Space Velocity of 1 Hour^{-1}

These suppositions are in substantial agreement with the observations that the isomerization of 1-pentene to an equilibrium mixture of 1-pentene and 2-pentene is much more rapid than formation of branched-chain pentenes, and that the formation of the latter is greatly accelerated by an increase in temperature. The concentration of protons on the surface is also important, since it has been found that the acid-treated aluminas are more active as catalysts than are the neutral aluminas (catalyst *B*).

Neutralization of the acid groups with alkali destroys the activity of the alumina completely for isomerization. Likewise, the commercial aluminas which contain sodium have not been found active at the experimental conditions used in this study. Prolonged heat treatment of the hydrogen fluoride–treated catalyst was found to drive off the hydrogen fluoride and thus reduce the isomerization activity of the catalysts eventually to that of pure alumina. Likewise, loss of water from phosphoric acid polymerization catalyst reduces the activity of this catalyst for isomerization, alkylation, and polymerization.

Concentration of the surface protons (as well as temperatures) is important from the standpoint of polymerization of the olefin feed. If the acid groups are numerous the concentration of adsorbed carbonium ions will be high, and the chances for polymerization are good. This is in partial agreement with the observation that high boiling material is formed over the acid-treated catalysts, whereas essentially only the double bond shift takes place over the neutral alumina.

Thus, it is possible to explain the mechanism of isomerization and polymerization of olefin hydrocarbons by aluminas by extending the ideas of the carbonium ion theory of reactions. These same ideas could be extended to the cracking of hydrocarbons by various catalysts such as the well known silica-alumina catalyst and the hydrofluoric acid–treated alumina. The latter catalyst has been found to be a potent cracking catalyst at temperatures above 425° C. for paraffin hydrocarbons. The data presented in this paper show the acid-treated aluminas to be active for the cracking of olefins at a temperature as low as 350° C.

SUMMARY

The reactions of 1-pentene and 2-pentene were studied over a limited range of temperatures and space velocities with the use of three different catalysts. These catalysts were similar in that they contained very little sodium and were either acidic or neutral in composition. The pure alumina gel catalyst *B* showed high activity for double bond shifting at low temperatures and produced little cracking or polymerization. Acid-treated aluminas were active in skeletal isomerization and gave good yields of branched pentenes even at very high space velocities. Shifting of the double bond in the *n*-pentene molecule appears to be a rapid reaction which is catalyzed by neutral alumina even at low temperatures. Skeletal isomerization requires higher temperatures and catalysts of more acid character. Branched-chain olefins may be prepared from either 1-pentene or 2-pentene, since equilibrium is rapidly established between these straight-chain olefins.

A reaction mechanism is proposed in which carbonium ions are formed by reaction between the olefin and protons on the acidic alumina surface. The distribution of products is explained by the various thermodynamic stabilities of the carbonium ions thus formed.

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Received May 31, 1946. Presented at the Texas Regional Meeting of the American Chemical Society, Austin, Texas, December 8, 1945.

Selenium Dioxide as a Lubricant Additive

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Selenium dioxide, although well known as an oxidizing agent, has been shown to retard the oxidation of drying oils. With several typical alcohols to increase its solubility, selenium dioxide was found to act as an antioxidant for lubricating oils. This paper describes the results of a number of bench and engine tests which indicate that the effectiveness of selenium dioxide is comparable with that of certain commercial antioxidants.

THE use of lubricant addition agents to inhibit oxidation or to decrease the extent of oxidation has been widely investigated during the past several years. Many thousands of tests have been run, and hundreds of different chemical compounds have been claimed as addition agents for lubrication oils.

The oxidizing action of selenium dioxide is well known (*6, 9, 14, 16*), but it is not so evident that selenium dioxide can also function as a powerful antioxidant (*10, 12, 13*). The antioxidant properties of this compound can be demonstrated by incorporating small quantities (0.1–0.5%) in drying oils, such as linseed or tung oil. Whereas pure linseed oil containing soluble cobalt dried in 7 hours when exposed in a thin layer to the atmosphere, a similar sample with the same amount of cobalt but also a small quantity of selenium dioxide incorporated in it did not dry after exposure for 1 week. Both of these drying oils, to which small quantities of selenium dioxide were added, remained wet after exposure for 1 week.

The purpose of this paper is to present data which show that the pronounced antioxidant action of selenium dioxide imparts desirable properties to lubrication oils and hence functions as a valuable lubricant addition agent.

METHODS OF ADDITION

Selenium dioxide is a white solid composed of monoclinic crystals having a density of 3.95 at 15° C. It sublimes at 317° C. to give a greenish yellow vapor, the color being caused by the SeO_2 and not by any impurities, and melts at 340° C. in a sealed tube. It is stable to high temperatures having a heat of formation of 56,360 calories at 18° C. Selenium dioxide is soluble in water and absorbs moisture from the air to form selenious acid, but this reaction is reversible at ordinary temperatures, and selenious acid effloresces on warm days to form the dioxide. Water at 70° C. will dissolve 176.3 moles of selenious acid per 1000 grams. It is practically impossible to remove the last traces of water from selenium dioxide since resublimed selenium dioxide that has been desiccated over phosphoric anhydride for a year still retains 0.045–0.088% water. Selenium dioxide has little or no solubility in organic solvents other than alcohols and related hydroxylic compounds.

Selenium dioxide is not soluble in lubricating oils, but it can be shown that suspensions of selenium dioxide in such oils impart greatly increased oxidation resistance to them. However, it is not desirable to use addition agents in the form of suspensions, and for this reason other methods of adding selenium dioxide to lubricating oils were investigated.

It has been found that selenium dioxide is soluble in most alcohols and that resulting selenium dioxide–alcohol solutions are sufficiently soluble in the lubricating oils to enable the required amount of selenium to be added. One part of selenium dioxide can be dissolved in two parts of each of the following alcohols at room temperature: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl, 2-nitrobutyl, capryl, isoamyl, *tert*-amyl, methylamyl, 2-ethylhexyl, *n*-octyl, *n*-decyl, *n*-undecyl, lauryl, diacetone, tetrahydrofuryl, benzyl, and cyclohexyl. In many cases considerably higher concentrations of selenium dioxide may be dissolved in the alcohol.

The mechanism of the action of alcohol as a mutual solvent for selenium dioxide and lubricating oils is not thoroughly understood. Astin, Moulds, and Riley (*2*) and Hinsberg (*7*) reported that selenium dioxide dis-

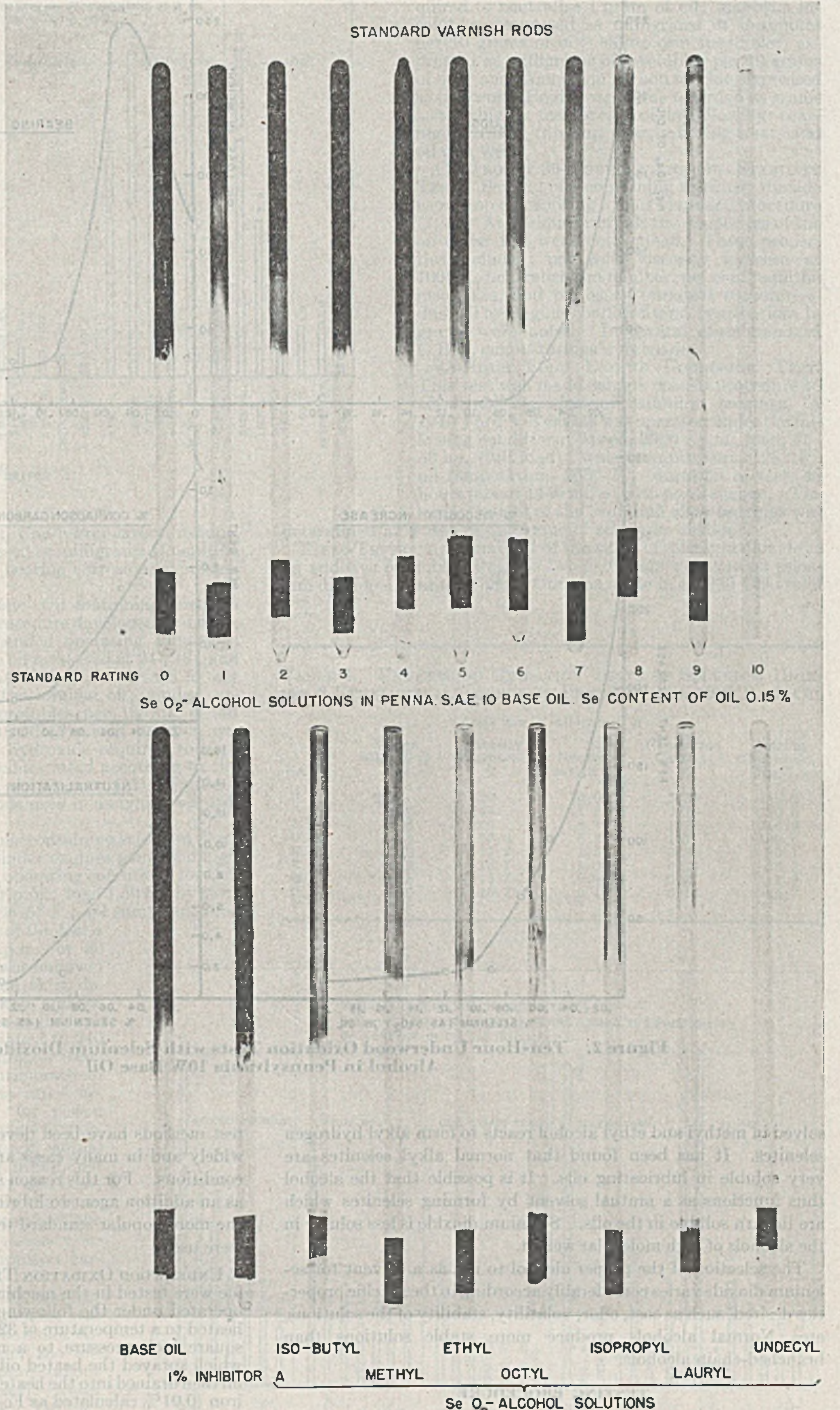

Figure 1. Set of Standard Varnish Rods Used in Assigning Varnish Rating

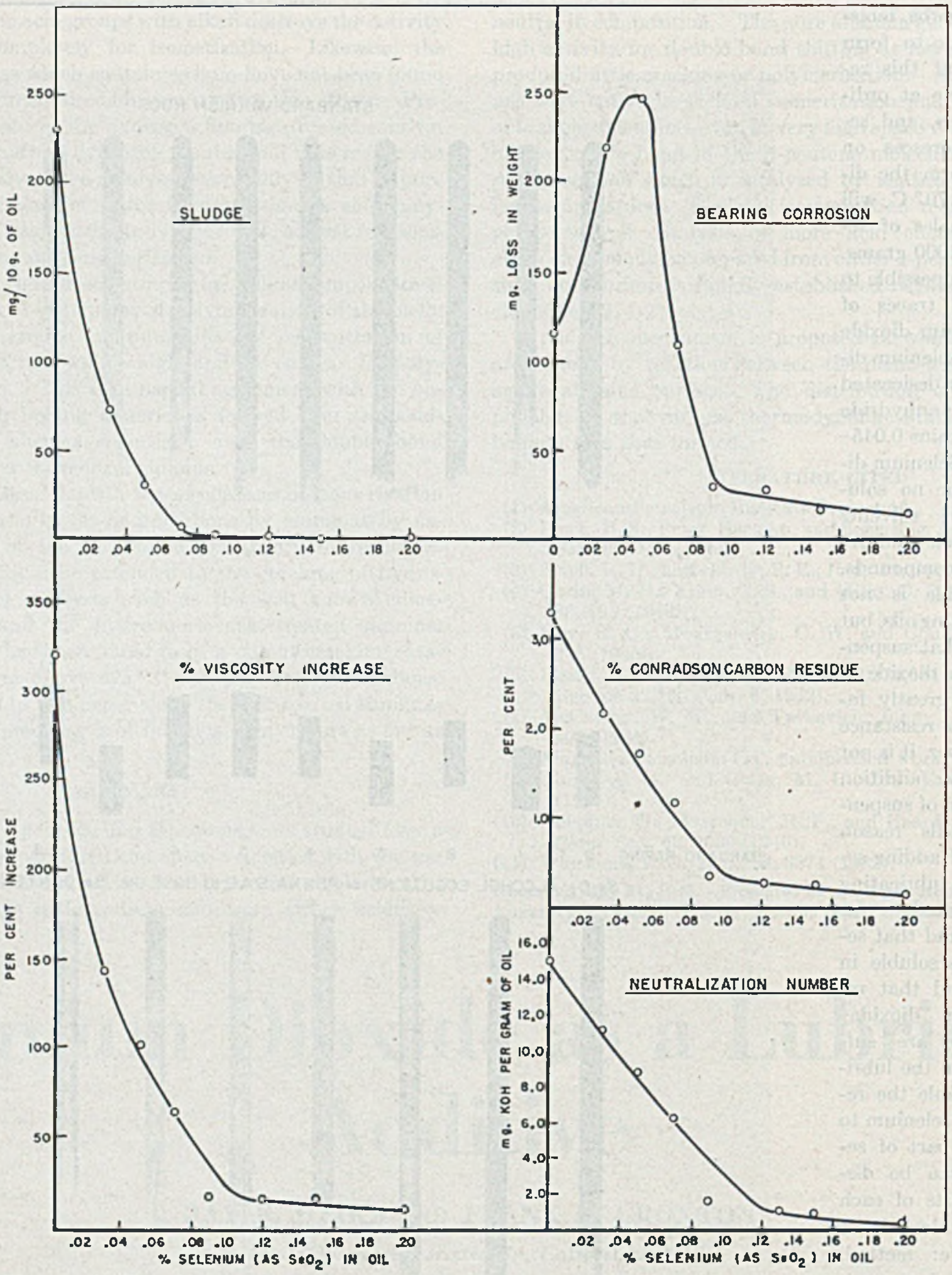

Figure 2. Ten-Hour Underwood Oxidation Tests with Selenium Dioxide–2-Ethyl Hexyl Alcohol in Pennsylvania 10W Base Oil

solved in methyl and ethyl alcohol reacts to form alkyl hydrogen selenites. It has been found that normal alkyl selenites are very soluble in lubricating oils. It is possible that the alcohol thus functions as a mutual solvent by forming selenites which are in turn soluble in the oils. Selenium dioxide is less soluble in the alcohols of high molecular weight.

The selection of the proper alcohol to use as a solvent for selenium dioxide varies considerably according to the specific properties desired, such as cost, odor, volatility, stability of the solutions, etc. Normal alcohols produce more stable solutions than branched-chain alcohols.

TESTING PROCEDURE

The literature contains many references to testing procedures for the evaluation of lubricating oil deterioration. By 1939 twenty-three different laboratory oxidation methods for testing lubricating oils had been published in the literature (*11*). More test methods have been developed since that time. They vary widely and in many cases are designed to meet certain specific conditions. For this reason selenium dioxide has been evaluated as an addition agent to lubricating oils according to a number of the more popular standard test procedures. The following tests were used:

Underwood Oxidation Test. Oils containing selenium dioxide were tested in the machine designed by Underwood (*15*) and operated under the following conditions: One gallon of oil was heated to a temperature of 325° F. and pumped at 10 pounds per square inch pressure to a manifold equipped with spray jets which sprayed the heated oil on copper-lead test bearings. The oil then drained into the heater reservoir for recirculation. Soluble iron (0.01% calculated as Fe_2O_3) in the form of iron naphthenate was added to all oils under test as a catalyst to accelerate oil deterioration. At the end of the 10-hour test period the following determinations were made: viscosity, expressed as per cent increase above the viscosity of the initial untested oil; neutralization number, expressed as milligrams of potassium hydroxide

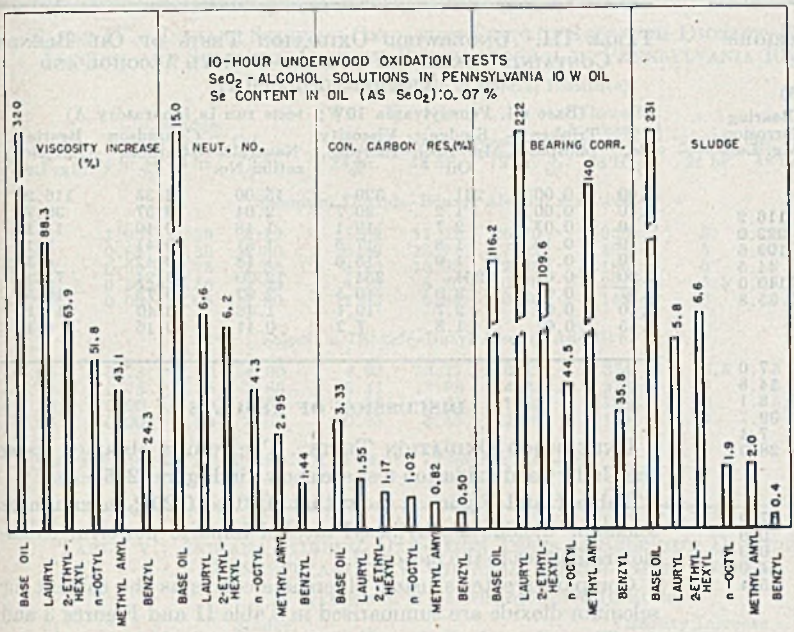

Figure 3

required to neutralize 1 gram of oil; Conradson carbon residue, expressed as per cent; sludge, expressed as milligrams of naphtha insolubles per 10 grams of oil; and bearing corrosion, expressed as milligram loss during the test.

Indiana Stirring Oxidation Test. Oil containing selenium dioxide was tested according to the procedure developed by Lamb, Loane, and Gaynor (*8*). Recommended operating conditions were followed. The properties of the oil measured at 24-, 48-, and 72-hour intervals were: viscosity at 100° F., expressed as per cent increase over the viscosity of the original oil; sludge, expressed as milliliters of naphtha insolubles per 10 ml. of oil according to A.S.T.M. Method D91–40 (*3*); acid number, expressed as milligrams of potassium hydroxide required to neutralize 1 gram of oil; and varnish values rated according to the method described by Lamb, Loane, and Gaynor (*12*). Figure 1 shows the set of standard varnish rods used in assigning varnish rating.

Lauson Engine Tests. Several oils containing selenium dioxide were tested in Lauson single-cylinder engines using the high piston temperature procedure. The operating conditions for this procedure are as follows: speed, 160 r.p.m.; load 1.50 hp. by two-blade fan; jacket temperature, 345 ± 5° F.; oil sump temperature, 225 ± 5° F. Prior to the start of the test a break-in run was made at 1200 r.p.m. for 30 minutes. Every 30 hours the engine was removed from its base and inspected. Piston skirt deposits and condition of rings were noted, and the crankpin bearings were weighed. The engine was then reassembled and the test continued to 240 hours unless ring sticking, oil ring filling, or bearing weight loss necessitated discontinuance of the test. The engine condition was rated according to the following system: for piston skirt condition, A excellent, B good, C fair, D poor, and E bad; for rings stuck, actual number of rings sticking; for ring filling, per cent of the oil ring filled with sludge; and bearing loss, the milligram loss suffered by the bearing during the run. At the end of the test the used oil was analyzed for per cent viscosity increase, neutralization number, Conradson carbon residue, and naphtha insolubles.

Chevrolet 66$^2/_3$-Hour Engine Oil Stability Test. An oil containing selenium dioxide was tested according to the standard Chevrolet engine oil stability test operating under the following conditions: speed, 3150 r.p.m. (about 60 m.p.h.); load, 30 hp. (road load); water temperature, 200° F.; oil temperature, 280° F.; duration of test, 66$^2/_3$ hours (no oil change), about 4000 miles. At the end of the test the properties of the crankcase oil were determined and the engine condition noted. The oil analyses included: viscosity, in Saybolt Universal seconds at 210° F.; neutralization number, expressed as milligrams of potassium hydroxide required to neutralize 1 gram of oil; naphtha insolubles, expressed as milligrams of insolubles per 10 grams of oil; chloroform insolubles, expressed as milligrams of insolubles per 10 grams of oil; and Conradson carbon residue, expressed as per cent. Engine wear was recorded as grams lost during the test for each of the following: bearing corrosion, top ring wear, mid ring wear, and oil ring wear.

Chevrolet 36-Hour Engine Oil Stability Test. Several oils containing selenium dioxide were tested according to this standard procedure (*1, 4*). At various intervals the properties of the oil under test were determined. These properties included: per cent viscosity increase at 100° F., neutralization number, per cent naphtha insolubles, and per cent Conradson carbon residue. The engine condition and bearing loss in grams were noted. In several cases standard C.R.C. engine ratings were made.

48-Hour Ford Engine Corrosion Test. This test was made using a special procedure to accelerate corrosion of cadmium bearings. A 1940 Ford V-8 engine was operated under the following conditions: speed, 2000 r.p.m., load, 45–50 hp. (full load); water temperature, 198° F.; oil temperature, 260° F.; duration of test, 48 hours (about 1440 miles) with no oil change. The loss in weight of the cadmium alloy bearings was determined as a test of the value of selenium dioxide.

Field Tests. As a final test of the value of selenium dioxide as an additive for lubricating oils two field tests were run on selenium dioxide–containing oils. One was made in a 1940 Chevrolet

Table I. Underwood Oxidation Tests of Selenium Dioxide–2-Ethylhexyl Alcohol in Pennsylvania 10W Base Oil

(Tests run in laboratory A)

Se, %	Sludge, Mg./10 G. Oil	Viscosity Increase, %	Neutralization No.	Conradson Carbon, %	Bearing Corrosion, Mg. Loss
0	231	320	15.0	3.33	116.2
0.03	72.0	144	11.2	2.18	220.0
0.05	29.3	103	8.70	1.73	246.0
0.07	6.6	63.9	6.20	1.17	109.6
0.09	2.0	17.2	1.60	0.36	30.1
0.12	0.8	16.7	1.08	0.29	28.3
0.15	0.8	15.7	0.90	0.27	17.9
0.20	2.0	10.7	0.45	0.16	15.7

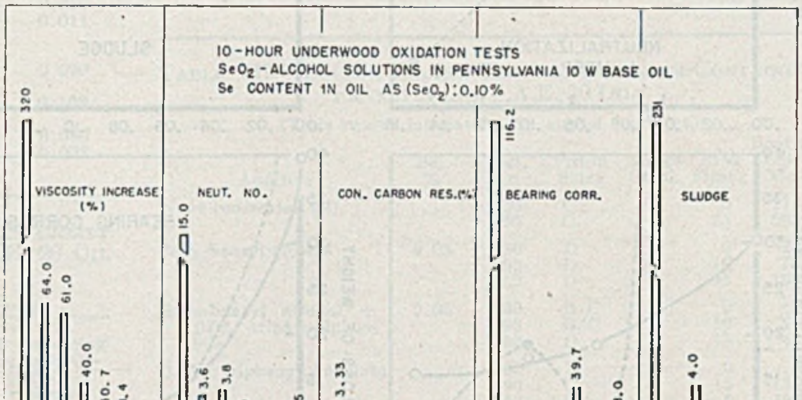

Figure 4

Table II. Underwood Oxidation Tests with Various Alcohols as Solvents for Selenium Dioxide

(Base oil, Pennsylvania 10W; tests run in laboratory A)

Alcohol	Sludge, Mg./10 G. Oil	Viscosity Increase, %	Neutralization No.	Conradson Carbon, %	Bearing Corrosion, Mg. Loss
Selenium Content of 0.07%					
Base oil	231	320	15.00	3.33	116.2
Lauryl	5.8	88.3	6.60	1.55	222.0
2-Ethylhexyl	6.6	63.9	6.20	1.17	109.6
n-Octyl	1.9	15.8	4.30	1.02	44.5
Methyl amyl	2.0	43.1	2.95	0.82	140.0
Benzyl	0.4	24.3	1.44	0.50	35.8
Selenium Content of 0.10%					
Butoxyethyl	0.6	64.0	3.60	1.14	7.0
Amyl	4.0	61.0	3.80	1.10	14.8
n-Butyl	2.4	40.0	2.30	0.87	8.1
Benzyl	1.2	30.7	2.04	0.57	39.7
Isobutyl	1.7	28.4	1.70	0.50	7.4
2-Ethylhexyl	2.0	22.0	2.50	0.36	28.0
Selenium Content of 0.15%					
2-Ethylhexyl	0.8	15.7	0.90	0.27	17.9
n-Butyl	1.4	11.3	0.58	0.58	0.0
Isobutyl	1.2	8.3	0.48	0.18	0.0
Benzyl	1.2	21.6	1.10	0.30	24.0
Benzyl + 0.07% triphenylphosphite	1.8	7.2	0.41	0.16	5.4

Table III. Underwood Oxidation Tests of Oil Blends Containing Selenium Dioxide–Benzyl Alcohol and Triphenylphosphite

(Base oil, Pennsylvania 10W; tests run in laboratory A)

Se, %	Triphenylphosphite, %	Sludge, Mg./10 G. Oil	Viscosity Increase, %	Neutralization No.	Conradson Carbon, %	Bearing Corrosion, Mg. Loss
0.00	0.00	231	320	15.00	3.33	116.2
0.10	0.00	1.2	30.7	2.04	0.57	39.7
0.10	0.07	2.7	19.1	1.48	0.40	11.1
0.10	0.10	1.8	17.5	1.51	0.41	8.1
0.10	0.15	1.9	15.6	1.18	0.42	5.3
0.00	0.07	264	254	12.20	3.24	75.1
0.07	0.07	3.0	10.5	2.92	0.73	10.5
0.10	0.07	2.7	19.1	1.48	0.40	11.1
0.15	0.07	1.8	7.2	0.41	0.16	5.4

truck which used S.A.E. 20 oil and ran for 6000 miles, changing oils every 2000 miles. The properties of the drain oil were determined after each change and the average of the three values recorded.

The second field test was run in a 1934 Oldsmobile convertible coupé immediately after the engine was overhauled. The oil was used for 2300 miles of driving without change or additions over a period of 3 months. The drain oil was then analyzed.

DISCUSSION OF RESULTS

Underwood Oxidation Tests. The results obtained using the Underwood oxidation test are shown in Figures 2–5.

Table I and Figure 2 show that 0.10 to 0.20% selenium as selenium dioxide-2-ethylhexyl alcohol imparts powerful oxidation resistance to the motor oil.

Comparative tests using different alcohols as the solvent for selenium dioxide are summarized in Table II and Figures 3 and 4. These data show that all the selenuim dioxide–alcohol solutions substantially increase the oxidation resistance of the base oil. At a concentration of 0.07% selenium, benzyl alcohol appears to be superior to the other alcohols tested at the same concentration. Similar comparisons at a selenium content of 0.10% are summarized in Table II and are shown in Figure 4. At this higher concentration the differences between the various alcohols are not so marked. Butoxyethyl, *n*-butyl, and isobutyl are superior to benzyl alcohol as regards bearing corrosion.

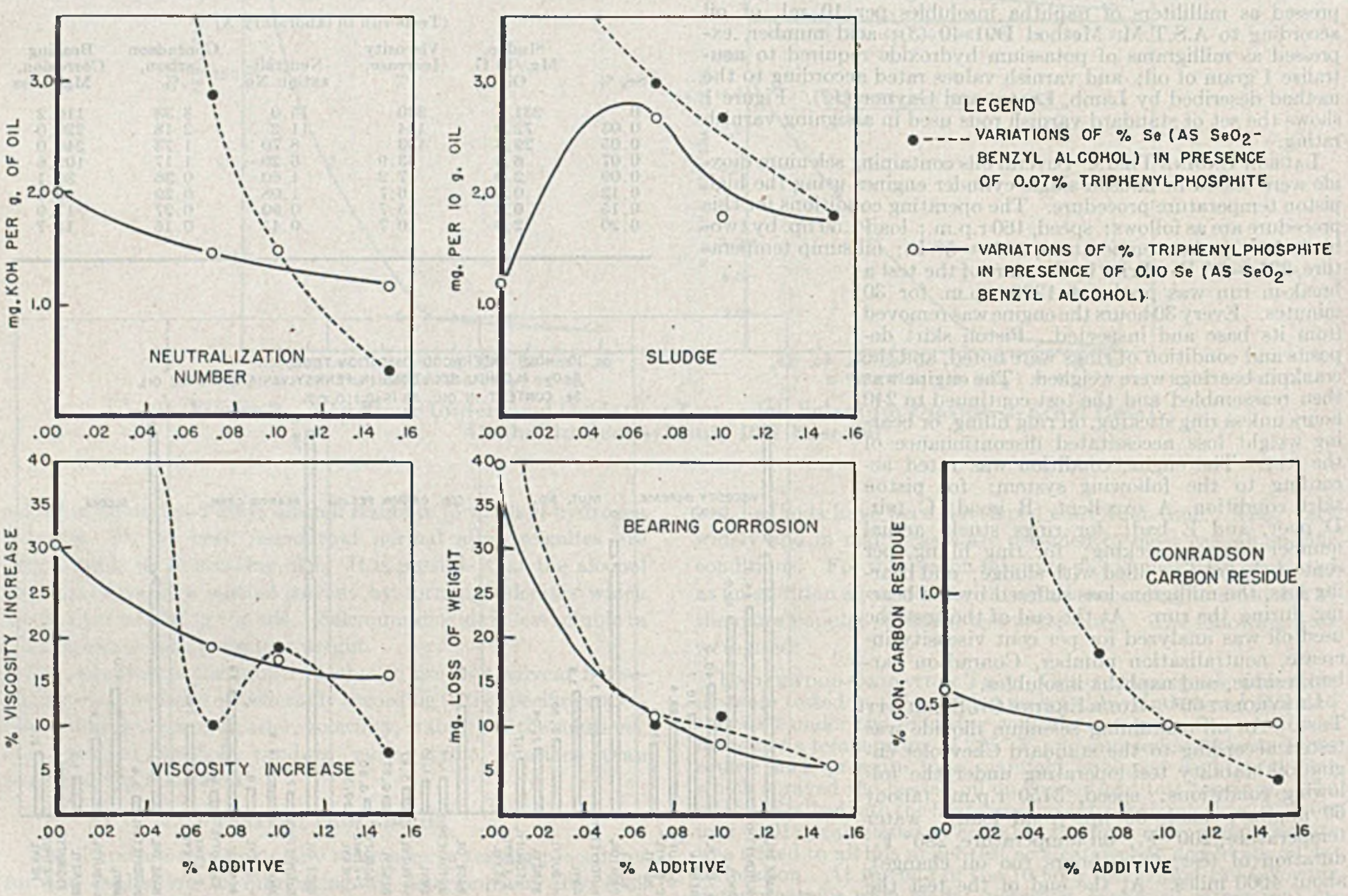

Figure 5. Ten-Hour Underwood Oxidation Tests with Combination of Selenium Dioxide–Benzyl Alcohol and Triphenylphosphite in Pennsylvania 10W Base Oil

TABLE IV. INDIANA STIRRING OXIDATION TESTS OF SELENIUM DIOXIDE–BENZYL ALCOHOL AND SELENIUM DIOXIDE–BUTYL ALCOHOL IN PENNSYLVANIA 10W OIL

(Tests run at Battelle Memorial Institute)

Se, %	Sludge, Ml./10 Ml. Oil 24 hr.[b]	48 hr.	72 hr.	Acid No. Increase 24 hr.	48 hr.	72 hr.	Viscosity Increase at 100° F.[a], % 48 Hr.	Varnish Rating 24 hr.	48 hr.	72 hr.
Selenium Dioxide–Benzyl Alcohol Additive										
0	1.95	4.39	5.12	11.69	17.12	26.26	953	8	4	5.0
0.05	0.83	3.30	4.80	6.89	15.77	17.62	431	5	2.5	2
0.10	0.60	1.75	2.65	4.86	10.33	12.88	185	6	2.0	2
0.15	0.50	1.50	2.05	4.19	8.20	10.70	221	6.5	5.5	5
0.25	0.00	1.05	1.90	1.93	6.69	10.80	143	10	5.5	5.5
Selenium Dioxide–Butyl Alcohol Additive										
0.05	0.73	3.40	4.00	4.94	13.17	16.42	334	5.5	3	3
0.10	0.78	3.30	3.85	5.41	13.98	14.33	373	6	4	3
0.15	0.00	1.50	2.53	1.96	8.77	11.82	188	10	5.5	5.5
0.25	0.00	0.60	2.05	0.63	3.55	12.20	165	10	10	10

[a] Viscosity increase not determined at 24 and 72 hours of testing.
[b] Testing time.

TABLE V. INDIANA STIRRING OXIDATION TESTS OF SELENIUM DIOXIDE–ALCOHOL IN PENNSYLVANIA 10W OIL AT 0.15% SELENIUM CONTENT

(Tests run at Battelle Memorial Institute)

Alcohol	Sludge, Ml./10 Ml. Oil 24 hr.[a]	48 hr.	72 hr.	Acid No. Increase 24 hr.	48 hr.	72 hr.	Viscosity Increase at 100° F., % 24 hr.	48 hr.	72 hr.	Varnish Rating 24 hr.	48 hr.	72 hr.
Methyl	0.00	0.53	1.35	0.29	2.46	6.35	41.6	109	225	10	9.5	9.5
Ethyl	0.00	0.95	1.70	1.10	5.15	7.74	56.6	140	271	10	7.5	7.0
Propyl	0.00	0.83	1.58	1.22	5.67	6.64	51.4	145	245	10	8.5	7.5
Isopropyl	0.00	0.55	1.18	0.29	3.35	5.72	35.1	102	233	10	9	6.5
Butyl	0.00	1.50	2.53	1.96	8.77	11.80	..	188	...	10	5.5	5.5
Isobutyl	0.15	1.00	2.85	1.53	5.10	7.75	54.4	196	500	10	9	8
Amyl	0.30	1.15	1.93	1.06	4.92	7.17	61.6	163	303	9.5	5.5	4.5
Isoamyl	0.05	0.50	1.35	0.75	2.78	5.17	43.3	97.4	212	10	8	7.5
Methyl amyl	0.25	0.83	2.15	1.92	5.40	8.31	53.5	175	327	10	6	5
2-Ethylhexyl	0.58	1.50	2.98	3.88	5.76	9.11	78.2	252	550	6	6.5	5
Undecyl	0.00	0.25	1.10	0.61	3.33	5.92	36.2	86.6	197	10	10	10
Tetradecyl	0.60	1.73	2.60	2.49	6.29	9.40	89.5	209	409	8	4	3
Lauryl	0.10	0.90	2.00	2.05	4.57	7.15	53.6	177	351	10	9.5	9.5
Benzyl	0.50	1.50	2.05	4.19	8.20	10.70	..	221	...	6.5	5.5	5
Base oil	1.95	4.39	5.12	11.69	17.12	26.26	..	953	...	8	4	5.0
Commercial oil *A*	0.10	0.95	2.80	1.32	4.05	12.31	27.9	165	Solid	10	10	10
Pennsylvania 10W base oil + 1% inhibitor *A*	0.80	3.55	6.50	5.50	15.39	20.65	..	452	...	1	1	1

[a] Testing time.

The selenium dioxide-benzyl alcohol solution allowed rather high bearing corrosion. However, it is much less than the bearing corrosion of Pennsylvania 10W base oil without additive. A survey by Georgi (5) showed that there was no apparent correlation between the Underwood copper-lead bearing corrosion data and full scale Chevrolet engine results using six reference oils ranging from very stable to very unstable oils. It has been found that the addition of small amounts of triphenylphosphite to the base oil in conjunction with the selenium dioxide–benzyl alcohol substantially reduces the bearing corrosion and still maintains satisfactory values for the other deterioration properties. The results of adding varying amounts of triphenylphosphite to an oil containing 0.10% selenium as selenium dioxide–benzyl alcohol are summarized in Table III and Figure 5. These data indicate that as little as 0.07% triphenylphosphite in conjunction with 0.10% selenium as selenium dioxide–benzyl alcohol reduces the bearing corrosion to a satisfactory value. Table III and Figure 5 also summarize the results of adding varying amounts of selenium as selenium dioxide–benzyl alcohol to an oil containing 0.07% triphenylphosphite. These data indicate that a combination consisting of 0.15% selenium as selenium dioxide–benzyl alcohol and 0.07% triphenylphosphite imparts desirable resistance to deterioration to the motor oil.

Table II summarizes the results obtained for a comparison of benzyl alcohol, 2-ethylhexyl alcohol, *n*-butyl alcohol, and iso-

TABLE VI. LAUSON ENGINE TESTS OF SELENIUM-CONTAINING PENNSYLVANIA S.A.E. 30 OILS

(Tests run in laboratory B; used oil analysis)

Additive	Se, %	Test, Hr.	Viscosity Increase, %	Neutralization No.	Conradson Carbon, %	Naphtha Insol., %
None (untreated oil)	..	90	54.2	3.00	1.76	0.030
SeO_2–benzyl alcohol	0.05	150	76.0	0.82	1.66	0.010
SeO_2–benzyl alcohol +0.07% triphenylphosphite	0.05	150	25.5	0.38	0.58	0.011
0.07% triphenylphosphite	..	150	49.5	2.55	1.29	0.090
1% commercial inhibitor *B*	..	150	39.5	0.38	1.30	0.108
SeO_2–benzyl alcohol	0.10	120	65.5	0.95	1.65	0.050
SeO_2–2-ethylhexyl alcohol	0.10	90	45.3	0.46	1.11	0.002

TABLE VIII. 66²/₃-HOUR CHEVROLET ENGINE OIL STABILITY TEST ON SELENIUM-CONTAINING PENNSYLVANIA S.A.E. 20 OIL

(Tests run in laboratory A)

	Composition of Oil Blends: Pennsylvania S.A.E. 20, no additive	Pennsylvania S.A.E. 20 containing 0.15% Se as SeO_2–benzyl alcohol & 0.07% triphenylphosphite
Used oil analysis		
Viscosity at 210° F.	164	70.2
Neutralization No.	3.17	1.15
Naphtha insolubles, mg./10 g.	480	37.2
Chloroform insolubles, mg./10 g.	74.3	2.50
Conradson carbon, %	4.72	2.78
Engine condition, grams loss		
Bearing corrosion	5.716 at 38 hr.	1.654
Top ring wear	0.064	0.068
Mid ring wear	0.024	0.046
Oil ring wear	0.400	0.091

TABLE VII. LAUSON ENGINE TESTS OF SELENIUM-CONTAINING PENNSYLVANIA S.A.E. 30 OILS

(Tests run in laboratory B; engine condition)

Additive	Se, %	Test, Hr.	Piston Skirt	Rings Stuck	Ring Filling	Bearing Loss, Mg.
None (untreated oil)	..	30	C	0	0	115
		90	C	0	25	562
SeO_2–benzyl alcohol	0.05	30	D	0	0	22
		90	D	0	10	78
		150	D	0	95	109
SeO_2–benzyl alcohol + 0.07% triphenylphosphite	0.05	30	B/C	0	0	2
		90	B/C	0	10	18
		150	D	1	15	44
0.07% triphenylphosphite	..	30	B	0	0	6
		90	C	0	15	15
		150	D	0	5	193
1% commercial inhibitor *B*	..	30	B	0	0	6
		90	C	0	0	27
		150	D+	0	0	99
SeO_2–benzyl alcohol	0.10	30	C	0	0	10
		60	D	0	5	20
		90	D	1	25	44
		120	C	1	60	118
SeO_2–2-ethylhexyl alcohol	0.10	30	C	0	0	1
		60	C	0	45	14
		90	D	0	60	20

Table IX. 36-Hour Chevrolet Engine Oil Stability Tests on Selenium-Containing Oils

Used Oil Analysis	Hours of Test	Pa. S.A.E. 20, No Addn. Agent[a]	Pa. S.A.E. 20 Containing 1.25% Commercial Inhibitor *B*[a]	Pa. S.A.E. 20 Containing 0.15% Se as SeO_2–Benzyl Alc. & 0.07% Triphenylphosphite[a]	Midcontinent S.A.E. 10, No Additive[b]	Midcontinent S.A.E. 10 + 0.15% Se as SeO_2–Benzyl Alc.[b]
Viscosity increase at 100° F., %	0	..	..	...	...	...
	8	..	..	...	...	...
	16	70.6	15.2	18.1	...	...
	24	..	..	...	...	...
	36	59.0	47.8	33.4	136	16.4
Neutralization No.	0	0.02	0.50	0.02	...	...
	8	2.99	0.21	0.21	...	...
	16	2.38	0.82	0.28	...	...
	24	2.17	1.85	0.33	...	...
	36	1.34	1.13	0.43	7.3	0.5
Naphtha insolubles, %	0	..	..	...	...	...
	8	..	..	...	...	...
	16	0.81	0.67	0.58	...	...
	24	..	..	...	...	...
	36	1.23	1.32	0.87	...	...
Chloroform insolubles, %	0	..	..	...	...	...
	8	..	..	...	...	...
	16	0.52	0.46	0.43	...	...
	24	..	..	...	...	...
	36	0.88	0.80	0.48	...	...
Conradson carbon, %	0	0.20	0.36	0.30	...	...
	8	..	..	...	...	...
	16	2.31	1.05	0.96	...	...
	24	..	..	...	...	...
	36	2.75	2.52	1.76	...	...
Bearing corrosion, grams loss	36	2.57 (18 hr.)	0.50	0.224	0.718	0.460

[a] Test run in laboratory A.
[b] Test run in laboratory C.

Table X. C.R.C. Ratings for 36-Hour Chevrolet Engine Oil Stability Test on Pennsylvania and Midcontinent Oils

	Midcontinent S.A.E. 10, No Additive[a]	Midcontinent S.A.E. 10 + 0.15% Se as SeO_2–Benzyl Alc.[a]	Pa. S.A.E. 20, No Addn. Agent[b]	Pa. S.A.E. 20 Containing 1.25% Commercial Inhibitor *B*[b]	Pa. S.A.E. 20 + 0.15% Se as SeO_2–Benzyl Alc. & 0.07% Triphenylphosphite[b]
Varnish deposit rating					
Piston skirts	2.0	8.0	9.5	9.5	10
Rocker arm cover plate	8.0	10.0	10.0	10.0	10
Push rod cover plate	9.0	10.0	10.0	10.0	10
Cylinder walls	2.5	8.5	9.5	9.5	10
Crankcase oil pan	1.5	9.5	10.0	10.0	10
Varnish total	23.0	46.0	49.0	49.0	50
Sludge deposit rating					
Rocker arm assembly	2.0	9.0	9.5	9.5	10.0
Rocker arm cover plate	4.0	9.0	9.5	10.0	9.5
Push rod cover plate	5.5	9.5	9.5	9.5	9.5
Oil screen	7.5	10.0	10.0	10.0	10.0
Crankcase oil pan	5.5	8.5	9.5	9.5	9.5
Sludge total	24.5	46.0	48.0	48.5	48.5
Varnish and sludge total	47.5	92.0	97.0	97.5	98.5

[a] Test run in laboratory C.
[b] Test run in laboratory A.

Table XI. 48-Hour Ford Engine Corrosion Tests on Pennsylvania S.A.E. 20 Oil Containing Selenium as Selenium Dioxide–Benzyl Alcohol

(Tests run in laboratory A)

Additive	Se, %	Weight Loss of Bearings, G.
SeO_2-benzyl alcohol + 0.07% triphenylphosphite	0.05	1.987
	0.10	0.110
	0.15	0.055

Table XII. Field Tests on Pennsylvania S.A.E. 20 Oil Containing 0.15% Selenium as Selenium Dioxide–Benzyl Alcohol and 0.07% Triphenylphosphite

	1940 Chevrolet Truck	1934 Oldsmobile Convertible Coupé
Miles driven	6000	2300
Miles between oil changes	2000	No change
Av. viscosity increase, %	7.77	0.307
Sludge	1.2 mg./10 g. oil	0.45 ml./10 ml. oil
Av. neutralization No.	1.03	4.53

butyl alcohol at a concentration of 0.15% selenium as selenium dioxide-alcohol solutions. These data indicate that butyl alcohol and isobutyl alcohol are as satisfactory as the combination of selenium dioxide–benzyl alcohol and triphenylphosphite on the basis of performance in the Underwood oxidation tester.

Indiana Stirring Oxidation Test. Table IV and Figure 6 summarize the results obtained using this test procedure when various amounts of selenium as selenium dioxide–benzyl alcohol and selenuim dioxide–butyl alcohol are added to a Pennsylvania 10W base oil. These data show that selenuim dioxide inhibits the oxidation of the base oil to a considerable extent and that approximately 0.15 to 0.20% selenium is the optimum quantity.

Numerous other alcohols were used as the solvent for selenium dioxide and the resulting solutions were tested according to this procedure. These data are summarized in Table V. All tests were run at 0.15% selenium content in the blended oil. Results obtained using 1% of inhibitor *A*, a commercial product, in the same base oil are included in the table. Also included are the results obtained using an inhibited commercial Pennsylvania base oil purchased on the open market.

These results show that all of the selenium dioxide–alcohol solutions impart substantially increased oxidation resistance to the base oil and that every selenium-containing oil is superior to oils containing 1% of inhibitor *A*. After 72 hours in the tester all selenium-containing oils are superior to the commercial oil *A* except for varnish ratings and two cases of sludge formation, which are about equal to the commercial oil. Undecyl, isoamyl, isopropyl, propyl, and methyl alcohols appear to be superior to the other alcohols tested at 0.15% selenium in the blended oil.

The varnish rods after 72 hours in the Indiana stirring oxidation tester are shown in Figure 1. These include a number of the rods from the tests summarized in Table V, all tests being at a selenium concentration of 0.15%.

Lauson Engine Test. The data obtained using this type of test are summarized in Tables VI and VII. Only one direct comparison between selenium-containing oils and the untreated oil is possible, since all selenium-containing oils were run for longer periods of time in the engine. In this one case (0.10% selenium as selenium dioxide–2-ethylhexyl alcohol), the selenium-containing oils are superior in all respects to the base oil. All selenium-containing oil gave lower neutralization numbers and Conradson carbon residues than the base oil, even though the former were

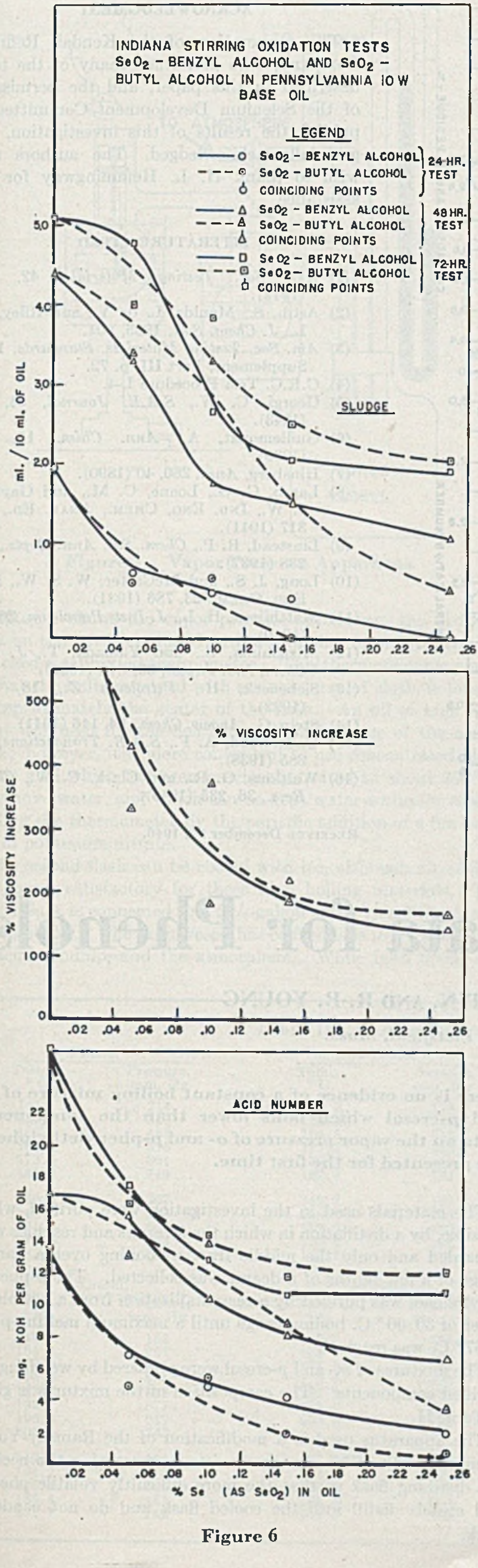

Figure 6

run nearly twice as long as the latter. Table VII shows that the selenium-containing oils gave superior engine condition, especially in regard to bearing corrosion. It should be noted that the selenium content of the oils tested in the Lauson engine are somewhat lower than the amount necessary for optimum performance as determined by Underwood oxidation and Indiana stirring oxidation tests.

Chevrolet 66²/₃-Hour Engine Test. The data obtained are summarized in Table VIII. A comparison between a Pennsylvania S.A.E. 20 base oil without inhibitor and the same base oil containing 0.15% selenium as selenium dioxide–benzyl alcohol shows that the selenium additive has substantially reduced oil deterioration and bearing corrosion under the conditions of this test.

Chevrolet 36-Hour Engine Test. The data obtained using this test procedure are summarized in Tables IX and X and are shown graphically in Figure 7. Tests were run using the selenium additive in both Pennsylvania and solvent-treated Midcontinent base oils. A marked improvement in the performance of the selenium-containing oils in comparison with the base oils is noted.

48-Hour Ford Engine Test. The results obtained are shown in Table XI and clearly indicate the excellent protection against bearing corrosion that results from the use of 0.10% or more of selenium as selenium dioxide–benzyl alcohol solution.

Field Tests. The results of the two field tests are summarized in Table XII. These data show that selenium dioxide has successfully inhibited the oxidation of the oil during the period of the test.

MECHANISM

The mechanism by which selenium dioxide functions as an antioxidant is not clearly understood. Observations made during the course of this investigation indicate that selenium dioxide performs several functions in lubricating oils. For instance, it has been observed that metals in contact with oils containing dissolved selenium dioxide acquire an adherent film probably composed of metal selenides. The formation of this film on the metal parts in contact with a lubricating oil would tend to reduce the catalytic effect of the metal on the oxidation of the oil. A reduction of this catalytic effect does not account for all of the observed antioxidant properties, since it does not explain the antioxidant action in cases where no metal parts are involved in the test, such as was the case in the drying oil experiments. The drying oil experiments indicate that in this case, since the oils contained soluble cobalt, the selenium dioxide may act as a metal deactivator as well as a metal passivator. Unpublished information, however, indicates that selenium dioxide exhibits substantial antioxidant action in the absence of metal in any form.

To account for this action of selenium dioxide as an antioxidant in lubricating oils, the following theory might be proposed: Selenites can be oxidized to selenates by the action of peroxides. Peroxides are thought to be intermediate products in the oxidation of lubricating oils which further catalyze the oil oxidation, giving oxidation *vs.* time curves which are S-shaped and exhibit the characteristics of autocatalysis. The selenium dioxide added to the oil, probably present as a selenite, may reduce the intermediate peroxides forming noncatalytic products and organic selenates, which, because of their unstable character, revert back to selenites. The mechanism would then be repeated, so that the rapid oxidation of the oil is thus effectively inhibited.

This theory is proposed only from limited observations, and it must be emphasized that data confirming it are lacking. Further experimental data are necessary before a complete explanation of the antioxidant action of selenium dioxide in lubricating oils can be given.

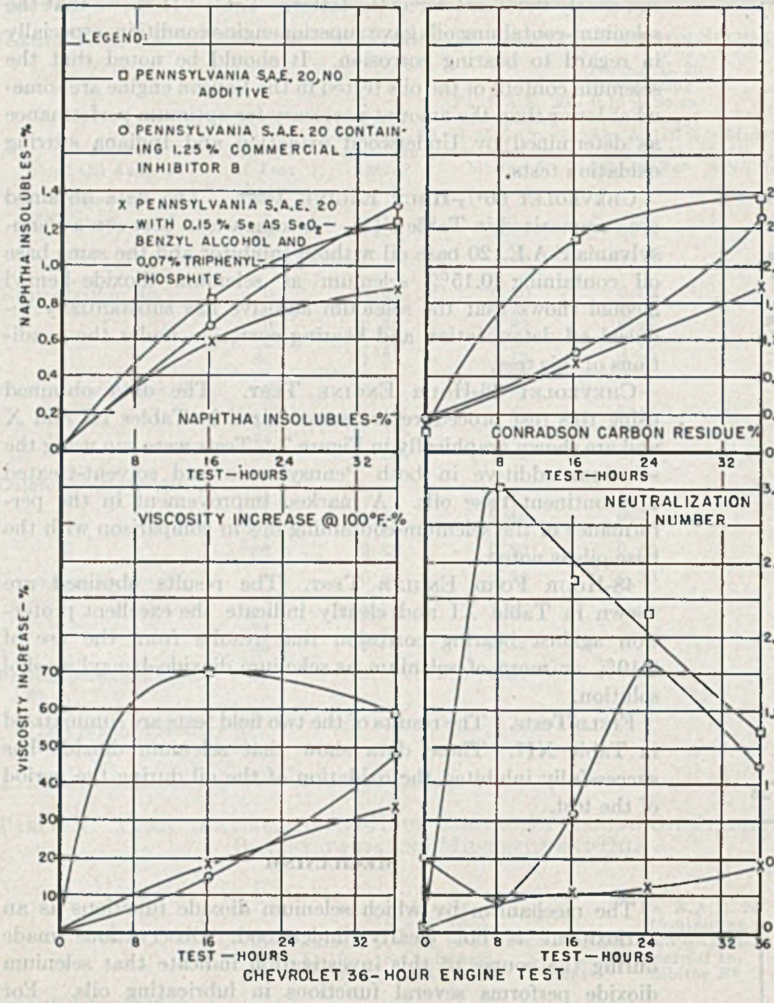

Figure 7

ACKNOWLEDGMENT

The cooperation of the Kendall Refining Company, who performed many of the tests described in this paper, and the permission of the Selenium Development Committee to publish the results of this investigation, are gratefully acknowledged. The authors also wish to thank H. L. Hemmingway for his assistance.

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Received December 26, 1946.

Vapor Pressure Data for Phenols

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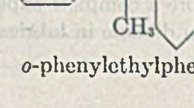
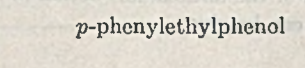
Vapor pressure data for phenol, *o*-cresol, *m*-cresol, *p*-cresol, four mixtures of *m*- and *p*-cresol, *o*-phenylethylphenol, and *p*-phenylethylphenol were determined by a modified Ramsay-Young procedure. The data show that there is no evidence of a constant boiling mixture of *m*- and *p*-cresol which boils lower than the components. Data on the vapor pressure of *o*- and *p*-phenylethylphenol are presented for the first time.

THE vapor pressure data for phenol, *o*-cresol, *m*-cresol, *p*-cresol, and four mixtures of *m*- and *p*-cresol were obtained in 1941 during an investigation of the possibility of the existence of a constant boiling mixture of *m*- and *p*-cresol. The boiling points of these two materials are very close together (Table I). The close proximity of the boiling points does not preclude the existence of a constant boiling mixture of the two materials. The data for *o*- and *p*-phenylethylphenol were determined in 1943. The structural formulas for the latter compounds are:



o-phenylethylphenol



p-phenylethylphenol

The materials used in the investigation were purified, where possible, by a distillation in which the foreruns and residues were discarded and only the middle fraction boiling over a narrow range of a few tenths of a degree was collected. The *p*-phenylethylphenol was purified by a recrystallization from a petroleum ether of 30–60° C. boiling range until a maximum melting point of 57° C. was reached.

The mixtures of *m*- and *p*-cresol were prepared by weighing the purified components. The composition of the mixtures is given in Table II.

The apparatus used is a modification of the Ramsay-Young equipment (*1*). The change consists in shortening the neck of the distilling flask so that the more difficultly volatile phenols and cresols distill into the cooled flask and do not condense back.

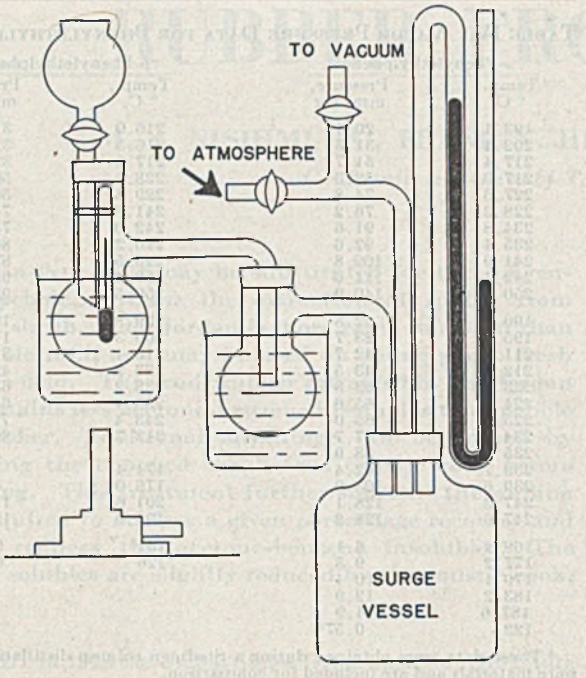


Figure 1. Vapor Pressure Apparatus

Figure 1 shows the vapor pressure apparatus; the distilling flask on the left is equipped with a dropping funnel, to which is attached a calibrated thermometer. This thermometer is placed so that the bulb, wrapped with several turns of cloth, is located at approximately the center of the flask. An oil of high flash point was used for the heating medium in some of the earlier work; however, it is more convenient to use concentrated phosphoric acid which has been previously heated to about 250° C. to remove water, and which can be kept water-white for ease in reading the thermometer by the periodic addition of a few crystals of potassium nitrate.

The second flask can be cooled with ice, although air cooling was found satisfactory for these high boiling materials. The cooled flask is connected to a $2^1/_2$-gallon surge vessel which acts as a reservoir. The surge vessel has connections to a manometer, a vacuum pump, and the atmosphere. While both open- and

Table I. Boiling Point in ° C. at 760 Mm. of *m*- and *p*-Cresols

m-Cresol	*p*-Cresol	Reference
202.8	202.5	(*2*)
201.0	202.32	(*6*)
202.8	202.	(*4*)
202.7	202.32	(*3*)
202.2	202.1	(*5*)

Table II. Composition of Mixtures

Mixture No.	*m*-Cresol, %	*p*-Cresol, %
1	80.77	19.23
2	60.07	39.93
3	40.06	59.94
4	20.73	79.27

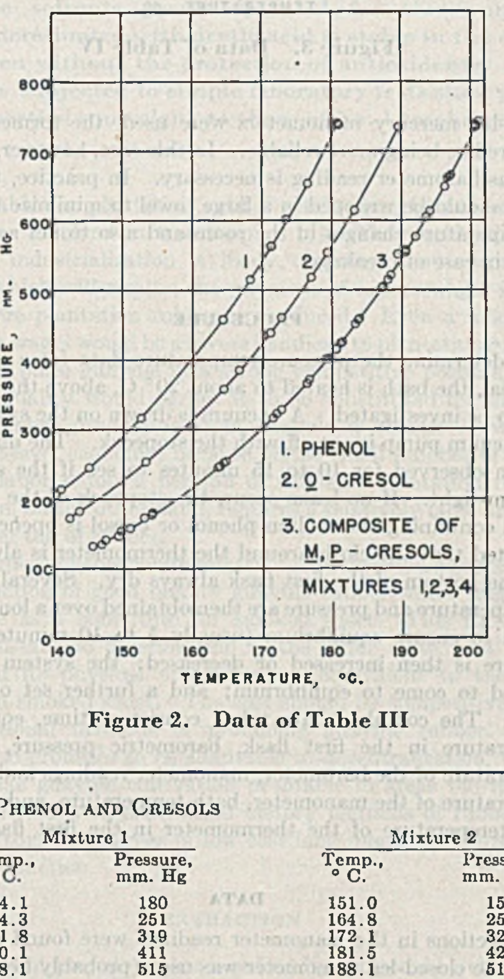


Figure 2. Data of Table III

Table III. Vapor Pressure Data for Phenol and Cresols

Phenol		*o*-Cresol		Mixture 1		Mixture 2	
Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg
141.1	214	142.3	173	154.1	180	151.0	158
152.6	317	153.3	253	164.3	251	164.8	253
164.4	458	164.5	358	171.8	319	172.1	320
168.3	515	171.2	439	180.1	411	181.5	426
173.5	601	183.3	615	188.1	515	188.1	514
181.0	740	189.8	734	194.1	609	194.0	606
				200.8	733	200.9	732
140.2	207	143.7	182	147.4	141	146.0	132
145.1	246	166.8	385	184.0	459	179.5	401
171.4	564	172.9	460	190.6	553	189.5	552
176.6	653	179.4	554	197.0	661	196.8	659
181.1	739	177.1	519	200.8	733	200.8	732

m-Cresol		*p*-Cresol		Mixture 3		Mixture 4	
Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg	Temp., ° C.	Pressure, mm. Hg
149.5	152	145.7	132	150.4	156	149.2	148
164.3	251	163.6	245	164.0	247	163.9	247
172.0	321	171.6	317	172.0	319	172.7	328
179.6	404	179.2	400	181.3	424	180.5	414
187.4	505	187.2	504	188.1	515	188.5	521
192.1	577	193.7	605	194.0	609	194.1	612
196.3	649	200.8	738	200.8	736	200.8	734
201.1	742						
149.6	153	153.0	172	146.9	138	146.9	136
154.1	178	183.8	458	176.8	371	176.4	367
176.4	366	190.8	557	184.0	459	183.6	454
183.4	451	197.1	664	190.5	552	191.0	551
201.1	742	200.9	738	196.7	660	197.0	662
				200.8	735	200.8	734

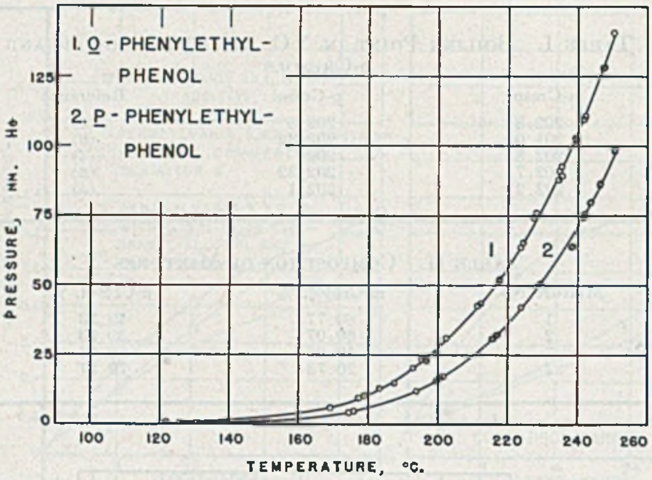


Figure 3. Data of Table IV

closed-leg mercury manometers were used, the former type is preferred as being more reliable. In this case, however, a simultaneous barometer reading is necessary. In practice, the surge vessel should be wrapped in a large towel to minimize the effect of temperature changes in the room and also to act as a safety guard in case of breakage.

PROCEDURE

To determine the pressure-temperature data for a particular material, the bath is heated to about 20° C. above the temperature to be investigated. A vacuum is drawn on the system, and the vacuum pump is cut off with the stopcock. The manometer is then observed for 10 to 15 minutes to see if the system is vacuum-tight. If no leaks occur, the stopcock of the dropping funnel containing the molten phenol or cresol is opened and so regulated that the cloth around the thermometer is always wet and the bottom of the first flask always dry. Several readings of temperature and pressure are then obtained over a long enough period to ensure equilibrium (usually 5 to 10 minutes). The pressure is then increased or decreased; the system is again allowed to come to equilibrium; and a further set of data is taken. The complete data taken consist of time, equilibrium temperature in the first flask, barometric pressure, ambient temperature of the barometer, manometer readings and ambient temperature of the manometer, bath temperature, and emergent stem temperature of the thermometer in the first flask, when necessary.

DATA

Corrections in the manometer readings were found necessary when the closed-leg manometer was used (probably because of a small amount of trapped air in the closed leg). The barometer and manometer readings were corrected to standard conditions. Emergent stem (when necessary) and calibration corrections were applied to the readings of the thermometer in the first flask. The corrected temperature and pressure data are presented in Tables III and IV and Figures 2 and 3.

Calculated Data. The data covering the relation of the reciprocal of the absolute temperature to the logarithm of the pressure may be expressed by the following formula:

$$\log P = \frac{-M}{T} + C$$

where P = pressure, mm. mercury
T = temperature, ° K.
M = slope of log pressure *vs.* reciprocal of absolute temperature line
C = intercept of this line at $1/T = 0$

Table IV. Vapor Pressure Data for Phenylethylphenols

o-Phenylethylphenol Temp., ° C.	*o*-Phenylethylphenol Pressure, mm. Hg	*p*-Phenylethylphenol Temp., ° C.	*p*-Phenylethylphenol Pressure, mm. Hg
193.1	20.1	216.0	31.5
202.4	31.5	216.5	32.1
217.4	51.7	217.0	32.5
217.6	52.3	228.9	50.2
227.6	74.8	229.3	50.6
228.2	76.2	241.8	74.7
234.8	91.6	242.0	75.7
235.4	92.6	246.2	86.7
241.9	109.8	246.5	87.1
242.1	111.6	250.4	98.1
250.3	140.9	250.5	98.9
196.8	22.8	199.8	16.4
195.6	23.7	200.3	17.0
211.6	42.7	215.4	31.6
212.2	43.5	223.8	42.4
223.8	63.8	238.2	63.7
224.3	65.6	238.4	64.1
225.0	65.0	243.4	79.7
234.6	87.7	243.7	80.1
235.6	88.9		
239.7	102.4	174.4	4.2
239.6	103.0	176.0	4.8
247.2	128.1	201.6	17.1
247.6	128.2	194.0	12.0
169.2	6.1	131	0.58[a]
177.2	9.3	126	0.41[a]
179.1	10.4		
183.2	12.9		
187.6	14.9		
122	0.57[a]		

[a] These data were obtained during a Stedman column distillation of the pure materials and are included for comparison.

A summary of the constants for the various materials is given in Table V. The graphs and calculated data show that, within the experimental limits of ±1 mm. of mercury for pressure and ±0.15° C. for temperature, there is no evidence of a constant boiling mixture of *m*- and *p*-cresol which boils lower than either constituent or any other mixture of the two. Although no special attributes are claimed for these data, a comparison with the literature (*2-6*) for the vapor pressure of phenol and of *o*-, *m*-, and *p*-cresol reveals that, except for *m*-cresol which is in disagreement by less than 5% at 140° C., the rest of the data are in agreement by 2.5% or less over the range 140° to 200° C. There are no data for comparison with *o*- and *p*-phenylethylphenols in the literature.

Table V. *M* and *C* Values

Material	*M*	*C*
Phenol	2510	8.395
o-Cresol	2520	8.308
m-Cresol	2650	8.457
p-Cresol	2680	8.524
Mixture 1	2650	8.457
Mixture 2	2690	8.545
Mixture 3	2690	8.545
Mixture 4	2700	8.566
Composite of mixtures 1, 2, 3, 4, and *m*- and *p*-cresol	2680	8.521
o-Phenylethylphenol	3800	9.531
p-Phenylethylphenol	3940	9.427

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Received August 17, 1946.

RUBBER FROM GUAYULE

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A Jordan-type mill may be substituted for the conventional pebble mill for the extraction of rubber from guayule shrub. The Jordan is more rapid in action than the pebble mill, and may be used on young shrub fresh from the field. The crude rubber extracted by the Jordan mill contains less acetone-benzene insolubles than pebble mill rubber. Additional advantage can be gained by subjecting the chopped shrub to a caustic cook before Jordaning. This treatment further shortens the milling time required to achieve a given percentage recovery and further reduces the acetone-benzene insolubles. The acetone solubles are slightly reduced by the caustic cook, and the stability and appearance of the crude rubber are improved. Vulcanizates from Jordan-extracted rubber, from either raw or caustic-cooked shrub, show physical properties somewhat superior to those of commercial guayule rubber extracted in pebble mills. Deresination of the Jordan-extracted rubber with acetic acid gives a product which is superior to guayule rubber deresinated with the solvents previously used for this purpose. Rubber deresinated with acetic acid is stable in the crude state, even without the protection of antioxidants. Vulcanizates subjected to simple laboratory tests show physical properties equivalent to those of No. 1 smoked sheet.

EARLY in 1942 the United States Department of Agriculture launched a comprehensive program to develop the guayule shrub (*Parthenium argentatun*) as a domestic source of natural rubber. In productivity it compares favorably with the plantation rubber tree (*Hevea brasiliensis*). Van Iterson (*10*) quotes figures which show that average plantation trees produce only about 300 pounds of rubber per acre per year. This figure includes only those trees in actual production, and omits the trees which are too young to be tapped. A rubber tree must be eight to twelve years old before it becomes productive. Cultivated guayule, on the other hand, is reported (*9*) to produce an average of 400 pounds per acre per year. Guayule lays down a new increment of rubber each year of its growth, and the sum total of all the annual increments is harvested in a single operation. The growth period from planting to harvest may be from two to seven years, or possibly longer. Planting, cultivation, and harvesting are adapted to mechanization and require a minimum of hand labor. They fit readily into the American pattern of large scale agricultural technique.

Guayule has enjoyed only a limited development because of the inferiority of the rubber produced from it. Guayule rubber tends to soften and sometimes liquefy in the crude state; when vulcanized, its physical properties are markedly inferior to those of vulcanized smoked sheet (plantation rubber). While small amounts of guayule can be advantageously blended with other types of rubber, it has not been found practical commercially to use it unblended. Doering (*3*) reported on service tests of tires and tubes made entirely of guayule rubber, and concluded it would be a poor substitute for plantation rubber. In spite of the substantial sums expended by the Department of Agriculture to improve guayule rubber by modifying the treatment of the shrub and the extraction process (*17*, page 477), no practicable process has yet been developed for the production of guayule rubber of a quality which would make it an acceptable substitute for smoked sheet. Reference is made to a process of latex extraction, which produces rubber of greatly improved quality. It is also known (*1, 18*) that the resin content of guayule can be reduced by microbial action (so-called retting), and that this results in improvement of the rubber. These processes demonstrate the possibility of substantial improvement in the quality of guayule rubber.

Certain economic factors made it advisable to investigate the possibilities of developing guayule rubber as an acceptable substitute for smoked sheet. An abundance of cheap labor is indispensable for plantation rubber production, because of the hand labor involved in tree tapping (*4*). The world-wide advance of industrialization is likely to bring about economic changes which will require the payment of higher wages in the areas where plantation rubber is produced. Even a moderate increase in wages would be a severe handicap to plantation rubber, and would place guayule in a strong competitive position, provided its quality would permit it to be substituted for smoked sheet. Rubber production from guayule is consistent with a high wage-level economy, because of the small number of man-hours of labor required per ton of rubber. Plantation rubber production, on the other hand, requires a relatively large amount of labor per ton of rubber.

The purpose of this communication is to describe a process for the production of good quality guayule rubber which might be acceptable as a substitute for smoked sheet. This rubber is highly resistant to deterioration in the crude state, and when vulcanized its physical properties are equivalent to those of vulcanized smoked sheet. The cost should be competitive with the traditional methods of producing guayule rubber. This process also promises to be adaptable to decentralization, which would make guayule cultivation profitable in areas too remote to be exploited with centralized factory methods of rubber extraction; thus large areas of low cost land might be utilized for rubber production.

EXTRACTION

Commercial guayule rubber is ordinarily extracted by chopping and crushing the shrub, and then grinding with water in a pebble mill for 90 minutes or longer. The milled slurry is discharged into tanks of water in which the wood fiber or bagasse sinks and the rubber, together with particles of cork, floats to the surface where it is skimmed off. The cork is water-logged by a subsequent treatment (either boiling or pressure), and after a second skimming the cork-free rubber is ready for drying. The pebble milling breaks up the tissue cells of the shrub which contain the rubber particles, initially of microscopic size, and causes them to agglomerate into larger particles. The agglomerated particles of rubber (called "worms") can be recovered as soon as they are large enough to float free from the sinking bagasse. Some small particles are always lost in the bagasse, and some bagasse fiber is always entrapped in the floating rubber. The factory process has been described in detail (*17*).

We have introduced two changes in this general method of processing the shrub. We cook the chopped shrub in caustic soda

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TABLE I. YIELDS FROM MILLING DUPLICATE SAMPLES OF SHRUB FOR 5, 10, 15, AND 25 MINUTES

Run No.	Grams Crude Rubber per 376 G. Chopped Shrub (Dry Wt.)			
	5 min.	10 min.	15 min.	25 min.
1	31.05	34.20	35.90	38.00
2	31.75	34.30	35.90	38.20
3	31.20	34.15	35.85	38.55
4	31.60	34.40	36.05	37.60
5	31.70	33.95	35.85	36.50
6	30.40	34.40	35.30	36.25
7	31.70	33.80	35.80	36.75
8	32.00	33.80	35.75	37.45
Av.	31.4	34.1	35.8	37.3

solution before milling, and use a steel mill resembling a paper pulp Jordan, instead of the pebble mill, for the comminution of the shrub and agglomeration of the rubber worms. The caustic cook softens the fiber of the shrub, and shortens the milling time required for a given degree of rubber recovery. It also eliminates the cork and improves the quality of the extracted rubber, particularly by reducing the quantity of insoluble impurities. The Jordan has certain advantages over the pebble mill, even for the milling of raw shrub. It is more rapid in action than the pebble mill, and is adaptable to both small and large scale operations. We can work with batches of 100 grams, while the smallest pebble mills that give satisfactory action require charges of about 5 kg.

Most of the work reported here was carried out in two miniature Jordan units[2]. We also made a few extractions with a commercial Jordan loaned by the Wood Conversion Company. This unit (known as a Claflin) was powered with a 20-horsepower motor, and was installed in the experimental plant of the Emergency Rubber Project, U. S. Forest Service, at Salinas, Calif. Several large Jordans were later installed at the factory operated by the Forest Service in Salinas, and these units were found to be effective in rubber recovery.

As might be predicted from an examination of various patents on the recovery of rubber from guayule (*11*), almost any mechanism which comminutes the shrub will produce a slurry from which rubber can be separated after dilution and flotation. There appears to be no record of Jordaning as a method of recovery, although Bradshaw (*2*) patented the use of a Jordan or similar machine to reduce the chopped shrub to fine particles preliminary to pebble milling. Our conclusion from three years' experience with a variety of Jordan-type mills is that quantity and quality of rubber recovered are less dependent upon design and construction of the mill than on technique of preparation of the shrub and conditions of operation of the mill. Every unit which we built was capable of extracting rubber and, if run long enough, was capable of high percentage recovery. The units which gave more rapid comminution also gave good recovery in shorter time. It would therefore be misleading to emphasize the structural details of any particular unit, especially since Jordans are already well known and fully described. Instead, attention will be given to the techniques of shrub preparation and operation of the mill.

PREPARATION OF SHRUB

Shrub was used from the local field and from various plantings in California which were maintained by the Emergency Rubber Project. Most of the work was done on shrub one to two years old, although some extractions were made with shrub three or more years old. The same technique was adequate in all cases, and it was not necessary to dry the shrub to any special moisture content before processing. The shrub, as received, was deleafed by immersing the tops in boiling water for 15 minutes and then beating on a cement floor. The deleafed shrub was washed to remove adhering lumps of soil and chopped to pass a 1/4-inch-mesh screen. This was generally done by passage through a power meat grinder, but equally good results were obtained with other methods of chopping. No crushing rolls were used. A coarse cut without much fine material makes circulation of the cook liquor and rinse water easier. Crushing gives too much fine material.

The chopped shrub was mixed, quartered, and mixed again. It was then divided into equal samples, of about 1 kg. each, by passing repeatedly through a Jones divider. Table I shows that duplicate samples prepared in this way give rubber yields in close agreement. Storage under refrigeration for several weeks does not alter the results obtained with duplicate samples stored in sealed cans.

One can from each batch of chopped shrub was taken for moisture determination and for double solvent analysis of resins and rubber hydrocarbon. Moisture was determined by drying at 60° C. in an air oven. This temperature is arbitrary. Higher temperatures drive off volatile materials other than water, some of which are lost at 60° also.

The material for double solvent analysis was dried thoroughly and ground to a fine powder; duplicate samples of 2.5 or 5 grams were extracted with acetone and then with benzene, following the Spence-Caldwell procedure (*16*). The acetone and benzene extracts were dried at 70° C. and weighed. Agerite Resin D (polymerized trimethyldihydroquinoline) was added to the benzene extract to retard oxidation during the drying operation. The percentage of acetone solubles and benzene solubles in the dry shrub was computed and used as a basis for establishing the rubber content of the other cans in the batch, on the assumption that the benzene solubles represent rubber hydrocarbon.

To extract crude rubber, the procedure was as follows: The shrub was first cooked in caustic with 5 parts water to 1 part dry weight of shrub, allowance being made for the moisture present in the shrub. The required amount of water and caustic was brought to a boil, and the shrub added to the boiling solution. The mass was boiled slowly for 30 minutes, time being taken from the moment when boiling started again after the chopped shrub was added.

The cooked mass was dumped into a wire basket and rinsed in slowly running water for about 30 minutes. The temperature of the rinse water was usually about 60° C. After rinsing, the liquor draining from the cooked chips had a pH of about 8.

MILL OPERATION

Milling was usually carried out with a ratio of 5 parts water to 1 part initial dry weight of shrub, no allowance being made for the loss in dry weight due to cooking. In charging the mill, it was assumed that the cooked chips were about 50% water. The required amount of water was measured out and put into the mill, the mill was set in motion so that the water was circulating, and then the shrub chips were added as rapidly as possible. This procedure was followed to avoid clogging the mill, which occurred readily if the entire charge was put in before circulation was started. One half gram of Agerite White (*sym*-di-β-naphthyl-*p*-phenylenediamine) was also added to each 500 grams dry weight of a mill charge to retard deterioration of the crude rubber. Agerite White was found to be the most effective antioxidant for retarding the decrease of benzene solubles and the increase in acetone solubles during storage of the crude rubber.

Figure 1 is a diagram of the setup. The slurry passes from hopper *H* into the small end of Jordan mill *L*. It is ground between the stationary and rotating blades as it passes to the large end of the cone, and enters return hose *R*, through which it is fed back into the hopper. Milling is usually continued for 15 or 30 minutes (time being taken from the moment when all the charge has been added) at about 60° C. At the end of the desired period valve *V* is turned to discharge the slurry into flotation tank *T*, and rinse water is poured into the hopper. A charge of 500 grams of shrub ground with 2. 5 liters of water would be discharged into a flotation tank containing about 10 gallons of water at 50° C.

The flotation tank is stirred violently with a stick for a moment after the slurry is run in, and then the surface is gently agitated to knock particles of bagasse off the curds of rubber as they float to the surface. After 5 minutes the rubber is skimmed and transferred to a kettle of water and boiled 30 minutes. In the case of raw shrub the boiling is necessary to remove cork. To avoid unnecessary differences in treatment of rubber from raw and cooked shrub, the rubber from cooked shrub is also boiled 30 minutes, although there is no cork to be water-logged. However, boiling eliminates some of the bagasse particles which are always trapped in the floating rubber. The boiling breaks up the rubber into fine particles and permits bagasse splinters to separate out, and the rubber forms a uniform layer which can be skimmed off on a wire screen for final drying.

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[2] Structural changes which improved the extraction efficiencies of these mills were made from time to time. These changes are responsible for differences in rubber recovery shown in different tables, in spite of comparable conditions.

Ordinarily a temperature of 60° C. was used for the flotation tank; a few experiments with temperatures from 5° to 85° C. showed no difference in the effect on rubber from raw shrub, but with rubber from cooked shrub, a low temperature in the flotation tank makes skimming easier because the worms are coarser.

In pebble milling it is believed that slow dilution of the slurry in the settling tank favors recovery of cleaner rubber; therefore some experiments were run to see if this were a significant factor in Jordan milling. The slurry was either diluted suddenly, by discharging into the empty settling tank and immediately dumping in a large volume of water, or diluted slowly in a very large mill hopper so that a large amount of water could be added, and then allowing the mill charge to flow slowly into the previously filled settling tank. Slow or fast dilution made no difference in the amount of crude rubber recovered or in the acetone solubles or benzene insolubles of the crude rubber.

The screens of skimmed rubber were dried in a circulating air oven at 40° C., usually for about 72 hours. The dried rubber was peeled off the screens, weighed, and sampled for determinations of moisture, acetone solubles, benzene solubles, and acetone-benzene insolubles. Bromination was used as a check on the benzene solubles, to support the assumption that this fraction represents rubber hydrocarbon. In the case of the rubber from raw shrub, not all the benzene solubles could be brominated, but with cooked shrub the rubber estimated as tetrabromide agreed well with the figure for benzene solubles, provided there had been no appreciable softening of the crude rubber prior to analysis. Softening is accompanied by a decrease in both the benzene solubles and the brominatable fraction of the benzene solubles. After softening has taken place, the brominatable fraction no longer shows a constant relation to the total benzene solubles but varies over a wide range.

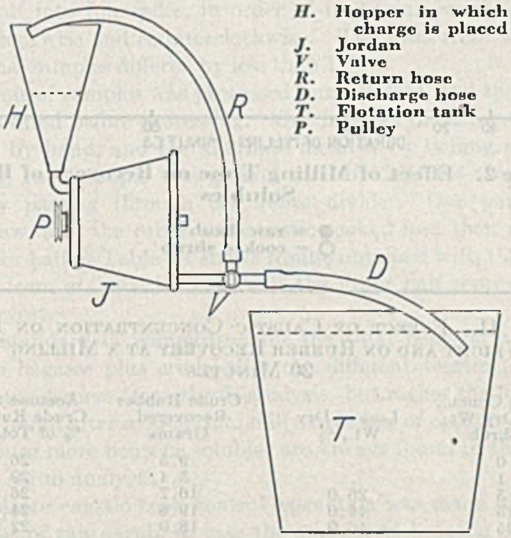
The bagasse was collected by straining the effluent from the flotation tank through a cloth bag. The dried bagasse was weighed and sampled for analysis of acetone and benzene solubles.

EFFECTIVENESS OF PROCESS

The efficiency of the extraction process may be determined in two ways. The rubber hydrocarbon (benzene solubles) of the crude rubber can be compared with the rubber hydrocarbon present in the sample of chopped shrub, on the basis of double solvent analysis of the shrub, or it may be compared with the total rubber hydrocarbon found in the bagasse plus the crude rubber. More rubber hydrocarbon was regularly found in the bagasse plus crude rubber than had been found by analysis in the initial shrub sample.

There are several possible explanations: Sampling errors might make the shrub analysis fail to represent the correct figure for rubber hydrocarbon content of the shrub sample. In this case it would be expected that the error would sometimes be in one direction and sometimes in the other, but we have nearly always found that the difference was in favor of mill extraction rather than shrub analysis. A second possibility is that the shrub analysis fails to extract all the benzene solubles present. Since we had no proper facilities for carrying out the sulfuric acid digestion specified in the Spence-Caldwell procedure, this possibility must be considered. But while the acid digestion may be necessary with older shrub where the rubber content is high, evidence is lacking that there is any need for it with young shrub such as we were using, where the percentage of rubber is low. At the Emergency Rubber Project laboratories in Salinas, where acid digestion was regularly used, analysis of the shrub generally showed less rubber hydrocarbon than did that of bagasse plus crude.

A third possibility is that the drying of the shrub sample preparatory for double solvent analysis results in some loss of rubber hydrocarbon, so that the thoroughly dried sample is not comparable with the moist shrub used for extraction of crude rubber. To test this possibility, chopped shrub was wetted and treated with various water-soluble antioxidants such as MTD (*m*-toluenediamine) prior to desiccation and fine grinding for analysis. This resulted in the recovery of more benzene solubles in the analysis, but never enough to make up the total found in bagasse plus crude by milling. We accept this effect of antioxidants as evidence that some rubber is ordinarily lost in the preparation of shrub samples for analysis, and that this is one of several possible reasons why more rubber is found by mill extraction than by analysis. Therefore it appears more logical to base extraction efficiency on rubber hydrocarbon found in bagasse plus crude than on shrub analysis. This method also avoids recovery figures higher than 100% which is common when calculations are based on shrub analysis. The figures for extraction efficiency in the following tables are based on benzene solubles in bagasse plus crude, but the rubber content on the basis of shrub analysis is specified so that this basis can be used if desired.



H. Hopper in which charge is placed
J. Jordan
V. Valve
R. Return hose
D. Discharge hose
T. Flotation tank
P. Pulley

Figure 1. Diagram of Miniature Jordan Setup

The effectiveness of the extraction technique depends not only on the completeness with which the rubber hydrocarbon is recovered, but also on the freedom of the crude rubber from objectionable impurities. The nitrogen content is generally small. The principal impurity is resin (acetone solubles), and the second is material insoluble in both acetone and benzene (designated "benzene insolubles" in the tables).

The tabular data show that the yield and quality of recovered rubber depend upon several controllable variables. But it cannot be assumed that the same combination of cooking and milling techniques will be optimal for all types of shrub, because the age, season of harvest, extent of drying after harvest, and other characteristics of the shrub influence the recoverability and quality of the rubber. Further experience may be expected to show the desirability of modifying the technique to compensate for differences in the condition of the shrub.

Although sodium hydroxide has been used to improve the quality of guayule rubber, a caustic cook followed by a milling technique appears to be an innovation. We tried treating the ground shrub with cold caustic solutions, cooking in a double boiler, open boiling, and pressure cooking. Cold soaking is less effective than hot processing. No attempt was made to establish the relative merits of the different methods of cooking, and open boiling was generally used because it is simple and effective. Cooking with other chemicals used in the paper pulp industry was also tried such as sodium hydrosulfite and combinations of sodium sulfide and sodium hydroxide. Sodium hydrosulfite gave rubber of poor quality. The use of sulfides had interesting effects on acetone solubles but showed no outstanding advantages over sodium hydroxide alone.

Table II shows the effect of caustic concentration. A charge of 500 grams of chopped shrub (290 grams dry weight) was cooked in a double boiler with 2.5 parts water to 1 part dry weight of

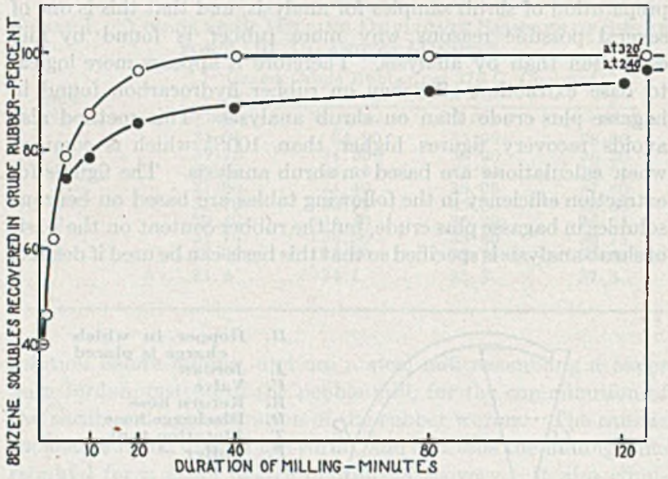


Figure 2. Effect of Milling Time on Recovery of Benzene Solubles

● = raw shrub
○ = cooked shrub

Table II. Effect of Caustic Concentration on Loss in Dry Weight and on Rubber Recovery at a Milling Time of 20 Minutes

Caustic Concn., % of Dry Wt. of Shrub	Loss in Dry Wt., %	Crude Rubber Recovered, Grams	Acetone Sols. in Crude Rubber, as % of Total Sols.
0	..	9.5	26.9
1	..	3.4	29.5
5	26.0	16.7	26.0
15	44.0	19.6	24.6
25	46.0	18.0	22.3

shrub for 30 minutes, rinsed, and milled for 20 minutes at about 85° C. A cook with 1% caustic gave poorer recovery than no caustic, and concentrations of 5% or higher were needed to improve recovery appreciably. Acetone solubles are also higher with the 1% cook than with the plain water cook. The acetone solubles are definitely lower with the higher caustic concentrations but it is evidently impossible to saponify more than a small part of the acetone soluble material.

Since the yield did not increase appreciably from 5 to 25% caustic, a concentration of 10% was arbitrarily selected, partly because this is approximately the concentration used in the paper pulp industry. However, the water-shrub ratio of 2.5–1 made such a thick mass that circulation was poor; later, when the use of the double boiler was abandoned, difficulty was experienced in getting a uniform cook, so the water-shrub ratio was raised to 5–1, and the caustic was raised to 20% of the dry weight of shrub to keep the concentration in water the same as before. A caustic concentration of 10% of the dry shrub is sufficient with a water ratio of 2.5–1, and this ratio is satisfactory with indirect heat or with mechanical circulation of the mass during the cook.

Table II shows the improvement in yield due to cooking, for an arbitrarily fixed milling time. Table III and Figure 2 show that the yield from raw shrub can be brought up to nearly the same level as the yield from cooked shrub by greatly prolonging the milling time. It is therefore incorrect to conclude from Table II that cooking increases the yield. It merely shortens the time required to reach a given level of recovery. For example, with raw shrub 96% of the total rubber hydrocarbon (benzene solubles) is recovered in the crude rubber after 240 minutes of milling; the same recovery is attained with cooked shrub after only 20 minutes, and after 40 minutes the cooked shrub gives a recovery of 99%. The insolubles are lower, and the acetone solubles continue to diminish with milling in sharp contrast to the raw shrub, where acetone solubles remain practically the same for all milling times.

In the case of both raw and cooked shrub (Figure 2), 70% of the rubber is recovered after less than 5 minutes of milling. The factory pebble mills, on the other hand, ordinarily recover only about 70% of the rubber from young shrub after about 1.5 hours of milling. The miniature Jordans can attain this level of recovery in even shorter time if the clearance between rotor and stator cones is decreased; but throughout the experimental runs reported here the clearance was kept large to minimize wear, in order to avoid confusing the effects of mill wear with those of factors under investigation.

The effect of pH has not yet been thoroughly investigated. Our experience indicated that milling at neutral or slightly acid pH values gives small rubber worms which are difficult to recover, and are high in insolubles and in acetone solubles. Slightly alkaline milling (pH 8–9) gives coarse worms which are easy to float, and are low in insolubles and acetone solubles. However, in the case of very fresh shrub, milled raw, alkalinity appears to be disadvantageous (Table VI).

Table IV shows that there is better recovery of rubber when the milling temperature is kept at 50° than at 90° C. There is no apparent difference in insolubles, but the acetone solubles are slightly lower at the lower milling temperature.

An important factor is the ratio of water to shrub during milling. Table V presents data on an experiment with raw shrub, in which the ratio was varied from 6–20 parts of water to 1 part of shrub. The shrub was milled at 80° C. Analysis indicated that each charge contained 33.5 grams of benzene solubles. Recovery of benzene solubles is much higher for the 6 to 1 ratio, for both long and short milling. Acetone solubles are also higher for the thicker slurry, although the difference is not striking. It is interesting to note that the acetone solubles are lower for the longer milling time and for the thinner slurry, but the benzene insolubles remain fairly constant regardless of milling time or water ratio. With thinner slurry, the total benzene solubles found are appreciably lower.

Table III. Dependence of Yield on Duration of Milling for Raw and Caustic-Cooked Shrub[a]

Milling Time, Min.	Analysis of Recovered Crude Rubber: Grams recovered	Analysis of Recovered Crude Rubber: Acetone sols., %	Analysis of Recovered Crude Rubber: Benzene insols., %	Total Benzene Solubles Found, Grams: In crude rubber	Total Benzene Solubles Found, Grams: In bagasse	Total Benzene Solubles Found, Grams: In bagasse + crude	% of Benzene Sols. Recovered in Crude Rubber
			Raw Shrub				
5	52.54	22.8	4.62	37.8	13.4	51.8	74.0
10	58.28	23.1	4.28	42.7	11.7	54.4	78.5
20	64.19	21.8	3.99	47.8	8.0	55.8	85.7
40	68.80	21.7	4.05	51.5	6.5	58.0	88.8
80	73.11	21.0	3.79	54.8	4.7	59.5	92.1
120	73.78	21.0	3.76	55.2	3.0	58.2	94.3
240	76.46	21.4	3.61	58.0	2.0	60.0	96.7
			Caustic-Cooked Shrub				
0.2	32.3	24.5	2.72	22.8	26.5	46.3	40.0
1.0	37.1	24.8	2.16	26.2	25.4	51.6	46.0
2.5	49.1	23.5	1.97	35.1	16.5	51.6	61.5
5.0	57.4	21.7	1.74	44.8	11.6	53.4	78.5
10	68.3	20.2	1.69	50.0	5.3	55.3	87.5
20	73.7	19.8	1.54	54.9	1.6	56.5	96.4
40	76.3	19.4	1.59	56.6	0.43	57.1	99.3
80	75.9	18.7	1.38	56.7	0.21	56.9	99.5
160	74.8	17.4	1.41	56.5	0.14	56.7	99.2
320	74.3	17.1	1.38	56.7	0.13	56.8	99.5
			Raw Shrub Controls for Cooked Series				
20[b]	63.7	20.5	6.00	47.6	8.9	56.5	84.2
20[c]	62.0	20.5	6.13	46.3	9.3	55.6	83.3
40	67.0	20.3	6.14	49.6	7.1	56.7	87.4
240	73.3	19.5	8.00	54.4	3.9	58.3	93.4

[a] Each set of values represents the average of two duplicate runs. Milling was at 50° C., with 6 parts water to 1 part dry weight of shrub. For the raw series, shrub analysis showed 54.4 grams of benzene solubles per 560 grams of dry matter. For the cooked series and the raw controls of this series, 525 grams of dry matter were used for each charge. No shrub analysis was made for this cooked series. The raw shrub controls of the cooked series are included to show that duplicate samples yield less rubber when extracted raw than when cooked before extraction.

[b] Start of cooked series.

[c] End of cooked series.

Table IV. Effect of Temperature on Recovery of Rubber

(Extns. from raw shrub milled 20 min. with 10 parts water to 1 part dry wt. of shrub; each charge contained 33.5 grams benzene sols.)

	Analysis of Recovered Crude Rubber			Total Benzene Sols. Found, Grams			Extn. Efficiency, % Benzene Sols. Recovered in Crude Rubber
Milling Temp., ° C.	Grams recovered	Acetone sols., %	Benzene insols., %	In crude rubber	In bagasse	In bagasse + crude	
50	33.32	20.6	3.95	25.4	7.3	32.7	77.7
50	34.68	19.4	4.30	26.5	7.5	34.0	77.9
90	21.39	21.4	3.58	16.1	12.9	29.0	55.5
90	24.67	21.5	4.75	18.4	11.5	29.9	61.5

Table V. Effect of Water-Shrub Ratio on Rubber Recovery

	Analysis of Recovered Crude Rubber			Total Benzene Sols. Found, Grams			Benzene Sols. Recovered in Crude Rubber, %
Water-Shrub Ratio	Grams recovered	Acetone sols., %	Benzene insols., %	In crude rubber	In bagasse	In bagasse + crude	
			20-Minute Milling Time				
6-1	33.25	22.7	4.04	24.7	7.9	32.6	76.0
6-1	37.33	22.7	4.80	27.6	6.9	34.5	80.0
10-1	31.53	22.5	4.00	23.2	10.6	33.8	69.0
10-1	30.16	23.2	3.44	22.2	9.6	31.8	70.0
20-1	23.78	22.3	4.60	17.7	14.4	32.1	55.0
20-1	23.78	20.6	4.54	17.3	13.6	30.9	56.0
			80-Minute Milling Time				
6-1	39.04	21.0	4.15	29.3	8.5	37.7	78.0
6-1	39.19	20.6	4.95	29.2	5.1	34.3	85.0
10-1	38.19	20.4	4.84	28.5	5.7	34.2	83.0
10-1	32.66	19.4	4.25	24.8	7.3	32.1	77.0
20-1	23.92	18.8	3.80	18.2	12.4	30.6	59.0
20-1	26.22	19.9	4.76	19.9	9.6	29.5	68.0

Thicker slurries have been used, especially in the case of cooked shrub, and good results have been obtained with ratios of 3.5 to 1. Thicker slurries require special precautions to ascertain that all parts of the mass have an equal chance for repeated passes through the mill. To avoid stilling, we used a narrow cylindrical receiver instead of the cone shown in Figure 1.

LOSSES OF BENZENE SOLUBLES

The condition of the shrub at the time of milling is believed to be an important factor in determining the amount of rubber recoverable by pebble milling. According to Lloyd (*12*) the rubber in guayule occurs in the form of latex particles confined within the parenchyma cells. It is known that the latex can be coagulated by partial drying of the shrub, and that the yield of rubber is better from dried than from fresh shrub. The improved yield from dried shrub is generally attributed to the coagulation of the latex, and it is believed that the milling of fresh shrub results in unavoidable losses of latex particles in the effluent, because of failure of pebble milling to agglomerate these particles into worms which can be skimmed after flotation. Such losses are believed to be especially serious with young shrub (one to two years old).

Our experience with the milling of caustic-cooked shrub did not produce any convincing evidence of appreciable losses of benzene solubles as latex particles in the effluent. It is always possible to recover more benzene solubles by milling cooked shrub than by shrub analysis, even from young shrub fresh from the field. Probably the caustic cook is an effective coagulant, but it is possible that the Jordan milling of raw shrub would result in appreciable losses of latex such as are believed to occur in pebble milling. To test this possibility, comparisons were made of total benzene solubles from fresh and from dried shrub, deleafed by hand to avoid coagulation of the latex by heat and deleafed by boiling in the usual way.

These experiments require the comparison of equivalent samples of whole shrub, subjected to different treatments prior to chopping. It is more difficult to sample whole than chopped shrub, and special precautions were taken to obtain aliquots as nearly comparable as possible. Two hundred uniform shrubs were harvested from our field at Manzanar (eighteen months old) and divided into size classes as quickly as possible by weighing on a spring balance. The exceptionally small and exceptionally large shrubs were rejected and the remaining individuals were dealt into four piles, in order of increasing weight, alternately clockwise and counterclockwise. The total fresh weights of the final samples differed by less than 1%.

One pair of samples was processed immediately, and the other pair was dried before processing. One member of each pair was deleafed by hand, and the alternate member by boiling. After deleafing, each sample was ground and divided into two equal parts by passing through the Jones divider. One part was milled raw, and the other was caustic-cooked and then milled. The upper half of Table VI shows results obtained with the eight samples from a single harvest, and the lower half represents a later harvest.

As a standard of comparison for the total benzene solubles found in bagasse plus crude after the different treatments, we did not use figures from shrub analysis, but rather the benzene solubles found after a 30-minute mill extraction of caustic-cooked shrub, since more benzene solubles are always found in this way than by shrub analysis.

A separate caustic cook control extraction was made for each treatment of raw shrub, in case the amount of benzene solubles should be altered by the treatment. In Table VI, the caustic cook run precedes the corresponding raw run or runs. The column headed "Benzene solubles unaccounted for" shows zero for the caustic cook extractions, implying that the highest possible figure for benzene solubles is obtained in this way.

Table VI shows that the total benzene solubles for the four control runs of the first harvest ranged from 36.4 to 42.5 grams, and for the two control runs for the second harvest, 35.9 and 31.1 grams. These differences might be regarded as evidence that the different treatments had actually altered the amounts of benzene solubles in the different aliquots, but such a conclusion is open to doubt because the differences might also be due to the inherent difficulties in sampling whole shrub. The purpose of these experiments was to seek evidence of latex losses in the milling of raw

Table VI. Effects of Shrub Condition and Preparation on Unaccountable Losses of Benzene Solubles

Preparation of Shrub				Analysis of Crude Rubber and Bagasse					
Condition	Deleafing method	Pretreatment of chips[a]	Milling time, min.	Acetone sols. in crude, %	Benzene insols. in crude, %	Benzene sols. in crude, grams	Benzene sols. in bagasse, grams	Total benzene sols. found, grams	Benzene sols. unaccounted for[b], %
Fresh	By hand	C.C.	30	27.0	2.4	36.0	0.4	36.4	0
	By hand	None	30	29.0	7.1	26.7	4.4	31.1	−14.4
	Boiling	C.C.	30	30.0	2.5	38.2	0.4	38.6	0
	Boiling	None	30	32.0	4.3	35.2	3.1	38.3	− 1.0
Dried	By hand	C.C.	30	28.0	1.6	39.6	0.5	40.1	0
	By hand	None	30	29.0	4.1	33.7	4.4	38.1	− 5.0
	Boiling	C.C.	30	32.0	2.5	39.8	0.4	40.2	0
	Boiling	None	30	31.0	5.3	37.5	5.0	42.5	+ 5.0
Fresh	By hand	C.C.	30	29.5	3.0	35.5	0.4	35.9	0
	By hand	None	30	30.6	6.5	27.0	3.7	30.7	−14.5
	By hand	None	120	27.6	6.5	32.2	2.2	34.4	− 4.2
	By hand	TSP in mill	30	31.0	4.5	12.9	10.1	23.0	−36.0
Dried	By hand	C.C.	30	28.0	2.0	30.7	0.4	31.1	0
	By hand	None	30	28.0	4.5	26.4	3.2	29.6	− 4.8
	By hand	None	120	26.5	4.0	29.1	1.8	31.9	+ 2.5
	By hand	TSP in mill	30	26.0	3.5	25.6	4.0	29.6	− 4.8

[a] C.C. = caustic cook; TSP = trisodium phosphate.

[b] Extent to which each raw milling falls short of accounting for the total benzene solubles found in the corresponding caustic-cook milling.

Table VII. Comparison of Guayule Rubbers on A.C.S. II and B.A.I.C. Formulas

		Before Aging			After Aging	
Source of Crude Rubber	Curing Time, Min.	Elongation at break, %	Modulus at 600%, lb./sq. in.	Tensile at break, lb./sq. in.	Tensile at break, lb./sq. in.	Loss in tensile, %
E.R.P., Salinas factory, Texas shrub[a]	60	860	570	2540	1012	60
	75	830	750	2560	810	68
	90	820	760	2790	553	80
	120	800	730	2625	619	76
Continental Mexican Rubber Co., Pedros unit	60	855	445	2355	685	71
	75	840	505	2410	435	82
	90	810	475	1930	264	86
	120	785	485	1775	1037	42
Miniature Jordan, raw shrub	60	875	405	2200	1702	22.6
	75	860	495	2480	1575	36.5
	90	820	580	2115	1093	48.0
	120	830	555	2375	1435	39.7
Miniature Jordan, caustic-cooked shrub	60	845	475	2735	1932	29.4
	75	855	495	2915	1832	37.0
	90	790	560	2260	1183	47.7
	120	780	540	2115	1617	23.4

[a] Formula II used only for this factory rubber, which contained 0.4% Tonox.

shrub. After the different aliquots of whole shrub had been pretreated they were ground, so that the control for each test run may be regarded as a correct sample, even though the controls may not be comparable among themselves because they represent different samples of whole shrub.

The results for the first harvest are consistent with the interpretation that the rubber must be coagulated to be fully recoverable. The fresh, hand-deleafed shrub showed 14.4% benzene solubles unaccounted for as compared to the caustic-cook control: deleafing by boiling reduced the loss to only 1%. Drying, which is also believed to coagulate the rubber, resulted in a loss of 5% in the case of hand deleafing and a gain of 5% for deleafing by boiling. This gain is to be regarded as a sampling error, or perhaps loss of some of the control rubber in the skimming process.

The second harvest was intended to show whether the losses in the case of fresh, hand-deleafed shrub were impossible to recover, or whether they could be recovered by longer milling. The harvest was again divided into four samples. With hand-deleafed fresh shrub milled 30 minutes, the unaccounted loss was 14.5%, in aggreement with the corresponding figure for the first harvest. When the milling period was lengthed to 120 minutes, the loss was reduced to 4.2%. In the case of the dried shrub, lengthening the milling time from 30 to 120 minutes reduced the loss from 4.8% to a gain of 2.5%. Our conclusion from these experiments is that, if the unaccounted losses of benzene solubles are due to uncoagulated latex, then Jordan milling, like boiling or drying, is capable of coagulating the latex. With fresh shrub, longer milling is required to attain a given level of rubber accounted for than with dried shrub.

Table VI also shows two 30-minute runs with raw shrub, in which the mill slurry was made alkaline with trisodium phosphate. The latter was tried to determine whether it would act as an emulsifying agent, leave more rubber in the form of latex, and hence increase the benzene solubles unaccounted for. With fresh shrub, trisodium phosphate raised the fraction unaccounted for to 36%, which is consistent with the hypothesis that trisodium phosphate causes more rubber to remain in finely divided form. In the case of dried shrub, trisodium phosphate did not change the benzene solubles unaccounted for. It made no substantial change in the yield, but the worms were coarse and easy to skim.

In conclusion it may be said that the miniature Jordans can recover close to 100% of the rubber hydrocarbon present in the shrub, either raw or caustic cooked. In either case the process is more rapid than pebble milling. Figure 2 and Table III show that, to obtain good recovery, sufficient time must be allowed for the milling operation. Other factors favoring good recovery are low milling temperature and low ratio of water to shrub. Our results do not indicate the need for special aging or conditioning of the shrub before the rubber is extracted, except to the extent that these treatments shorten the duration of milling required to attain a given percentage recovery of benzene solubles. Caustic cooking surpasses other treatments in its effect on shortening milling time, and also makes a substantial reduction in benzene insolubles and a small reduction in acetone solubles.

DERESINATION WITH ACETIC ACID

The crude rubber extracted in miniature Jordans, whether from raw or cooked shrub, is not much more stable than ordinary commercial guayule rubber extracted in pebble mills. The physical properties of vulcanizates of Jordan-milled rubber have been found to be somewhat superior to those of ball-milled rubber, probably because of the lower benzene insolubles. But the crude rubber, whether from caustic-cooked or raw shrub, generally tends to soften and eventually to liquefy, like the rubber from pebble mills. The caustic cook delays softening and liquefaction, but does not prevent it. Tonox (*p-p'*-diaminodiphenylmethane) is known to be a good preservative for crude guayule rubber, and we found that 0.5% Tonox, milled into the Jordan rubber from caustic-cooked shrub, prevents softening indefinitely. The rubber from raw shrub, whether Jordan- or pebble-milled, eventually softens even if treated with Tonox. In any case, Tonox is not an ideal preservative because it acts as a secondary accelerator when the rubber is compounded and cured, and Tonox-treated rubber is less resistant to Geer oven aging than rubber without Tonox.

The softening of guayule rubber is generally attributed to its high resin content, and deresination has often been recommended as a means of making it an acceptable substitute for smoked sheet. Various solvents have been used for deresination of guayule (*8*), and it is reported that the removal of the resins, far from protecting the crude against deterioration, makes it extremely unstable and subject to liquefaction. However, when the deresinated rubber is preserved with Tonox, it is much more stable than the Tonox-treated resinous rubber and can be kept in the crude state indefinitely without deterioration. Morris *et al.* (*13*) report from physical tests with deresinated guayule rubber that it is superior to resinous, but that the elongation and tear resistance are low, and that deresination does not offer sufficient advantages to justify the expense.

Guayule resin is a mixture of a large number of components, and it is reasonable to expect that the effect of the various components on the rubber will differ appreciably. Exploratory experiments showed that, if the bark and the wood were separated and then extracted, the rubber from the wood contained less resin but was more prone to liquefaction than the rubber from the bark. This suggests that deterioration may be dependent upon character as well as quantity of resin.

Haagen-Smit and Siu (*5*) studied the oil obtained from guayule by steam distillation, separated it into forty-five fractions, and kindly supplied us with samples of the various fractions, which we tried on guayule rubber. Some of these fractions were much more potent than others in bringing about oxidation and deterioration of the rubber. Some seemed to exert a preservative effect. The deteriorative effect was associated with the presence of oxygen in the molecule. A suggestion was made that it might be possible to extract the oxygen-containing resins with cold concentrated sulfuric acid. Although it did extract material from the rubber, no concentration of acid was found which would act as an effective solvent without damaging the rubber. Experiments were then made with hydrochloric, nitric, and phosphoric acids, and with organic solvents such as acetone, dioxane, methanol, ethanol, glycerol, acetic acid, etc. Hydrochloric and nitric acids produced objectionable changes in the rubber, suggestive of breakdown. Phosphoric acid did not seem to damage the rubber but was too viscous to give good extraction. The organic solvents all caused more or less swelling of the rubber, and the solvent-extracted rubber was extremely prone to deterioration as soon as it was washed and dried. The acetic acid, on the other hand, did not cause swelling of the rubber nor any apparent breakdown. Rubber extracted with acetic acid and washed in water was light gray, not sticky, and tougher than ordinary guayule. We still have samples of the first batch, prepared in July 1944. Although no antioxidant has been added other than the Agerite White used in milling, this rubber has shown no tendency to soften or liquefy. Exposure to a temperature of 70° C. for 48 hours in the Geer oven fails to make this rubber flow, although ordinary guayule rubber becomes almost liquid with this treatment. The rubber deresinated with acetic acid can be handled on the compounding mill as easily as smoked sheet. It does not stick to the rollers objectionably and is very easy to process. The properties of the cured rubber are given in the next section.

To deresinate the rubber with acetic acid, it is first dried on screens in the ordinary way. The dried sheets are porous like rubber sponge. If the sheets are carefully peeled from the drying screens, the porosity is not lost, and it seems to be an important factor in successful deresination. The sheets are stacked in crocks, separated by layers of filter paper, and covered with glacial acetic acid. The acetic acid is changed occasionally. After extraction, the rubber is washed in running water until no odor of acid remains, and dried. This rubber still contains 2.5 to 4.5% acetone solubles (depending on the length of extraction and the thickness of the sheets extracted), 1.5% acetone-benzene insolubles, and more than 90% brominatable benzene solubles. The loss in weight due to deresination is 17 to 19%.

The acetic acid is used repeatedly so that it becomes quite dark. The acid that has been used longest contains, presumably, a concentrate of the substances causing deterioration. If it is diluted with equal parts of water, a cloudy yellow precipitate appears. This floats to the surface after standing, and leaves a clear colorless layer of acetic acid and water. The oily precipitate can be filtered off or taken up in ether. If the precipitate is separated by filtration and exposed to air, it deteriorates rapidly, and the stages of deterioration are closely similar to the course of deterioration of resinous guayule rubber. Attempts are being made to identify the deterioration of guayule rubber with some fraction or fractions contained in this extract.

Whether or not acetic acid deresination proves to be practicable on a commercial scale, the results described here demonstrate the possibility of preparing from guayule a crude rubber which is free from tendency to liquefy.

CURING AND PHYSICAL TESTING

For physical testing, 400-gram samples of crude rubber were compounded on a laboratory mill equipped with 6-inch-diameter rollers, following A.S.T.M. procedure. The temperature of the rollers was 130–140° F. The compounded sheets were allowed to rest 24 hours before curing. Cures were made in a four-cavity A.S.T.M. mold; each cavity was 6 inches square and 0.075 inch deep. Curing temperature was 257° F. (20 pounds steam), checked from time to time by a mercury thermometer inserted in a pool of mercury in a steel plate between the plattens of the press. The cured slabs rested 24 hours before samples were cut for testing modulus at 600% elongation, ultimate elongation, and tensile strength at break. Aging tests were made by exposing samples to rapid air circulation in the Geer oven at 100° C. for 24 hours.

No one compounding formula has been accepted as standard in studying the physical properties of guayule rubber. Spence and Boone (*15*) used a pure gum formula containing diphenylguanidine (DPG) as the only accelerator. Hauser and leBeau (*6*) used formulas containing a combination of mercaptobenzothiazole (Captax) and DPG. Morris *et al.* (*13*) tried out a number of accelerator combinations and reported that dibenzothiazyl disulfide together with zinc dimethyl dithiocarbamate gave the best all-round characteristics for guayule. Hauser and leBeau (*7*) showed that the acetone solubles in guayule rubber influence the amounts of stearic acid and sulfur required to give satisfactory cure; since the quantity and character of acetone solubles may differ widely from one sample of guayule to another, it can hardly be expected that a single formula will be satisfactory for comparing different types of guayule and for comparing guayule with smoked sheet. Therefore, it seemed best to modify the formula in accordance with the requirements of the rubber, and in this way seek to give a more significant comparison of properties than could be achieved with any single formula.

We had neither time nor material for a thorough study of all the variables in even a simple pure-gum formula. The work of Hauser and leBeau clearly indicated the importance of accelerator and stearic acid in relation to guayule resin, and we confined our modifications of formulas almost entirely to these two factors. The sulfur requirement merits more attention than we have given it, especially in relation to aging, but in general we followed Hauser and leBeau in adhering to a concentration of 3 parts of sulfur per 100 rubber.

The pure gum formulas recommended by the A.C.S. Division of Rubber Chemistry for the testing of Hevea rubber (*14*) were used:

	A.C.S. I	A.C.S. II	B.A.I.C.
Rubber	100	100	100
Zinc oxide	6	6	6
Stearic acid	0.5	4.0	4.0
Sulfur	3.5	3.5	3.5
Captax	0.5	0.5	1.0

A.C.S. formula I is for testing good grades of smoked sheet, and the formula II is for wild and slow-curing rubbers. Formula I does not give a satisfactory cure with any guayule rubber. Formula II has been extensively used by the U. S. Forest Service Emergency Rubber Project at Salinas for testing guayule, but most of the rubber tested contained about 0.5% Tonox as a stiffener and preservative. Tonox acts as a secondary accelerator, enhances the activity of the Captax, and therefore constitutes a modification of formula II which should not be overlooked. Guayule rubber which contains no Tonox gives a soft and unsatisfactory cure with formula II. For rubber without Tonox the Emergency Rubber Project doubled the amount of Captax in formula II and called this the B.A.I.C. formula.

Table VIII. Comparison of Mexican, Salinas, and Miniature Jordan Rubber, on Formula A

Source of Crude Rubber	Curing Time, Min.	Before Aging: Elongation at break, %	Before Aging: Modulus at 600%, lb./sq. in.	Before Aging: Tensile at break, lb./sq. in.	After Aging: Elongation at break, %	After Aging: Tensile at break, lb./sq. in.	Loss in tensile, %
E.R.P., Salinas factory, Texas shrub (Tonox)	28	875	635	2805	735	2140	56
	35	830	840	3225	665	1300	60
	40	815	870	3105	665	1260	59
	45	770	960	2830	650	1340	53
	60	780	1143	3130	635	1465	53
	80	770	1125	3125	610	1300	58
E.R.P., Salinas factory, local cultivated shrub. Tonox painted on bale	20	790	1120	3560	700	1755	51
	30	790	1315	3715	990	1580	59
	45	745	1527	3633	1300	1775	51
	60	695	1477	3280	1450	1665	50
Continental Mexican Rubber Co., Pedros unit	28	810	765	2890	655	1795	38
	35	820	910	3125	630	1645	47
	40	800	835	2940	600	1520	39
	45	790	920	2950	580	1430	51
	60	780	900	2810	580	1460	48
	80	765	925	2855	580	1670	41
Miniature Jordan, raw shrub	35	766	1066	3176	550	2100	34
	45	780	1240	3460	550	1910	45
	60	710	1920	3480	560	1935	44
	80	710	1250	3280	630	2615	20
Miniature Jordan, caustic-cooked shrub	30	795	900	3445	560	1715	50
	40	775	1150	3285	570	1965	40
	50	785	1140	3590	580	2260	37
	60	750	1225	3280	635	2800	15
	75	730	1290	3130	620	2420	23

TABLE IX. EFFECT OF STEARIC ACID CONCENTRATION ON AGING RESISTANCE OF RUBBER FROM CAUSTIC-COOKED SHRUB

		Before Aging			After Aging		
	Curing Time, Min.	Elongation at break, %	Modulus at 600%, lb./sq. in.	Tensile at break, lb./sq. in.	Elongation at break, %	Tensile at break, lb./sq. in.	Loss in tensile, %
Formula A, 3 parts stearic acid	25	850	445	2630	650	1917	27
	35	815	650	2895	660	2540	12
	40	815	710	3050	...	..	..
	50	820	630	2855	650	2113	26
	60	790	720	2635	...	..	..
	90	780	770	2690	690	2280	15
Formula B, 2 parts stearic acid	25	850	495	2790	...	..	..
	40	830	600	3020	700	2255	25
	60	780	670	2540	760	2665	−5[a]
	75	790	670	2820	760	2790	1.1
	90	795	640	2795	750	2320	17

[a] A negative value for loss in tensile indicates a gain.

Table VII compares various samples of guayule rubber on the B.A.I.C. formula with formula II used for Salinas rubber which contained Tonox. The high elongation and low modulus characteristic of guayule rubber are evident. The Mexican rubber is inferior to the others in every property tested. The Salinas rubber has the highest modulus, probably because of the presence of Tonox and consequent better cure. In resistance to Geer oven aging, the Salinas and Mexican rubbers were markedly inferior to the rubber extracted in miniature Jordans from both raw and caustic-cooked shrub.

Members of the Product Control division of the Los Angeles tire plant, U. S. Rubber Company, where the tests were made, judged all four of these vulcanizates, including the Tonox-treated rubber from the Salinas factory, to be soft and incompletely cured. Exploratory tests showed that less sulfur and stearic acid, together with a little added DPG, gave more satisfactory cure. Table VIII compares these four rubbers on a formula used for a large number of physical tests, which has proved superior to the A.C.S. II or B.A.I.C. This was called formula A, later modified to formula B:

	Formula A	Formula B
Rubber	100	100
Zinc oxide	5	5
Sulfur	3	3
Stearic acid	3	2
Captax	1	1
DPG	0.5	0.5

In the case of the Tonox-treated Salinas rubber, the Captax and DPG were cut to 0.5 and 0.25 part, respectively, to compensate for the accelerating effect of Tonox. A second sample of Salinas factory rubber, from a batch preserved with JZF instead of Tonox is included. In this case 1 part Captax and 0.5 part DPG were used, to correspond with tests on the other rubbers without Tonox; but it was later found that the exterior of the bale had been painted with a Tonox solution, so that an unknown amount of tonox was included. This probably accounts for the very rapid curing of the sample.

Table VIII shows that the rubber extracted in miniature Jordans, both from raw and cooked shrub, is superior to the Mexican rubber, and approximately equal to the Salinas rubber in tensile strength. The Jordan rubber is definitely superior in resistance to Geer oven aging. Table IX shows that the aging resistance of the rubber from caustic-cooked shrub can be further improved by using less stearic acid. The rubber was extracted in the 20-horsepower Claflin-type Jordan operated at Salinas. This rubber was tested on formulas A and B, providing 3 parts and 2 parts of stearic acid, respectively. The marked effect of stearic acid on Geer oven aging appears to be a peculiarity of guayule rubber. Smoked sheet does not show this response (Table XI).

It was suggested that the caustic cook might result in the presence of alkali in the finished rubber, and that the alkali might cause poor aging of the vulcanizates. The figures for effect of Geer oven aging shown in the preceding tables do not confirm this suggestion. In most cases the aging resistance of the rubber from caustic-cooked shrub is remarkably good, especially considering that no preservative was added during compounding. The crude rubber had been protected against softening by addition of Agerite White to the mill charge during extraction; however, separate tests have shown that Agerite White (0.5 part per 100 rubber) is without appreciable effect on the rate of cure and Geer oven aging of the cured samples, so the observed aging resistance is to be interpreted as a quality of the rubber itself. Tests were made to determine if incomplete washing of the cooked chips would result in poor aging resistance of the vulcanizates, but the results were negative. Longer washing of the cooked chips gave no appreciable advantage over a short rinse.

The possibility remains that the caustic cook damages the rubber in some way, but that the damage is concealed by the superiority of the caustic-cooked rubber in other respects. If the caustic cook could be avoided entirely, and its advantages achieved by some other means, the rubber might possibly show other advantages which are not obvious because of damage from the caustic cook.

TABLE X. COMPARISON OF FORMULAS FOR COMPOUNDING GUAYULE RUBBER DERESINATED WITH ACETIC ACID

(Base formula: 100 parts rubber, 5 zinc oxide, 3 sulfur)

		Before Aging			After Aging		
Variables in Formula	Curing Time, Min.	Elongation at break, %	Modulus at 600%, lb./sq. in.	Tensile at break, lb./sq. in.	Elongation at break, %	Tensile at break, lb./sq. in.	Loss in tensile, %
Stearic 2, Captax 1, DPG 0.5	30	725	..	5020	...	..	..
	40	685	..	4550	...	..	..
Stearic 1, Captax 0.5, DPG 0.1	45	920	355	2500	790	3030	−21[a]
	60	890	530	3120	750	2780	11
	90	865	490	2770	710	2090	24
	120	855	560	2895	690	1740	40
Stearic 1, Captax 0.8, DPG 0.2	20	830	760	3080	670	2750	11
	30	770	1170	3500	665	3305	6
	60	750	1530	3750	620	2560	32
Stearic 2, Captax 0.8, DPG 0.2	10	950	210	1515	...	..	..
	15	815	745	3190	480	745	69
	20	775	1205	3670	...	..	..
	30	745	1880	3960	375	820	79
	50	720	2090	3950	315	420	89
	80	685	2055	3500	355	590	83
Stearic 2, Captax 0.60, DPG 0.15	20	880	400	2050	355	285	87
	30	800	770	3025	310	275	91
	40	780	1090	3260	...	..	..
	50	760	1275	3470	260	255	93
	65	755	1320	3400	...	..	..
	80	765	1275	3415	285	280	92

[a] A negative loss in tensile indicates a gain.

These tests on rubber extracted in Jordans from raw and from caustic-cooked shrub show that resiniferous guayule rubber can be compounded to give pure-gum tensiles up to about 3500 pounds per square inch and reasonably good resistance to aging in the Geer oven. Compared with samples of guayule rubber extracted in the conventional pebble mills in Mexico and at Salinas, the Jordan-extracted rubber shows definite superiority. A characteristic common to all the guayule rubber tested is that Captax and DPG gave good cures, but much more accelerator was required than is ordinarily provided in formulas for smoked sheet.

The rubber prepared by deresination with acetic acid is quite different from the resinous rubber and, in some respects, is more similar to smoked sheet. The first samples were compounded on formula B, which was found to give more acceleration than necessary. A series of formulas with less acceleration were tried, in order to find the curing requirements, and comparisons were made with smoked sheet. Table X shows the results obtained with acid-deresinated rubber compounded in various ways, beginning with formula B. The remarkably

Table XI. Effect of Reduced Stearic Acid Content on Aging Resistance

		Before Aging			After Aging		
Stearic Acid per 100 Parts Rubber	Curing Time, Min.	Elongation at break, %	Modulus at 600%, lb./sq. in.	Tensile at break, lb./sq. in.	Elongation at break, %	Tensile at break, lb./sq. in.	Loss in tensile, %
		Guayule Rubber					
1.0	40	800	1050	3780	625	2265	40
	50	780	1160	3550	550	1650	53.5
	65	750	1180	3350	565	2100	37.3
0.5	40	810	710	3040	705	2475	30.7
	50	810	780	3155	735	2855	9.5
	65	800	810	3135	715	2620	16.4
		Smoked Sheet					
1.0	30	725	2155	4245	235	280	95
	50	685	2510	4025	200	220	95
	75	660	2490	3550	215	250	93
0.5	30	735	1990	4250	300	370	92
	50	710	2370	4245	265	425	90
	75	670	2460	4080	235	410	90

Table XII. Results of Physical Tests on No. 1 Smoked Sheet

(Base formula: 100 parts rubber, 5 parts zinc oxide, 2 parts stearic acid, 3 parts sulfur)

	Before Aging			After Aging		
Curing Time, Min.	Elongation at %	Modulus at 600%, lb./sq. in.	Tensile at break, lb./sq. in.	Elongation at break, %	Tensile at break, lb./sq. in.	Loss in tensile %
			Captax 0.60, DPG 0.15			
20	760	1320	3530	250	330	91
30	715	2190	4060	...	..	....
40	680	2580	3810	...	..	....
50	690	2855	3990	150	205	97
65	630	2700	3115	...	..	...
80	655	2640	3390	150	165	95
			Captax 0.8			
20	875	440	2320	...	..	....
30	815	760	2710	665	3595	−33[a]
50	765	1135	3150	615	3190	− 1.3
80	745	1360	3385	610	3005	11
120	720	1405	3100	400	950	66

[a] A negative loss in tensile indicates a gain.

high tensile of 5000 pounds per square inch is superior to any value reported for guayule rubber deresinated by other methods, and is definitely above the tensiles ordinarily obtainable with smoked sheet, even when DPG is used in addition to Captax.

Formula B gives too little elongation, and provides more acceleration than is required by this rubber. The next formula tried was A.C.S. I (standard for smoked sheet) with only 0.5 part Captax and no DPG. This failed to give a full cure, even after 120 minutes in the press. The 120-minute cure gave an elongation of 1100% without breaking, and a modulus of only 345 pounds per square inch at 1050% elongation. Since it was impossible to approach a satisfactory cure with the A.C.S. formula, formula B was used with various proportions of Captax, DPG, and stearic acid until a good cure was achieved. The next three batches in Table X show the modifications of formula B and the results obtained.

The next to last batch shows excellent tensile and modulus and satisfactory elongation, but the aging resistance is poor. It was first thought that this might be due to too much acceleration, so another batch (last in Table X) was tried with 0.6 part Captax and 0.15 DPG. The elongation is good, tensiles are lower, but aging resistance is still very poor. Table XI shows that this is because the stearic acid is too high. Although 2 parts of stearic acid were not too much for the resinous rubber, it is responsible for bad aging in the acid-deresinated rubber. Table XI, with the same formula as the last batch in Table X except for stearic acid, shows that aging resistance is better with 1 part of stearic acid and still better with 0.5 part, although in this case the modulus and tensile are appreciably reduced. More work is needed to establish the best combination of stearic acid and accelerators for this rubber.

Table XII shows some tests with smoked sheet, for comparison with those in Table X for the acid-extracted rubber. The first batch is on the same formula as the last batch of Table X. The smoked sheet gives lower elongation, but higher modulus and tensiles. Aging resistance is very poor and, in the case of the smoked sheet, cannot be improved by reducing the stearic acid, as shown by the lower half of Table XI. This formula obviously gives too much acceleration for smoked sheet. The second series of Table XII shows that if the DPG is omitted and the Captax content raised to 0.8 part, the elongation and aging resistance are greatly improved, but the maximum tensile falls below that of the acid-extracted rubber for corresponding tightness of cure.

These comparisons show that guayule rubber deresinated with acetic acid can be compounded and cured on formulas with less acceleration than is required for resinous guayule. Although the amount of acceleration required is much closer to the amount required for curing smoked sheet, the deresinated guayule still requires more acceleration than the smoked sheet. The fully cured guayule has physical properties and resistance to Geer oven aging equivalent to smoked sheet, and the guayule will stand more DPG than the smoked sheet without sacrifice of aging resistance, especially if the stearic acid is kept low. By increasing the DPG to the proportions used with resiniferous guayule, the tensile strength of the acid-deresinated guayule can be raised to 4000 and 5000 pounds per square inch, or above the range of tensiles ordinarily reported for smoked sheet.

ACKNOWLEDGMENT

The work reported in this communication was done at the California Institute of Technology and the Manzanar Relocation Center of the War Relocation Authority. Grateful acknowledgment is made to the War Relocation Authority and the U. S. Army for administrative support; to the U. S. Forest Service, the Earhart Foundation, the Kirkhill Rubber Company, and the U. S. Rubber Company for financial support; and to the Los Angeles Standard Rubber Company and U. S. Rubber Company for cooperation and advice in the compounding and physical testing of the rubber. Helpful cooperation was also received from many individuals, and special gratitude is due the evacuees at Manzanar, people of Japanese descent, who worked on the guayule project in many different capacities, often under very adverse conditions.

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Received May 20, 1946.

Copolymers of Butadiene with Halogenated Styrenes

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Some twenty halogenated styrenes have been copolymerized with butadiene in a typical emulsion polymerization formula. Based on laboratory evaluations of small samples, the quality of most of the copolymers was approximately equivalent to that of GR-S. There were indications that the copolymers containing 2,5-dichlorostyrene, 3,4-dichlorostyrene, and *p*-cyanostyrene were superior to GR-S in several respects.

IN SEEKING new copolymers of butadiene which might show rubberlike properties superior to those of the styrene copolymer, the authors were led by numerous reports on chlorostyrene derivatives (*4*) to make a study of halogenated styrenes. The chlorostyrenes are potentially available in quantity and should be reasonably cheap. The present work was undertaken to obtain fundamental information on the copolymerization of these halogenated styrenes with butadiene as well as to learn what relative advantages and disadvantages the various copolymers would have as substitutes for rubber. In addition to various halogenated styrenes the copolymerization of *p*-cyanostyrene and some derivatives is included in this report.

The methods of preparation of the new halogenated styrenes have been reported elsewhere (*13*). The known compounds were made by the standard methods. The mixed mono-, di-, tri-, and tetrachlorostyrenes were furnished by the Electrochemical Department of E. I. du Pont de Nemours & Company, Inc. The 2,5-dichlorostyrene was furnished by the Monsanto Chemical Company.

POLYMERIZATION

Most of the monomers were charged at a 25:75 weight ratio with butadiene in a typical emulsion polymerization recipe and polymerized as nearly as possible to 77% conversion. A few of the more promising styrenes were also tested at a 15:85 ratio and at a ratio of x:75, where x is the molar equivalent of 25 parts of styrene. Halogen analysis showed to what extent the styrene had entered the copolymer.

Table I shows that some of the monohalogenated styrene copolymerizations went at a slightly slower rate than did the control. Thus *o*- and *p*-chlorostyrene, *m*- and *p*-fluorostyrene, and *m*-bromostyrene gave a slower over-all rate; on the other hand, *m*-chlorostyrene, the mixed chlorostyrenes, and *o*- and *p*-bromostyrene gave a normal conversion in 11 hours. It is possible that traces of inhibiting impurities in the monomers were responsible for some of these anomalous results. Among the dichlorostyrenes the 2,3-, 2,4-, and mixed isomers had a normal rate; the 2,6-isomer slowed the polymerization considerably; and the 2,5- and 3,4-isomers (on the basis of data not shown) copolymerized somewhat more rapidly than styrene. The tri- and tetrachlorostyrenes gave progressively slower polymerization rates. Very little pentachlorostyrene appeared in the copolymer. *p*-Cyanostyrene copolymerized normally. α-Chlorostyrene caused the emulsion to break, perhaps because the halogen alpha to the ring was no longer protected by its position on an olefinic carbon atom once polymerization had begun, so that it was hydrolyzed to give hydrochloric acid; in any event, the breaking of the emulsion prevented any appreciable polymer formation.

The ratio at which the two monomers enter a copolymer is quite significant in relation to the properties of the product, for it determines whether there is homogeneity of structure from one molecule to the next. Wall (*15*) has defined the value α as the exponent in the equation:

$$\frac{n_x}{n_x^0} = \left(\frac{n_y}{n_y^0}\right)^\alpha$$

where n_x and n_y are the number of unpolymerized molecules of two monomers, x and y, after a given time of polymerization has elapsed, when n_x^0 and n_y^0 molecules of the two monomers were present at the beginning of the reaction. Wall points out that only in an ideal copolymerization, where α is unity, do the mono-

TABLE I. EMULSION COPOLYMERIZATION OF BUTADIENE AND HALOGENATED STYRENES AT 50° C.

Comonomer	Wt. Ratio, Butadiene: Styrene	Time, Hr.	Conversion, %	Benzene Soly., %	[η]	Halogenated Styrene, %
Styrene	75:25	11	77	98	2.12	..
o-Chlorostyrene	75:25	11	66	96	1.09	23.3
	75:33.5	19	74	100	2.06	29.7
	85:15	14½	72	92	1.89	14.2
m-Chlorostyrene	75:25	11	78	94	1.82	25.0
p-Chlorostyrene	75:33.7	12	67	100	1.64	26.7
Mixed chlorostyrenes	75:25	11½	77	95	1.55	25.8
α-Chlorostyrene	75:25	36	0	...	..	..
2,3-Dichlorostyrene	75:25	11½	75	94	1.16	27.5
2,4-Dichlorostyrene	75:25	12	76	95	1.65	23.0
2,5-Dichlorostyrene[a]	75:25	11	80	99	1.52	28.2
	75:41.6	12	89	99	2.05	38.1
2,6-Dichlorostyrene	75:25	16	72	90	1.92	14.3
3,4-Dichlorostyrene[a]	75:25	12	80	93	1.78	27.3
	75:41.6	12	81	100	1.89	36.2
	85:15	12	77	94	2.06	16.4
3,5-Dichlorostyrene	75:25	9½	75	99	1.24	27.1
Mixed dichlorostyrenes	75:25	11⅔	75	96	1.52	26.2
Mixed trichlorostyrenes	75:25	14½	71	93	1.60	20.0
Mixed tetrachlorostyrenes	75:25	37	80	46	1.13	24.1
Pentachlorostyrene[a]	75:25	12	65	100	Low	3.9
m-Fluorostyrene	75:25	12	70	96	1.44	24.3
p-Fluorostyrene	75:25	14	71	96	2.01	[b]
o-Bromostyrene	75:25	11½	79	99	1.63	26.8
m-Bromostyrene	75:25	13	75	92	1.55	26.6
p-Bromostyrene	75:25	10	74	92	1.19	23.4
p-Cyanostyrene	75:25	10½	72	97	1.34	26.1
p-Carboxystyrene[a]	75:25	22	41	13	0.44	[b]
p-Carboxystyrene (Na salt)[a]	75:25	20	100	12	0.47	[b]
p-Carbomethoxystyrene[a]	81:19	15	59	100	1.33	[b]

[a] Not evaluated.
[b] Not analyzed.

mers enter the polymer in the ratio at which they are charged, but that for monomer pairs having α values between $^1/_2$ and 2 the homogeneity of monomer distribution throughout the polymer chains is reasonably great. Table I shows the fractions of the halogenated styrenes found in the copolymers by halogen analysis (except for the fluoro- and cyanostyrenes which were analyzed by other means); from these fractions the α values have been calculated (Table II). Only those for 2,6-dichlorostyrene and pentachlorostyrene with butadiene do not fall within the limits proposed. The symbol y has been assigned to butadiene in these calculations, in order that a value of α greater than unity will indicate that the substituted styrene enters the polymer faster than does the butadiene.

TABLE II. VALUES OF α FOR EMULSION COPOLYMERIZATION OF BUTADIENE AND HALOGENATED STYRENES, 50° C., AS FOUND AT 75:25 CHARGING RATIO AND CONVERSIONS SHOWN IN TABLE I

Substituted Styrene	α
Styrene (*14*)	0.61
o-Chlorostyrene	0.85
m-Chlorostyrene	1.0
Mixed monochlorostyrenes	1.1
2,3-Dichlorostyrene	1.3
2,4-Dichlorostyrene	0.80
2,5-Dichlorostyrene	1.6
2,6-Dichlorostyrene	0.31
3,4-Dichlorostyrene	1.4
3,5-Dichlorostyrene	1.3
Mixed dichlorostyrenes	1.2
Mixed trichlorostyrenes	0.59
Mixed tetrachlorostyrenes	0.89
Pentachlorostyrene	Very low
m-Fluorostyrene	0.93
o-Bromostyrene	1.3
m-Bromostyrene	1.2
p-Bromostyrene	0.84
p-Cyanostyrene	1.1

It is evident that there is no correlation between the over-all polymerization rate and the rate at which the comonomer enters, except that 2,6-dichlorostyrene and pentachlorostyrene both have abnormally low rates and low α values. Of the styrenes examined, the *o*- and *m*-bromo- and all the dichlorostyrenes except the 2,4- and 2,6-isomers enter the copolymer most rapidly, in all cases faster than the butadiene. With the dichlorostyrenes the quality of the rubber seems to be directly related to the relative rate of entry, for the 2,5- and 3,4-isomers give the best copolymers and the 2,4- and 2,6-isomers the poorest.

MONOMERS. The mixed mono-, di-, tri-, and tetrachlorostyrenes were furnished by the Electrochemical Department of E. I. du Pont de Nemours & Company, Inc. The following data accompanied these samples:

Monochlorostyrenes	
Chlorostyrene content (Br_2 titration), %	97.5
d_4^{15}	1.099
n_D^{25}	1.5638
B.p. around 2 mm., ° C.	38.0–42.0
Dichlorostyrenes	
d_4^{15}	1.285
n_D^{20}	1.5812
B.p. at 2 mm., ° C.	67–70
Stabilizers	*p-tert*-amylphenol and diphenylamine, 0.1% each
Trichlorostyrenes	
Trichlorostyrene content (Br_2 titration), %	88
d_4^{15}	1.408
n_D^{20}	1.5951
B.p. at 2 mm., ° C.	105–110
Stabilizer	Hydroquinone
Tetrachlorostyrene	
d_4^{15}	1.509
n_D^{20}	1.6066
B.p. at 3 mm., ° C.	126–129
Stabilizers	*p-tert*-amylphenol and diphenylamine, 0.1% each

The mono- and trichlorostyrenes were used as received. The di- and tetrachlorostyrenes were washed with 5% sodium hydroxide and water, dried, and distilled at reduced pressure in a nitrogen atmosphere.

2, 5-Dichlorostyrene was furnished by the Monsanto Chemical Company. It was washed and dried before use. The methods of preparation of the monohalostyrenes have been reported by Brooks (*2*) and Marvel and co-workers (*3*). The transformation of styrene to α-chlorostyrene was made according to the directions of Biltz (*1*) and of Emerson and Agnew (*5*). Pentachlorostyrene was prepared from ethylbenzene by methods found in the patent literature (*11*). *p*-Cyano-, *p*-carbomethoxy-, and *p*-carboxystyrenes have been described (*12*).

The physical constants of the styrenes used in this study are given in Table III.

Butadiene was the special purity grade supplied by the Phillips Petroleum Company; it was passed over sodium hydroxide pellets and condensed in a dry-ice trap.

POLYMERIZATION. The polymerizations were carried out in 4-ounce screw-cap bottles (or, in a few instances, in 28-ounce crown-cap bottles) whose caps were fitted with rubber disk gaskets lined with heavy tin foil. The charge for a 75:25 run was as follows in parts by weight:

Butadiene	75.0 parts
Substituted styrene	25.0
Soap (Procter and Gamble silica-free flakes)	5.0
Water	180.0
Potassium persulfate	0.30
Dodecyl mercaptan, pure	0.35

The soap was dissolved in 170 parts of water and charged into the bottle with 10 parts of freshly prepared 3% potassium persulfate solution. The substituted styrene, containing the proper proportion of dodecyl mercaptan, was added, and the mixture was shaken and thoroughly chilled in ice water. Slightly more than 75 parts of butadiene was poured into the weighed bottle, and the excess was allowed to boil off to remove air before the cap was put in place. The bottles were rotated end over end for the specified time in a bath at 50° ± 1° C.

TABLE III. PHYSICAL CONSTANTS OF THE HALOGENATED STYRENES

	B.p., ° C.	Pressure, Mm.	n_D^{20}
o-Chlorostyrene	67–9	3–3.5	1.5638
m-Chlorostyrene	60–1	3	1.5620
p-Chlorostyrene	65	6–7	1.5648
α-Chlorostyrene	75–6	17	1.5612
2,3-Dichlorostyrene	93–5	4–5	1.5834
2,4-Dichlorostyrene	81	6	1.5828
2,6-Dichlorostyrene	70–2	4–5	1.5754
3,4-Dichlorostyrene	84	4	1.5750
3,5-Dichlorostyrene	59	1	1.5745 (25°)
Pentachlorostyrene	140–2	0.5	1.5965
m-Fluorostyrene	30–2	2	1.5170
p-Fluorostyrene	57–9	13–14	1.5156
o-Bromostyrene	64–5	3	1.5914
m-Bromostyrene	74–5	3	1.5903
p-Bromostyrene	88	12	1.5950 (19°)
p-Cyanostyrene	102–4	9	1.5781

The cooled latex was mixed with 25 parts of a 10% suspension of phenyl-β-naphthylamine in soap solution and coagulated with a saturated sodium chloride solution containing 2.3% of concentrated sulfuric acid. The rubber was washed repeatedly with water, cut or broken into small pieces, and dried overnight at 70–80° C. in a vacuum oven at 85 mm. In calculating conversion the residual fatty acid and antioxidant were taken into account. It was assumed, perhaps without justification, that the unpolymerized styrene would be removed by the vacuum drying.

ANALYSIS. Samples were prepared for halogen analysis by twice dissolving the polymer in benzene and precipitating it with methanol, then drying in the vacuum oven. Fluorostyrene content was determined by comparison of the ultraviolet ab-

Table IV. Analyses[a] of 75:25 Copolymers

Comonomer	Halogen Found, %	Carbon, %		Hydrogen, %		Ash, %	Total
		Calcd.[b]	Found	Calcd.[b]	Found		
o-Chlorostyrene	5.97	84.3	82.66	9.7	9.87	0.9	99.4
m-Chlorostyrene	6.40	84.0	83.73	9.6	9.71	...	99.8
2,3-Dichlorostyrene	11.3	79.8	79.33	9.1	9.36	...	100.0
2,4-Dichlorostyrene	9.44	81.2	81.16	9.4	9.35	...	100.0
2,5-Dichlorostyrene	11.58	79.4	79.61	9.0	8.90	...	100.1
2,6-Dichlorostyrene	5.85	84.1	83.38	10.0	10.04	...	99.3
3,4-Dichlorostyrene	11.2	79.6	77.90	9.0	9.10	...	98.2
3,5-Dichlorostyrene	11.1	79.8	77.94	9.0	8.65	...	97.7
o-Bromostyrene	11.7	79.2	79.25	9.1	9.23	...	100.2
m-Bromostyrene	11.6	79.3	79.58	9.2	9.42	...	100.6
p-Bromostyrene	10.2	80.4	78.52	9.4	9.08	...	97.8
p-Cyanostyrene	2.83[c]	87.6	86.12	9.6	9.82	...	98.8

[a] These microanalyses were carried out by H. S. Clark of the Illinois State Geological Survey.

[b] Calculated from halogen content.

[c] Per cent nitrogen.

sorption spectra of the copolymer and of pure polyfluorostyrene (*9*).

The carbon, hydrogen, and halogen analyses (Table IV) indicated that a few of the samples contained from 1 to 4% of methanol; it is likely that an even larger residue of benzene remained, for benzene constituted three fourths of the purifying solvent, yet it would not affect the carbon-hydrogen ratio noticeably. It may be concluded that the true halogen contents, and consequently the proportions of halostyrenes, were higher than they appeared to be in these samples. This does not alter the fact that most of the substituted styrenes enter the copolymer more rapidly in relation to butadiene than does styrene.

Characterization of Polymer. The solubility of the material was normally determined by allowing a 0.4-gram sample, cut into small pieces, to stand 48 hours in 100 ml. of dry benzene in a closed bottle at room temperature (*7*). The liquid was decanted and filtered through a 100-mesh screen to remove gel; a 5-ml. aliquot was pipetted into a tared aluminum pan. When the solvent had evaporated, the pan was dried 2 hours in a circulating air oven at 70–80° C. and weighed.

The gel-free solution was diluted with 2 parts of dry benzene, and its flow time was measured in an Ostwald viscometer at 25° C. From this value and the flow time for dry benzene the intrinsic viscosity, $[\eta]$, was computed by the following formula:

$$[\eta] = \frac{\ln t - \ln t_0}{c}$$

where t, t_0 = flow times of soln. and solvent

C = concn. of polymer, grams/100 ml. soln. (*7*)

EVALUATION

The copolymers were evaluated in the following tread-type recipe, in parts by weight:

Copolymer	100.0
EPC carbon black	50.0
Zinc oxide	5.0
Stearic acid	1.5
Paraflux[a]	5.0
Santocure	1.2

Sulfur varied, when sample size permitted, to give optimum physical properties

[a] A petroleum-type softener supplied by C. P. Hall Company.

The behavior of the rubber on the mill was noted in each case. Although the Mooney viscosity values varied widely, the mill behavior was in no case markedly different from that which would have been experienced with butadiene-styrene copolymers made to the same viscosity.

Stress-strain properties were determined by the Goodrich microtechnique (*6*). Hysteresis temperature rise at 212° F. was determined using the Goodrich flexometer (*10*) with a 55-pound load and a $17^1/_2\%$ stroke. Flexing results are reported in terms of the number of flexures required for an initiated crack to grow to an arbitrary rating of eight (about 75% of a 1-inch width). A De Mattia machine was used, operating at 300 cycles per minute with a stroke of $2^1/_4$ inches in a room maintained at 82° F. and 45% relative humidity.

Quality index (*8*) is defined as the ratio of the observed flexures to the flexures of a similar GR-S tread stock having a hysteresis temperature rise equal to the observed hysteresis temperature rise. The relation between flexing and hysteresis temperature rise for a GR-S tread stock compounded with EPC black and for the particular test conditions used here is expressed by the following equation (*8*):

$$\log_{10} \text{flexures} = 0.0126\Delta T + 4.28$$

where ΔT is the hysteresis temperature rise above 212° F. as determined using the Goodrich flexometer with a 55-pound load and a $17^1/_2\%$ stroke. The significance of the quality index has been discussed by Juve (*8*).

On the basis of the test results obtained (summarized in Table V) the following conclusions were reached:

1. In general, copolymers of the monohalogenated styrenes are equal in quality to GR-S. However, those of *o*-chlorostyrene, both 75–25 and 75–33.5, appear to be somewhat superior to GR-S, and those of the *m*-chlorostyrene and the *m*-fluorostyrene may possibly be superior.

2. Copolymers of the dichlorostyrenes, with the exception of the 2,5- and 3,4-, give quality indexes about equal to that of GR-S. These two isomers, particularly the latter, show an appreciable improvement. Since the rate of entry of these materials into the polymer during polymerization is greater than that of styrene, the combined halogenated styrene content is greater than that of the styrene in GR-S. Comparison should, therefore, be made with butadiene-styrene copolymers having an equivalent styrene content, since an increased styrene content results in an improvement in quality index (*8*).

3. The mixed tri- and tetrachlorostyrenes are both definitely inferior to styrene.

4. The *p*-cyanostyrene copolymer gave a high quality index and good stress-strain properties. However, from its composition it would be anticipated that its low temperature properties would be poor.

These conclusions are based on the results obtained in copolymers made in the particular recipe given and may or may not apply to copolymers made in other polymerization systems. In several cases the Mooney viscosity of the copolymer differed widely from that of standard GR-S. Had it been possible to adjust the viscosity of the product to that of standard GR-S, the results and conclusions might have been somewhat different.

SUMMARY

Butadiene has been copolymerized in a typical emulsion polymerization recipe with each of the monochloro, monobromo-, monofluoro-, and dichlorostyrenes, with the mixed mono-, di-, tri-, tetra-, and pentachlorostyrenes, and with *p*-cyanostyrene and several of its derivatives. While 2,5- and 3,4-dichlorostyrene copolymerized with butadiene more rapidly than does styrene itself, 2,6-dichlorostyrene and the mixed tri-, tetra-, and pentachlorostyrenes copolymerized at a slower rate than did the control. 2,5-Dichlorostyrene entered the copolymer much more rapidly, and 2,6-dichlorostyrene and pentachlorostyrene much more slowly, then does styrene itself. The mono- and dihalogenated styrenes in general gave copolymers whose quality indexes were about equal to that of GR-S; *o*-chlorostyrene, 2,5-

TABLE V. EVALUATION OF COPOLYMERS

Comonomer	Ratio, Butadiene: Comonomer	Mooney Viscosity[a]	Sulfur, Parts	Cure, Min. at 280° F.	300% Modulus, Lb./Sq. In.	Tensile, Lb./Sq. In.	Elongation, %	Hysteresis Temp. Rise, ° F.	Flexing[b]	Durometer Hardness	Quality Index (8)
No. 1 *o*-chlorostyrene	75:25	..	1.75	75	600	2750	685	105	1,280,000-8	..	3.3
				150	750	2600	640	70	730,000-8	..	5.1
GR-S control[c]	....	..	1.75	75	550	2700	740	45[d]	350,000 8	..	..
				150	600	3150	750	42[d]	420,000-8	..	
No. 2 *o*-chlorostyrene	75:33.5	51	1.75	75	1090	3880	607	109	880,000-8	74	1.9
				150	1200	4140	586	56	760,000-8	67	7.8
GR-S control	....	..	..	75	910	3050	607	..	310,000-8	59	..
				150	940	3170	575	47	200,000-8	65	2.6
No. 3 *o*-chlorostyrene	85:15	59	2.0	60	700	3140	710	..	..	..	..
				75	890	3320	665	..	385,000-8	64	..
				150	..	..	..	76	160,000-8	64	0.92
GR-S control	....	..	..	60	550	2790	790	..	......	..	..
				75	760	3490	713	97	286,000-8	57	0.86
				150	950	3140	633	62	190,000-8	60	1.6
No. 4 *m*-chlorostyrene	75:25	..	2.0	45	500	2700	860				
				75	800	3300	760	..	2,000,000-3	..	..
				150	900	3800	720	122	2,000,000-6	..	3.0+
GR-S control	....	..	2.0	45	500	2700	825	..	......	.	..
				75	950	3500	745	63	480,000-8	..	4.0
				150	1100	3550	620	53	430,000-8	..	4.6
No. 5 *p*-chlorostyrene	75:33.7	..	..	30	600	2450	685	..	......	..	..
				45	950	2350	505	81	570,000-8	..	2.8
				75	1125	3000	550	..	......	..	..
GR-S control	....	..	2.0	45	400	2450	875	..	......	..	..
				75	600	3300	755	78	330,000-8	..	1.8
				150	950	3050	630	58	210,000-8	..	2.0
No. 6 mixed monochlorostyrenes	75:25	..	2.0	45	250	1850	1000	..	......	..	..
				75	650	3500	815	..	380,000-8	..	..
				150	1000	3500	670	44	230,000-8	..	3.3
GR-S control	....	..	2.0	45	200	1550	980	..	......	..	..
				75	600	3100	750	69	320,000-8	..	2.3
				150	900	3000	640	51	260,000-8	..	3.0
No. 7 *m*-fluorostyrene	75:25	..	1.75	45	700	2825	840	..	......	..	..
				75	1050	2700	700	110	2,000,000-2	..	4.2+
				150	1000	2200	550	..	......	..	..
GR-S control				Same as That under No. 5 *p*-Chlorostyrene							
No. 8 *p*-fluorostyrene	75:25	..	2.0	45	425	2725	795	..	......	..	..
				75	700	3400	710	77	400,000-8	..	2.2
				150	825	2800	550	57	270,000-8	..	2.7
GR-S control				Same as That under No. 5 *p*-Chlorostyrene							
No. 9 *o*-bromostyrene	75:25	..	1.75	75	1200	2850	525	60	320,000-8	..	2.9
				150	1500	2650	465	53	210,000-8	..	2.3
GR-S control	....	..	1.75	75	950	2800	575	57	410,000-8	..	4.1
				150	1300	3050	525	46	290,000-8	..	4.0
No. 10 *m*-bromostyrene	75:25	..	1.75	75	1400	2750	450	67	170,000-8	..	1.2
				150	1700	2700	410	51	170,000-8	..	2.0
GR-S control	....	..		Same as That under No. 1 *o*-Chlorostyrene							
No. 11 *p*-bromostyrene	75:25	..	2.0	45	250	2350	980	..	......	..	..
				75	725	2700	700	98	280,000-8	..	0.8
				150	925	3000	600	66	180,000-8	..	1.3
GR-S control	....	..		Same as That under No. 6 Mixed Monochlorostyrenes							
No. 12 2,3-dichlorostyrene	75:25	25	1.75	75	710	3700	715	71	260,000-8	60	1.7
				150	920	3790	655	51	250,000-8	62	3.0
GR-S control	....	..		Same as That under No. 2 *o*-Chlorostyrene							
No. 13 2,4-dichlorostyrene	75:25	..	2.0	45	450	2300	780	..	......	..	..
				75	750	2900	610	85	330,000-8	..	1.4
				150	1050	2850	530	58	180,000-8	..	1.7
GR-S control	....	..		Same as That under No. 5 *p*-Chlorostyrene							
No. 14 2,5-dichlorosytrene	75:41.6	..	1.75	45	1200	3400	635	..	......	..	..
				75	..	2900	475	99	1,450,000-8	..	4.2
				150	2000	3100	465	..	......	..	..
GR-S control	....	..		Same as That under No. 5 *p*-Chlorostyrene							
No. 15 2,6-dichlorostyrene	75:25	..	1.75	75	1200	2450	505	62	110,000-8	..	0.9
				150	1450	2050	390	56	100,000-8	..	1.0
GR-S control	....	..		Same as That under No. 9 *o*-Bromostyrene							
No. 16 3,4-dichlorostyrene	75:41.6	..	..	45	850	3275	610	83	1,950,000-8	..	9.2
				60	1175	3750	610	..	......	..	..
GR-S control	....	..		Same as That under No. 5 *p*-Chlorostyrene							
No. 17 3,4-dichlorostyrene	85:15	59	1.75	75	800	3540	674	86	300,000-8	63	1.3
				150	1000	3470	607	74	270,000-8	63	1.7
GR-S control	....	..		Same as That under No. 3 *o*-Chlorostyrene							
No. 18 3,5-dichlorostyrene	75:25	23	2.0	75	680	3300	733	98	1,560,000-8	63	4.8
				150	940	3300	627	83	750,000-8	67	3.5
GR-S control	....	..	2.0	75	740	3250	713	97	960,000-8	53	3.0
				150	940	3740	674	66	420,000-8	57	3.2
No. 19 mixed dichlorostyrenes	75:25	..	2.0	45	400	2500	.880	..	......	..	..
				75	800	3400	695	89	950,000-8	..	3.7
				150	1200	2800	480	73	320,000-8	..	2.0
GR-S control	....	..		Same as That under No. 4 *m*-Chlorostyrene							
No. 20 mixed trichlorostyrenes	75:25	..	1.75	75	550	2850	725	98	340,000-8	..	0.9
				150	675	3000	700	64	240,000-8	..	1.9
GR-S control	....	..		Same as That under No. 1 *o*-Chlorostyrene							
No. 21 mixed tetrachlorostyrenes	75:25	48	2.0	75	1030	2900	607	65	120,000-8	57	0.92
				150	1330	3150	513	56	70,000-8	61	0.71
GR-S control	....	45	2.0	75	950	3020	648	58	640,000-8	62	6.1
				150	1100	1990	433	50	330,000-8	63	4.0
No. 22 *p*-cyanostyrene	75:25	26	1.75	75	1120	3150	580	83	2,000,000-5	67	9.2+
				150	1180	3200	540	102	1,660,000-8	76	4.4
GR-S control	....	..		Same as That under No. 2 *o*-Chlorostyrene							

[a] Mooney value at end of 4-minute run using the large rotor at 212° F.

[b] Rating of crack length at the number of flexures shown. A rating of 1 means no crack and 10 is complete failure.

[c] With each experimental polymer or group of polymers a GR-S control was run. The values obtained for the control are shown in Table V along with those for the experimental polymer. Because of differences from time to time in the materials used and inadvertent differences in mixing, curing, and testing, conclusions as to the quality of the experimental polymers are based on its properties compared with the appropriate control.

[d] This control showed exceptionally low hysteresis.

and 3,4-dichlorostyrenes, and *p*-cyanostyrene all gave copolymers with quality indexes higher than that of GR-S. The mixed tri- and tetrachlorostyrenes gave copolymers of inferior quality.

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Received August 29, 1946. This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

Evaluation of Sodium-Catalyzed Copolymers of 1,3-Butadiene and Styrene

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The properties of tread-type vulcanizates of sodium-catalyzed butadiene-styrene copolymers have been found to differ considerably from those of similar vulcanizates of emulsion-polymerized butadiene-styrene copolymers of identical monomer composition. These differences provide a good basis for further work relating polymer structure to properties. Sodium butadiene:styrene copolymers were not so flexible at low temperatures as emulsion copolymers of the same composition; however, in processing quality and in balance of flex crack growth and hysteresis, the sodium copolymers exhibited real advantages. In general, the properties of sodium copolymers were comparable to those of emulsion copolymers of higher styrene content.

Sodium-catalyzed butadiene-styrene copolymers of monomer ratio 75 butadiene:25 styrene by weight were prepared at the University of Illinois (*5*). Evaluations were carried out simultaneously at The B. F. Goodrich Company and the United States Rubber Company. Preliminary studies indicated that the properties of the sodium copolymers were different in several respects from those of emulsion-polymerized copolymers of identical butadiene-styrene composition.

Evidences of differences in molecular structure have been reported (*5*) and undoubtedly result from different mechanisms of polymerization. The work reported here was carried out to determine the suitability of sodium-catalyzed butadiene-styrene copolymers as general-purpose synthetic rubbers, and to provide a background for studies relating structure of elastomeric materials to their physical behavior.

DESCRIPTION OF COPOLYMERS

The sodium-catalyzed copolymers evaluated in the two laboratories were all of 75 butadiene:25 styrene composition. The abbreviation S-BS, coined by the University of Illinois workers, is used hereafter to denote these copolymers.

The method of preparation of the samples which were evaluated followed either the "standard" method, the "interrupted" method, or the "increment addition of monomers" method as described by Marvel *et al.* (*5*).

The precise method of preparation of a particular sample is not given in the present report, since preliminary tests showed that, for equal intrinsic viscosity and benzene solubility, approximately equal results were obtained by the three methods of preparation.

Table I gives control data on the polymers tested. Each test sample is a blend of a number of experimental runs. Intrinsic viscosity and Mooney viscosity were determined on mill-massed blends. Gel determinations were made at the University of Illinois, and the range of solubilities for the different batches included in each test sample is reported.

The butadiene-styrene emulsion copolymers used as controls were from standard plant GR-S production. The emulsion

Table I. Control Data

Code	Intrinsic Viscosity	% Sol. in Benzene	Mooney Viscosity[c] at 212° F.,
S-BS I	4.9	90–100	79
S-BS II[a]	2.0	100	50
S-BS III	5.0	89–99	84
S-BS IV	3.7	89–100	98
30° C.–S-BS	4.6–5.9[b]	86–97	..
50° C.–S-BS	2.27–3.25[b]	89–100	62

[a] Polymer S-BS I refined by 15 passes on a cold tight mill.
[b] Represents range of intrinsic viscosities on polymers blended.
[c] Mooney viscosity at end of a 4-minute run using the large rotor.

system is persulfate-catalyzed, and the polymerization proceeds by means of a free radical mechanism. The ratio of the comonomers was 72 weight % butadiene : 28 weight % styrene in the feed and approximately 75 butadiene : 25 styrene by weight in the product. Intrinsic viscosities of the samples used varied but in all cases approximated 2.0; all samples had essentially complete solubility. Mooney viscosities varied in the range 45–55.

A high styrene emulsion copolymer, coded J-99, was prepared in the United States Rubber laboratory at 50° C., using the same type of polymerization GR-S recipe just described with the exception that the initial feed contained butadiene and styrene, respectively, in the weight ratio 40:60. Conversion was carried to 72% of monomer charge. Accurate Mooney viscosity could not be determined because of slipping. However, it was estimated to be in the range 50–60.

Another high styrene emulsion copolymer was prepared in the B. F. Goodrich laboratory at 50° C., in which the charging ratio of the monomers was 1 part butadiene to 1 part of styrene. The combined styrene in the finished copolymer was 47.90%. In addition, the modifier was adjusted to give a Mooney viscosity of 50 ± 5 at 77% conversion.

EXPERIMENTAL METHODS

The physical tests used in the evaluation work fall into four main types of classification: (*a*) processability, (*b*) stress-strain, (*c*) flex crack growth–hysteresis balance, and (*d*) low temperature flexibility. The following tread-type recipes, in parts by weight, were used in the two laboratories:

The B. F. Goodrich Company

Copolymer	100.00
EPC carbon black	50.00
Zinc oxide	5.00
Paraflux	5.00
Stearic acid	1.50
Santocure	1.20

Sulfur varied, when sample size permitted, to give optimum properties

United States Rubber Company

Copolymer	100.00
EPC carbon black	50.00
Zinc oxide	5.00
Bardol	5.00
Captax	1.50
Sulfur	2.00
BLE antioxidant	1.50

Evaluation tests were usually run on the crude copolymer. However, in some special cases (noted elsewhere in this paper), heat-treated and chemically softened copolymers were also evaluated.

Processability: Mill Compounding and Fabrication. Plasticity was measured by the method of Schultz and Bryant (*8*) and by the Mooney rotary disk plastometer (*6*). All Mooney viscosity measurements were made at 212° F. using the large rotor. Objective laboratory processing measurements were made to evaluate mill compounding and fabrication qualities by the methods of White, Ebers, and Shriver (*9*). The behavior of the rubber on cold milling was also noted. One large sample was mixed in an internal mixer maintained at 320° F.

Stress-Strain. Room temperature stress-strain properties were determined at the B. F. Goodrich laboratories using small dumbbell specimens (*1*). All other stress-strain measurements at both laboratories were made on standard dumbbell specimens. The instruments were not cross-calibrated, so determinations at the two laboratories are not necessarily comparable.

Flex Crack Growth–Hysteresis Balance. Hysteresis temperature rise was measured at the B. F. Goodrich laboratory as the temperature rise in °F. above 212° F. using the Goodrich flexometer (*4*) with a 55-pound load and a $17^{1}/_{2}$% stroke. Flexing results are reported by that laboratory in terms of the number of flexures required for an initial crack to go to an arbitrary rating of eight (about 75% of a 1-inch width). A De Mattia machine was used, operating at 300 cycles per minute with a stroke of $2^{1}/_{4}$ inches in a room maintained at 82° F. and 45% relative humidity. B. F. Goodrich data are reported as a quality index, which is defined as the ratio of the observed flexures to the flexures of a similar GR-S tread stock having a hysteresis temperature rise equal to the observed hysteresis temperature rise. The relation between flexing and hysteresis temperature rise for a GR-S tread stock compounded with EPC carbon black and for the particular test conditions used here is expressed by the following equation (*3*):

$$\log_{10} \text{flexures} = 0.0126\,\Delta T + 4.28$$

where ΔT is the hysteresis temperature rise above 212° F. as determined using the Goodrich flexometer with a 55-pound load and a $17^{1}/_{2}$% stroke.

The significance of the quality index has been discussed by Juve (*3*).

At the United States Rubber laboratories, cut growth was measured by flexing a De Mattia bend-flexing specimen with a circular groove through an 85° arc at 287 cycles per minute. A pin hole is placed in the center of the groove to start cut growth;

Table II. Processability Data from United States Rubber Company Laboratories

Code	S-BS I	S-BS II	S-BS IV	GR-S	J-99
Description	Sodium, 75:25	Sodium, 75:25	Sodium, 75:25	Emulsion, 72:28	Emulsion, 40:60
Brittle point, ° C.	−24	−24	−30	−65	−12
Initial viscosity (Mooney, large rotor, 4-minute run at 212° F.)	79	50	98	45	Slipped
Shrinkage, %	20.5	6.0	23.0	47	31
Rugosity	0.25	0.13	0.21	0.62	0.14
Carbon black stiffening	....	....	29	35	....
Final viscosity (Mooney, large rotor, 4-minute run at 212° F.)	80	64	....	56	52

Table III. Stress-Strain Data from United States Rubber Company Laboratories

Polymer code	S-BS III[a]	S-BS IV[b]	GR-S	J-99
Description	Sodium, 75:25	Sodium, 75:25	Emulsion, 72:28	Emulsion, 40:60
Brittle point, ° C.	−24	−30	−60	−12
Cure, min. at 292° F.	25	30	25	25
Green tensile, lb./sq. in.	2350	2500	2100	2100
Stress at 300% elong., lb./sq. in.	750	800	550	500
Elongation at break, %	590	560	650	640
Green tensile at 212° F., lb./sq. in.	1000	1000	770	1100
Elongation at break, %	410	370	430	760
Aged tensile (aged 48 hr. at 212° F.), lb./sq. in.	2050	2200	1700	2500
Elongation at break, %	220	300	200	250
Cure, min. at 292° F.	50	50	50	50
Green tensile, lb./sq. in.	2000	2500	2700	2700
Stress at 300% elong., lb./sq. in.	1200	1450	1050	1300
Elongation at break, %	400	420	510	460
Green tensile at 212° F., lb./sq. in.	710	725	940	1500
Elongation at break, %	260	230	300	510
Aged tensile (aged 48 hr. at 212° F.), lb./sq. in.	1500	1900	1700	2000
Elongation at break, %	190	290	180	190
Cure, min. at 292° F.	180	..	180	180
Green tensile, lb./sq. in.	2050	..	2300	2400
Stress at 300% elong., lb./sq. in.	..	..	1700	2100
Elongation at break, %	280	..	360	320
Green tensile at 212° F., lb./sq. in.	730	..	990	1300
Elongation at break, %	180	..	260	270
Aged tensile (aged 48 hr. at 212° F.), lb./sq. in.	1950	..	2100	2500
Elongation at break, %	200	..	240	230

[a] 5.0 parts stearic acid added during compounding.

[b] 4.0 parts stearic acid added during compounding. Emulsion polymers prepared on soap normally retain 3–5 parts fatty acid.

TABLE IV. EVALUATION OF SODIUM-CATALYZED 75 BUTADIENE:25 STYRENE COPOLYMERS

(Data from The B. F. Goodrich laboratories)

Identification	Mooney Viscosity[a]	Sulfur, Parts	Cure at 280° F., Min.	300% Modulus, Lb./Sq. In.	Tensile, Lb./Sq. In.	Elongation, %	Hysteresis Temp. Rise above 212° F., ° F.	Flexing	Quality Index
30° C. S-BS	..	1.75	30	1015	3060	580	49	770,000–8	9.6
			45	1415	2700	425	43	460,000–8	7.2
50° C. S-BS	62	2.0	75	960	2400	580	43	550,000–8	8.4
			150	1190	2390	530	37	550,000–8	10.0
GR-S control	47	1.75	75	1020	3380	648	79	690,000–8	3.6
			150	1040	2810	567	58	440,000–8	4.2
Emulsion-polymerized 50 butadiene–50 styrene	54	1.75	75	1200	3900	593	64	1,552,000–8	9.5
			150	1600	4000	527	53	604,000–8	6.8

[a] Mooney viscosity (at end of a 4-minute run) at 212° F. and using the large rotor.

TABLE V. EVALUATION OF 30° C. SODIUM-CATALYZED 75 BUTADIENE:25 STYRENE COPOLYMER

(Data from The B. F. Goodrich laboratories)

Property	S-BS untreated		S-BS softened with 1% JMH		S-BS internally mixed at 320° F.		GR-S control	
Cure, min. at 280° F.	75	150	75	150	75	120	75	120
Tensile at room temp., lb./sq. in.	2375	2375	2025	2425	1600	2050	2200	2350
Elongation at room temp., %	575	510	510	500	735	575	615	575
300% modulus at room temp., lb./sq. in.	.....	...	1000	1250	500	900	800	1050
Tensile at 212° F., lb./sq. in.	.....	...	....	...	...	730	640	....
Elongation at 212° F., %	.....	...	....	...	...	455	420	....
% of elong. retained at 212° F.	.....	...	....	...	...	79	68	....
300% modulus at 212° F., lb./sq. in.	.....	...	....	...	...	380	330	....
Tensile aged 10 hr. in air bomb, lb./sq. in.	.....	...	....	...	...	1960	1690	....
Elongation, aged 10 hr. in air bomb, %	.....	...	....	...	...	560	430	....
300% Modulus, aged 10 hr. in air bomb, lb./sq. in.	.....	...	....	...	...	950	1110	....
% of elong. retained on aging	.....	...	....	...	...	97	70	....
Hysteresis temp. rise at 212° F., ° F.	71	370	75	58	...	92	119	....
Flexing × 10^{-3}	2000–7[a]	740–8[a]	2000–6[a]	690–8[a]	990–2[a]	2000–3[a]	990–2[a]	2000–3[a]
Quality index	13	13.4	11	6.6	...	7.2	2.0	2.2
Permanent set, %	27.9	12.1	22.8	21.0	...	45.0	...	....
Durometer hardness	.....	...	....	...	54	57	55	60
Schopper rebound, %	.....	...	....	...	20	20	34	35
Extrusion plasticity, cc./min.	.....	...	....	...	6.53	....	7.18	....

[a] First number indicates number of flexures; second number is an arbitrary rating of size of crack at end of flexing period.

results are given in kilocycles required for growth of the pin hole to a cut 1 inch long. All results reported are the averages of simultaneous tests on three specimens. Hysteresis measurements were made on the torsional hysterometer (*7*). Values for hysteresis are reported as a logarithmic decrement, *K*, which is proportional to the fractional energy loss per cycle of damped oscillation, when the fractional energy loss per cycle is small.

LOW TEMPERATURE FLEXIBILITY. As a measure of low temperature flexibility, Young's modulus was determined for the temperature range + 30° to −30° C. by the method of Green and Loughborough (*2*). Brittle points are reported as the highest temperature in ° C. at which a 1-inch square, 0.1-inch thick specimen will shatter under the impact of a 290-gram weight dropped from a height of 20 inches. The weight is guided during fall through a slot, and the contact end is fitted with a 1/4-inch movable ball bearing.

RESULTS OF EVALUATION TESTS

PROCESSABILITY: MILL COMPOUNDING AND FABRICATION. The S-BS copolymers broke down nicely on a cold mill and gave no difficulty in mixing. On a laboratory mill S-BS showed more tack than GR-S. However, when mixed in an internal mixer maintained at 320° F., the S-BS compound crumbled near the end of the mixing period. S-BS copolymers can be softened by JMH, a proprietary chemical peptizing agent (manufactured by the J. M. Huber Company).

The results of a typical set of processability tests are given in Table II. These data show S-BS to be equal or superior to GR-S in most processing characteristics. The processing properties of preplasticated S-BS (S-BS II) were outstanding. It is indicated that S-BS can be economically compounded, and that satisfactory calendered and extruded products can be fabricated with less filler than is required for GR-S. The high styrene emulsion polymer J-99 was demonstrated to have essentially the same processing advantages as S-BS.

STRESS-STRAIN. Tables III, IV, and V give test results typical for S-BS and for standard GR-S. Data are also included for two high styrene emulsion copolymers, so that a comparison of sodium and emulsion copolymers can be made on an equivalent brittle point basis. These data represent S-BS to have stress-strain properties in the same range as GR-S at room temperature, at 212° F., and after accelerated aging tests. However, S-BS

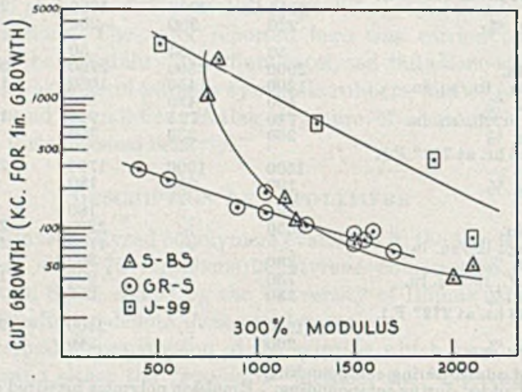

Figure 1. Cut Growth Plotted against Modulus

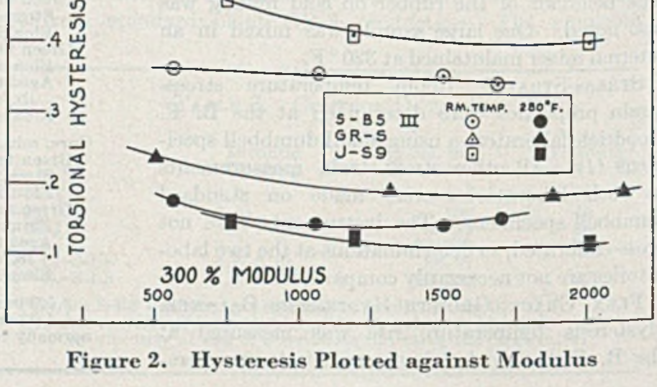

Figure 2. Hysteresis Plotted against Modulus

vulcanizates retain a higher percentage of their room temperature elongation at 212° F. and after accelerated aging than do GR-S vulcanizates. These data indicate an improvement in these properties for S-BS over GR-S.

The testing program was not sufficiently extensive to demonstrate any effect on stress-strain properties of polymerization temperature changes and molecular weight changes over the ranges studied.

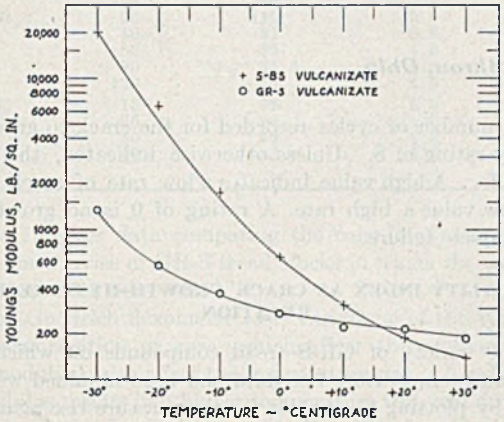

Figure 3. Low Temperature Properties of S-BS and GR-S Vulcanizates

Since extensive compounding studies could not be made with the limited amount of material available, no definite conclusions can be arrived at concerning the optimum stress-strain possibilities. However, it is indicated that no exceptional advantages over GR-S are to be expected. In the single test made, the high styrene vulcanizates showed 212° F. stress-strain properties better than those of the control. These values are particularly outstanding and have seldom been duplicated in GR-S.

Flex Crack Growth–Hysteresis Balance. Figure 1 summarizes the data obtained at the United States Rubber laboratories relating cut growth to modulus. The modulus values reported are stress at 300% elongation measured at room temperature. The data were for different stocks measured at different times; also minor compounding changes were made. The $\log_{10}$ (KC for 1-inch growth) is plotted against modulus for convenience. The graph indicates that the cut growth of S-BS is far superior to that of GR-S at low modulus but approximately equivalent at high modulus. On the other hand, the high styrene emulsion copolymer retained its good cut growth properties at high modulus. Hysteresis was measured at room temperature and 280° F. Figure 2 presents results of S-BS, GR-S, and high styrene polymer. Although at room temperature the hysteresis of the S-BS was inferior to GR-S, the more important measurement at 280° F. showed the S-BS to be definitely better. The data presented in the graph are the only measurements that were made for high styrene polymers.

The balance between flex crack growth and hysteresis temperature rise above 212° F. as reflected by quality index ratings (Tables IV and V) show that S-BS is much superior to GR-S in this property. Also, their excellent quality indices are but slightly lowered by heat treatment, chemical softening, or milling of the copolymer.

These data indicate that S-BS has a flex cracking–hysteresis balance superior to that of GR-S through the whole modulus range. This balance appears to be particularly favorable for low modulus stocks. The good cut growth of the high styrene emulsion polymer allows some compromise in that property in favor of improving hysteresis; the flex cracking–hysteresis balance is indicated to be equal to or better than that of S-BS except for low modulus, undercured stocks.

Low Temperature Flexibility. This property indicates more clearly than any other that a significant difference must exist between the structures of sodium and emulsion polymers of the same butadiene-styrene composition. The S-BS is definitely inferior to GR-S with respect to low temperature flexibility. For a reduction in temperature from +30° to −30° C. an S-BS tread compound increased in Young's modulus from 140 to 20,000 pounds per square inch, while a control GR-S compound increased only from 190 to 1300 pounds per square inch (Figure 3). Brittle points of cured S-BS were determined to be −24° and −30° C.; a value of −20° C. was obtained for raw S-BS. These values compare with −60° and −65° C. for tests on cured GR-S. These comparisons are probably typical of butadiene-styrene copolymers prepared by the two methods over a wide range of composition. Emulsion polybutadiene was determined to have a brittle point of −85° C. for a vulcanized stock, whereas sodium polybutadiene had a brittle point of −62° C. for a vulcanized stock and −50° C. for a raw stock. The high styrene emulsion copolymer was prepared with a 40 butadiene: 60 styrene feed, and the brittle point was determined to be −12° C.

SUMMARY

Sodium-catalyzed butadiene-styrene copolymers (S-BS), of composition 75 weight % butadiene:25 weight % styrene, have been compounded in tread type recipes. Evaluation tests showed properties significantly different from those of GR-S, the emulsion-phase free radical-catalyzed copolymers of identical monomer composition.

1. The processing characteristics of S-BS are considerably superior to those of GR-S, although one experience with a high temperature internal mix may indicate some limitation. Objective laboratory processing tests show that S-BS resembles high styrene emulsion copolymers in that it can be satisfactorily fabricated from stocks containing less filler than is required in GR-S stocks for similar uses.

2. Stress-strain properties based on limited compounding studies are similar to those of GR-S.

3. The flex crack growth–hysteresis balance for S-BS vulcanizates is much superior to that of GR-S vulcanizates. Vulcanizates of emulsion polymers of high styrene content also had a flex crack growth–hysteresis balance superior to that of GR-S vulcanizates.

4. The low temperature properties of S-BS vulcanizates are inferior to those of GR-S vulcanizates. Brittle points and low temperature Young's modulus of S-BS vulcanizates are much higher than those of GR-S vulcanizates.

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Received October 10, 1946. This work is a joint contribution of The B. F. Goodrich Company and the United States Rubber Company. It was carried out as a cooperative project under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

Crack Growth in GR-S Tread Stocks

RELATION TO STATE OF CURE AND COMPOSITION

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Two of the most serious troubles encountered with GR-S in tire use are excessively rapid crack growth and high temperature build-up in the tread composition. One characteristic may be improved at the expense of the other by variations which affect the state of cure. The relations between these properties, when measured under a specific set of conditions, were studied and empirical formulas developed which are valid for a wide variety of compounding modifications. A knowledge of these relations permits the ready evaluation of experimental polymers or suggested compounding modifications which are intended to provide a more favorable balance between these properties. An improvement in this balance may be expressed as a ratio which for convenience has been termed a quality index.

ONE of the most serious deficiencies of GR-S vulcanizates is their poor resistance to crack growth during flexing. This weakness is a major concern in the use of GR-S in tire treads, but it is also a serious handicap in other products which are subjected in service to repeated flexing. A second serious deficiency is their high heat generation during flexing.

It has been the general experience of tire technologists that GR-S treads, which possess the properties usually associated with an undercure or a low state of cure, give good resistance to crack growth (*2, 3, 4, 6, 8*). These properties are low modulus, high elongation, high permanent set, low resilience, and high temperature build-up on flexing. As these properties are changed by advancing the state of cure, the resistance to crack growth declines precipitously, while the temperature build-up improves. A satisfactory solution to the problem must provide a more favorable balance between these properties either by an improved compounding technique or by the development of an improved polymer. It was the purpose of the work reported here to study the relation between these two properties using the conventional De Mattia crack growth test and the Goodrich flexometer test (*5*) to measure the properties.

The choice of the latter test was dictated by two considerations. First, its use focuses attention on one of the properties in which GR-S is deficient, and, second, it is a good measure of the relative state of cure. Relations similar to the one developed here could, no doubt, be developed with any of the test methods ordinarily used to measure or estimate the state of cure, provided they are reasonably sensitive.

TEST METHODS

The temperature rise measurements used in this study were run in the Goodrich flexometer at 212° F. with a 55-pound load and a stroke of 17.5%. ΔT is the rise in temperature above 212° F. after 25 minutes in the machine. All crack growth tests, except where otherwise noted, were run on a De Mattia flexing machine at 300 cycles per minute and a stroke of $2^{1}/_{4}$ inches, in a room maintained at 82° F. and at 45% relative humidity. The crack was initiated by means of a No. 2 needle and the number of cycles recorded for the crack to grow to an arbitrary rating of 8. Unless otherwise indicated, this is the flexing life. A high value indicates a low rate of crack growth and a low value a high rate. A rating of 0 is no growth, and 10 is complete failure.

QUALITY INDEX AS CRACK GROWTH-HYSTERESIS RELATION

A wide variety of GR-S tread compounds on which crack growth and temperature rise data had been obtained were first studied by plotting the values for temperature rise against the logarithm of the flexing life. The curve representing the median value for this series of observations and the two parallel curves representing the spread, which included 90% of the values, are illustrated in Figure 1. The equation for the average curve is:

$$\log \text{flexing life} = 0.0126\,\Delta T + 4.28 \qquad (1)$$

The compounds included in this group, which numbered 268, represented variations in sulfur ratio, accelerator ratio, kind of accelerator, degree of cure, plasticated and crude GR-S, aging of the crude GR-S at various temperatures, aging of the vulcanizates, and minor variations in the GR-S. All compounds, however contained 45 to 50 parts of either EPC or MPC black. As a check the data for an additional group of 146 compounds were plotted, and it was found that all values fell within the limits shown, and that 71 of the cases were above the average line and 74 cases below.

Undoubtedly cases were included in this plot which should not have been included in the light of subsequent findings; thus the spread in results for a particular level of temperature rise is somewhat wider than it should be. Also it should not be implied that, if a careful examination were made, one would not find a consistent difference between a stock containing 45 parts of EPC black and one containing 50 parts of MPC black.

However, with these considerations discounted there is still an appreciable dispersion of crack growth results for a specific temperature rise level, which would indicate either poor precision of the test methods or less dependence between the two properties than is indicated by Equation 1. Subsequent tests have shown that the former is the case. The temperature rise measurement is subject to a small error, but the precision of the crack growth test is poor. Also the two measurements are made on different specimens cured in different molds and, frequently, on different days. The cure rate of the stocks may vary appreciably from day to day as the result of a gain or loss in moisture resulting from humidity changes (*1, 7*). Also, the hysteresis specimen is either cut from a 1-inch thick block or molded into a 0.7-inch-diameter, 1-inch high pellet, and the state of cure in these thicker specimens may not be strictly in the same relation to that of the thinner flexing specimens when different compounds are being compared.

Table I illustrates the application of Equation 1 to variations in time of cure for a typical GR-S tread stock cured for varying lengths of time at three curing temperatures.

Table I. Effect of Curing Time

(Recipe, parts by weight: GR-S 100, Captax 1.0, DPG 0.2, sulfur 2, zinc oxide 5, Age Rite HP 1, MPC black 47, Paraflux 10)

Cure: Temp., ° F.	Cure: Time, Min.	ΔT, ° F.	Log Flex: Obsvd.	Log Flex: Calcd.
260	60	106	5.9	5.6
	90	78.5	5.5	5.3
	120	63	5.1	5.2
	180	46.5	4.9	4.9
	240	43.5	4.7	4.8
	300	42	4.6	4.8
280	25	112	5.6	5.7
	40	81	5.0	5.3
	60	59	4.9	5.0
	90	45.5	4.6	4.8
	120	43	4.6	4.8
300	15	96	5.9	5.5
	25	65	4.9	5.1
	40	46	4.8	4.9
	60	43	4.6	4.8

Table II gives data comparing the calculated and observed flex life for a series of GR-S tread stocks in which the sulfur and accelerator ratios were varied.

In the Goodrich flexometer test, variations of the type listed in the composition or cure, which affect the modulus (300% static modulus), also affect the temperature rise. A reduction in the modulus results in a higher temperature rise, and an increase results in a lower temperature rise. For all such recipe variations Equation 1 represents the temperature rise–crack growth relation. However, other variations in composition may be made for which this equation does not apply. These are changes which simultaneously either increase or decrease both temperature rise and modulus. Changes of this type include variations in the concentration of carbon black and the use of certain high melting resins or pitches.

Table II. Effect of Variations in Sulfur and Accelerator Ratios

(Base recipe, parts by weight: GR-S 100, zinc oxide 5, MPC black 47, Paraflux 10, Age Rite HP 1)

Compd.	Sulfur Ratio	Accelerator Ratio, Captax/ 0.2 DPG	ΔT, ° F.	Log Flex: Obsvd.	Log Flex: Calcd.
A	1	1.5	118	5.6	5.8
B	1	2.0	123	5.6	5.8
C	1	2.5	76	5.6	5.2
D	2	0.75	80	5.1	5.3
E	2	1.0	68	4.9	5.1
F	2	1.5	62	5.0	5.1
G	3	0.5	67	4.9	5.1
H	3	0.75	45	4.8	4.8
I	3	1.0	48	4.9	4.9

On the basis of data of 774 compounds representing variations in composition of this type, an empirical equation has been derived which represents the approximate relation between crack growth, hysteresis temperature rise, and the 300% static modulus:

$$\text{log flexing life} = 5.42 + \frac{\Delta T}{336} - \frac{M}{2000} \qquad (2)$$

To illustrate the application of this equation the EPC black loading in a GR-S tread type recipe was varied from 20 to 75 PHR (parts per hundred on the rubber). Table III shows the modulus, the temperature rise, the observed flexing and the flexing calculated with Equation 2.

Although Equation 1 is satisfactory for recipe variations which result in variations in the state of cure and for time of cure variations, Equation 2 is more accurate for application to all other recipe variations which do not involve carbon blacks or pigments other than EPC or MPC. In some compounding studies, and in particular in the evaluation of experimental polymers, it is frequently impossible to be certain that changes in temperature rise are due to state of cure variations or to inherent differences in the hysteresis properties of the mixture or the polymer.

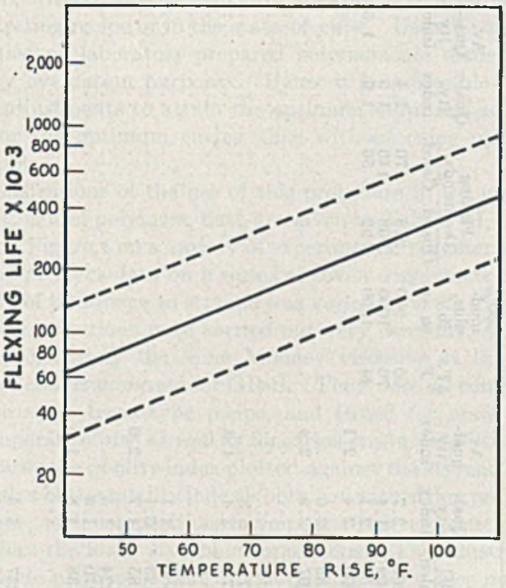

Figure 1. Flexing *vs.* Temperature Rise for State-of-Cure Variations

A more favorable balance between these two properties may be evidenced by an improved flexing life at the same temperature rise level or an improved temperature rise at the same flexing life level, or various intermediate combinations. As a convenient expression of the degree of improvement obtained, either by compounding modifications or by polymer improvements, the author uses the term "quality index," which is defined as the ratio of the observed flexing life for the experimental material to either: (*a*) the calculated flexing life, using Equation 1, of a GR-S tread compound containing the normal loading of EPC or MPC black and having a temperature rise equal to that of the experimental material, or (*b*) the calculated flexing life, using Equation 2, of a GR-S tread compound containing EPC or MPC black and having a modulus and temperature rise equal to that of the experimental material.

A high quality index for a particular polymer, for example, does not necessarily mean that the over-all performance of a tire tread made from it will be superior to that of a GR-S tread. The quality index indicates only the relative excellence with respect to crack growth and temperature rise, and gives no information on the numerous other properties on which the performance of a tire tread depends.

By this definition the quality index for a GR-S tread stock when compounded within the limits given should be 1.00—that is, the calculated and observed flexing values should be the same. However, for several reasons there may be differences which will result in quality indexes higher or lower than 1.00. For the reasons already given, in discussing the precision of test methods one would expect an appreciable variation due to this cause. In addition, the composition and quality of commercial GR-S is not a constant. For example, the styrene ratio has not

Table III. Effect of Variations in Loading of EPC Black

(Recipe, parts by weight: GR-S 100, Paraflux 10, zinc oxide 5, Age Rite HP 1, sulfur 1.75, Santocure 1.2, EPC black as shown)

Loading, PHR	300% Modulus, Lb./Sq. In.	ΔT, ° F.	Log Flex: Obsvd.	Log Flex: Calcd.
20	350	46	5.5	5.4
30	500	54	5.4	5.3
40	800	72	5.3	5.2
50	1000	94	5.2	5.2
60	1650	115	4.9	4.9
75	2450	[a]	...	...

[a] Blew out during the test.

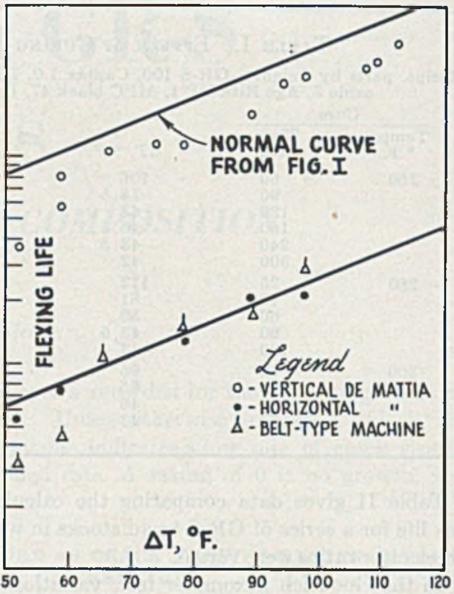

Figure 2. Comparison of Various Flexing Machines

been permanently fixed, and this, as will be shown later, has a pronounced effect on this balance of properties. Also, the degree of carbon black dispersion has some effect. Thus when comparisons are made between a control and an experimental material, it is necessary to give weight to the quality index obtained on the control. The formulas thus supply a reference base to which both the experimental material and the control can be compared.

None of the compounds used in deriving these formulas contained carbon blacks other than EPC or MPC. In order to determine the effects of other blacks a series of compounds was made up based on the following carbon blacks in parts per hundred on the rubber:

Statex A	50
Statex B	50
Statex 93	50
Philblack A	40
Acetylene black	35
Kosmos 40	40
Gastex	50

In addition, mixtures of each of these blacks with EPC were tried on the basis of replacing 10 and 20 parts of the EPC with each of them. For each black and for each mixture at least two levels for temperature build-up were secured, either by varying the time of cure or by recipe variations affecting the state of cure.

Both crack growth and hysteresis tests were run in quintuplicate from specimens cured from the same batch. Tests were run on different days over a period of several months.

The average results are given in Table IV, and the ratio of the observed life to the calculated flexing life using Equation 2 is shown.

The results given in Table IV indicate that a slight but definite improvement results from the substitution of these blacks for EPC black. Although it appears that Statex 93 gives slightly better results than the other blacks, it would be necessary to repeat the test a number of times to be certain that the improvement was beyond the experimental error of the observations.

No work has been done on compounds in which all the carbon black was replaced by an inorganic

Table IV. Crack Growth and Hysteresis Tests

Black	10 PHR Replacement of EPC Black						20 PHR Replacement of EPC Black						Total Replacement							Control, 50 PHR EPC Black					
	ΔT, ° F.	300% modulus, lb./sq. in.	Flexing (thousands) Obsvd.	Flexing (thousands) Calcd.	Quality index	Av. quality index	ΔT, ° F.	300% modulus, lb./sq. in.	Flexing (thousands) Obsvd.	Flexing (thousands) Calcd.	Quality index	Av. quality index	Parts Black[a]	ΔT, ° F.	300% modulus, lb./sq. in.	Flexing (thousands) Obsvd.	Flexing (thousands) Calcd.	Quality index	Av. quality index	ΔT, ° F.	300% modulus, lb./sq. in.	Flexing (thousands) Obsvd.	Flexing (thousands) Calcd.	Quality index	Av. quality index
Statex A	98	600	508	257	2.2		102	500	432	295	1.4		50	102	600	708	263	2.7		90	900	248	170	1.4	
	72	625	248	210	1.2		72	750	366	240	1.5			62	750	245	169	1.4		76	1000	208	140	1.5	
	54	950	242	129	1.9		62	1000	266	126	2.1			61	800	336	159	2.1		44	1600	92	56	1.6	1.5
	51	1000	135	117	1.2	1.6	56	900 (?)	172	138	1.2	1.5		47	1100	244	100	2.4	2.1	...	...	...	...	...	...
Statex B	90	600	372	246	1.5		85	850	415	178	2.3		50	54	900	278	135	2.0		...	...	...	...	...	...
	66	750	248	178	1.4		78	975	236	148	1.6			55	1100	310	107	2.9	2.4	...	...	...	...	...	...
	60	900	236	142	1.6		54	1400	220	76	2.9			...	...	...	...	...	...	...	...	...	...	...	...
	51	1050	218	112	1.9	1.6	44	900	188	126	1.5	2.1		...	...	...	...	...	...	...	...	...	...	...	...
Statex 93	138	550	1218	360	4.6		93	1000	530	159	3.3		50	91	900	932	174	5.3		...	...	...	...	...	...
	97	1100	664	145	2.4		71	1100	294	120	2.4			44	1300	270	79	3.4	4.3	...	...	...	...	...	...
	79	1200	266	112	2.2		65	1300	212	85	2.5			...	...	...	...	...	...	...	...	...	...	...	...
	57	1400	174	78	3.4	3.1	45	1550	117	60	1.9	2.5		...	...	...	...	...	...	...	...	...	...	...	...
Philblack	87	900	406	169	2.4		81	700	444	204	2.2		40	111	700	596	560	1.1		...	...	...	...	...	...
	63	950	226	138	1.6		64	1100	222	115	1.9			57	1000	388	123	3.1		...	...	...	...	...	...
	52	1200	204	47	4.3	2.8	48	1150	116	100	1.2	1.8		38	1200	142	85	1.7	2.0	...	...	...	...	...	...
Kosmos 40	106	500	460	310	1.5		85	750	505	200	2.5		40	61	500	336	224	1.5		...	...	...	...	...	...
	74	700	233	195	1.2		66	1100	284	115	2.5			61	350 (?)	498	270	1.5		...	...	...	...	...	...
	68	850	176	159	1.1		58	1250	256	93	2.7	2.6		39	800	214	138	1.8	1.6	...	...	...	...	...	...
	58	1000	195	123	1.6	1.3	...	...	...	...	...	...		...	...	...	...	...	...	...	...	...	...	...	...
Acetylene black	104	600	404	270	1.8		91	900	296	174	1.7		35	81	500	398	257	1.5		...	...	...	...	...	...
	74	1000	214	138	1.5		77	1300	150	100	1.5			67	650	288	200	1.4		...	...	...	...	...	...
	61	1200	192	100	1.9		56	1350	156	83	1.8	1.7		44	950	174	120	1.4	1.4	...	...	...	...	...	...
	50	900 (?)	140	132	1.1	1.5	...	...	...	...	...	...		...	...	...	...	...	...	...	...	...	...	...	...
Gastex	96	800	481	210	2.3		93	850	498	190	2.6		50	...	...	...	...	...		...	...	...	...	...	...
	79	900	340	159	2.1		69	900	382	148	2.6			51	810	414	147	2.8		...	...	...	...	...	...
	60	1200	234	100	2.3		54	1000	288	120	2.4	2.5		44	950	274	121	2.2	2.5	...	...	...	...	...	...
	47	1500	136	64	2.1	2.2	...	...	...	...	...	...		...	...	...	...	...	...	...	...	...	...	...	...

[a] The different values given for each black represent different states of cure.

Table V. Effect of Addition of Nonblack Pigments

(Base recipe, parts by weight: GR-S 100, EPC 45, zinc oxide 5, Santocure 1.5, Turgum 10, Sulfur 2.0)

Pigment Added to Standard Tread Recipe, Parts	ΔT, ° F.	Flexing (Thousands)		Quality Index
		Obsvd.	Calcd.	
Control	78	170	182	0.94
Atomite Whiting, 15	62	120	115	1.04
Atomite Whiting, 25	76	170	195	0.87
Mica, 4	59	180	105	1.71
Clay, 7.5	61	110	112	0.98
Clay, 15	92	1110	276	4.0
Yellow iron oxide, 15	100	300	390	0.77
Soapstone, 5	79	180	186	0.97
Soapstone, 10	110	370	468	0.79

pigment. However, some data have been obtained on compounds in which varying amounts of inorganic pigments were added to the normal complement of EPC black.

The results obtained are shown in Table V. With the exception of the stock containing 15 parts of clay, the calculated flex life agrees well with the observed flex life. The exception is no doubt an illustration of the laminating or anisotropic effect described by Breckley (*2*). The crack growth results from this type of compound should be much higher than the calculated values.

All of the data used in these derivations and illustrations were obtained on a single De Mattia type flexing machine. It was of interest to determine whether a similar relation applied to other machines.

A series of six tread compounds with varying proportions of curing agents was tested on two other machines. The first, known as the horizontal De Mattia, is similar to the one used as the standard except that it is operated at 500 cycles per minute with a stroke of 2 inches. The second was a belt-type machine not previously described in the literature, in which molded samples of $^1/_4$-inch-square cross section, having the same transverse groove as the standard De Mattia sample, are fastened to a belt run over small diameter pulleys at a rate which gives the sample 400 flexures per minute. The results are reported as the number of cycles to produce a crack 80% of the total width of the sample. In both tests twelve samples of each stock were tested on each machine.

The results are illustrated in Figure 2. The belt-type machine is about as severe as the horizontal high speed De Mattia, and both are considerably more severe than the vertical De Mattia. The slopes of the curves are approximately the same as that of the curve shown in Figure 1, which indicates that Equation 1 will apply to a variety of flexing machines with a suitable revision of the constant.

The rate of crack growth in GR-S tread compounds increases rapidly with an increase in testing temperature. To determine how the curve relating crack growth to hysteresis temperature rise is shifted by an increase in testing temperature, the six compounds used in this comparison were tested on the belt-type flexing machine at 158° and at 212° F. Figure 3 shows the results obtained at these temperatures as well as at room temperature.

One of the primary reasons for the study of this relation between crack growth and temperature rise was for the purpose of evaluating supposed improvements in the GR-S type of copolymer with respect to these deficiencies of GR-S, without the necessity for making precise adjustments in the testing recipe or in the state of cure. Usually only small quantities of laboratory-prepared polymers are made for preliminary evaluation purposes. Hence it is impossible to make recipe adjustments to attain the optimum sulfur and accelerator ratios or the optimum curing time without using up most of the sample.

As illustrations of the use of this procedure in the evaluation of experimental polymers, data are given in Tables VI, VII, and VIII and Figure 4 on a variety of experimental polymers.

Table VI gives data on a series of seven copolymers in which the ratio of butadiene to styrene was varied from 85:15 to 50:50. The polymerizations were carried out very carefully, so that all had approximately the same Mooney viscosity at the normal degree of conversion used for GR-S. They were all compounded into the same tread-type recipe, and tested for crack growth and temperature rise as well as for stress-strain properties. Figure 4 shows the quality index plotted against the styrene content. Although a better quality index is obtained with higher proportions of styrene, such compositions have poorer low temperature properties than the lower styrene compositions. This illustrates the point made previously that a high quality index does not necessarily ensure the presence of other properties which are important in tire tread service.

Table VII shows results for a series of copolymers employing various chlorinated derivatives of styrene in the standard GR-S

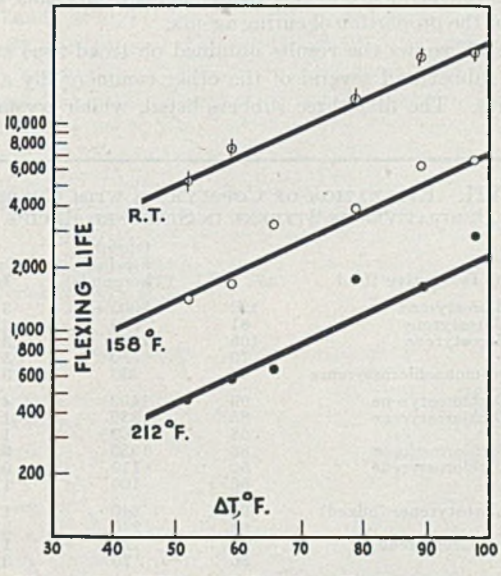

Figure 3. Effect of Testing Temperature

Table VI. Evaluation of Copolymers with Same Tread-Type Recipe

Charging Ratio, Butadiene/Styrene	Conversion, %	Mooney Viscosity, 212° F., 4-Min.	Combined Styrene, %	Cure, Min. at 280° F.	300% Modulus, Lb./Sq. In.	Tensile, Lb./Sq. In.	Elongation, %	Flexures	ΔT, ° F.	Quality Index	Av. Quality Index
85/15	76.6	53	13.3	75	1250	3180	553	210,000-8	Blew out	..	
				150	1340	2190	447	130,000-8	77	0.73	0.73
78/22	76.7	51	21.6	75	1010	3690	661	250,000-8	98	0.76	
				150	1270	3080	513	196,000-8	70	1.4	1.1
75/25	78.3	53	24.05	75	1180	3700	606	290,000-8	92	1.1	
				150	1570	3450	527	220,000-8	65	1.8	1.5
72/28	78.5	53	27.50	75	1290	3900	607	290,000-8	91	1.1	
				150	1300	3360	527	248,000-8	66	1.9	1.5
69/31	78.2	52	29.90	75	1190	3670	622	366,000-8	88	1.5	
				150	1350	3340	518	296,000-8	63	2.5	2.0
65/35	78.8	53	33.00	60	1050	3580	620	454,000-8	91	1.7	
				150	1320	3840	567	274,000-8	59	2.6	2.2
60/40	77.5	53	37.60	75	1270	4090	661	694,000-8	82	3.3	
				150	1390	4010	620	362,000-8	61	3.2	3.3
50/50	77.6	54	47.90	75	1200	3900	593	1,552,000-8	64	9.5	
				150	1600	4000	527	604,000-8	53	6.8	8.2
X-125 GR-S	..	..	...	75	1010	3580	700	420,000-8	103	1.1	
				150	910	3400	661	270,000-8	88	1.1	1.1

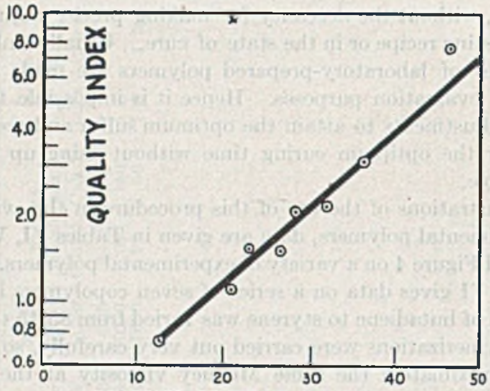

Figure 4. Quality Index as Function of Styrene Content

polymerization recipe. They were all compounded using the same recipe with EPC black.

In some cases an experimental polymer gives a temperature rise value for equal modulus widely different from that obtained from GR-S. In this case Equation 2 should be used in calculating the quality index. Table VIII gives data on two copolymers in which vinyl pyridines were used in place of styrene. In this table the two values for each recipe variation represent two different cures, 75 and 150 minutes at 280° F. These data illustrate the independence of the quality index from either the time of cure or the proportion of curing agents.

Table IX shows the results obtained on tread-type stocks of natural rubber and several of the other commercially available synthetics. The first three rubbers listed, which crystallize on stretching, are considerably superior to GR-S; also, several of the experimental polymers shown in Table VII are superior to GR-M, one of the crystallizable rubbers. Apparently the ability to crystallize, although desirable in providing a favorable balance between temperature rise and crack growth (as well as in other properties), is not an essential requisite to the attainment of a reasonably favorable balance. (Those rubbers showing a high quality index in Table VII do not show evidence of crystallization when examined by x-ray technique.) The more favorable balance observed by certain of the experimental rubbers must be due to certain structural differences from standard GR-S, probably a greater degree of linearity.

Table VII. Evaluation of Copolymers with Chlorinated Derivatives of Styrene in Standard Recipe

Styrene Derivative Used	ΔT, ° F.	Obsvd. Flexing (Thousands)	Quality Index
m-Chlorostyrene	122	2000+	3.0+
p-Chlorostyrene	81	570	2.8
o-Chlorostyrene	105	1280	3.2
	70	730	5.1
Mixed monochlorostyrenes	44	230	3.3
2,5-Dichlorostyrene	99	1450	4.2
2,4-Dichlorostyrene	85	330	1.5
	58	180	1.7
3,4-Dichlorostyrene	83	1950	9.5
2,6-Dichlorostyrene	62	110	0.9
	56	100	1.0
Trichlorostyrenes (mixed)	98	340	1.0
	64	240	2.0
Tetrachlorostyrene	65	120	1.0
	56	70	0.7

Table VIII. Evaluation of Copolymers with Vinyl Pyridine Replacing Styrene

Styrene Replaced by	300% Modulus, Lb./Sq. In.	ΔT, ° F.	Flexing (Thousands) Obsvd.	Flexing (Thousands) Calcd.	Quality Index
2-Vinylpyridine (Santocure 1.2, sulfur 1.75)	1650	70	930	63.5	14.6
	2000	57	480	39	12.3
2-Vinylpyridine (Altax 0.15, sulfur 1.6)	1150	80	1590	123	12.9
	1700	60	910	56	16.2
5-Vinyl-2-methylpyridine					
Santocure Sulfur					
1.2 1.75	1920	57	280	42.6	6.6
	1590	58	240	62.8	3.8
1.2 1.5	2000	69	260	42.2	6.2
	1480	69	300	76.8	3.9
1.2 1.25	1010	70	290	66.6	4.4
	1510	63	280	72	3.9
1.0 1.75	..	..	350	..	..
	1850	50	430	44	9.8
0.8 1.75	1620	66	290	64	4.5
	2090	57	320	35	9.1
0.6 1.75	1740	64	290	54	5.4
	..	62	250	..	...

Table IX. Results on Tread-Type Stocks

Rubber	ΔT, ° F.	Obsvd. Flexing (Thousands)	Quality Index
Natural	64	2000+	16+
GR-I	79	2000+	10.5+
GR-M	67	480	3.5
Hycar OR-15	87	316	1.3

SUMMARY

A quantitative relation has been established between rate of crack growth and temperature rise, as determined in the Goodrich flexometer test, for GR-S tread stocks compounded with the normal quantities of EPC or MPC blacks. This was shown in Equation 1. The relation is valid for all variations which affect the state of cure—that is, time of cure, sulfur or accelerator variation, retarding or activating softeners, etc.

For other variations in the tread composition, such as an increase or decrease in the loading of the EPC or MPC black, Equation 2 holds. This relation is valid for all other known recipe modifications which do not involve carbon blacks other than EPC or MPC.

Improvements in the balance between flex cracking and temperature rise, obtained by compounding or by an improvement in the polymers, may be expressed as the ratio of the observed flexing life to the calculated flexing life using the equation appropriate to the case. This ratio is termed the quality index.

Coarser blacks substituted for the EPC or MPC blacks give an improvement in the balance between temperature rise and crack growth.

The slope of the curve relating crack growth to heat rise is the same for a variety of flexing machines and for various testing temperatures.

Knowledge of this relation has made it possible to evaluate, with some confidence, compounding changes intended to improve the resistance to crack growth without a sacrifice in temperature build-up, and also to evaluate small quantities of experimental polymers without the necessity for precise adjustments in either the proportions of curing agents or curing time.

ACKNOWLEDGMENT

The assistance of C. H. Schroeder, M. M. Goff, L. O. Schroyer, and C. T. Rood in the accumulation of the data for this study is gratefully acknowledged, as is the preparation of the varying styrene series by R. J. Houston. The polymers containing chlorinated styrenes and 5-vinyl-2-methyl pyridine were prepared at the University of Illinois under the direction of C. S. Marvel. The 2-vinyl pyridine copolymers were made by The Goodyear Tire and Rubber Company.

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Received April 18, 1946. Presented before the Division of Rubber Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

DENSITIES OF CELLULOSE ESTERS

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Densities of cellulose, cellulose acetates, acetate propionates, and acetate butyrates have been measured by the Archimedes and flotation methods. They have also been calculated from unit molecular weights and unit molecular volumes based on the densities of regenerated cellulose and the various acids. Observed and calculated results agree within two units in the second decimal place. Regenerated cellulose samples were found to have a density of about 1.52. The densities of other cellulose samples varied, depending upon their origin and degree of purity. Observed cellulose ester densities varied with composition reaching values as low as about 1.28 for the triacetate and 1.16 for the tributyrate. The Archimedes method is preferred for film samples, but the flotation method is useful for powders and fibrous samples. In the measurement of densities it is necessary to select immersion media which do not dissolve or swell the sample. Water or aqueous cadmium sulfate solutions were used for esters of high propionyl or butyryl content, and carbon tetrachloride or mixtures of carbon tetrachloride and benzene or tetrabromoethane and xylene were used for cellulose acetates and mixed esters of low propionyl or butyryl content. Calculated approximate values are also presented for simple fatty acid esters from formate to stearate.

THE density of a manufactured article is of practical importance and interest because most raw materials are purchased by weight, whereas the amount required for a finished object depends on its volume. Materials of lower density thus have a price advantage on a volume basis over materials of higher density. It is therefore desirable to know the densities of commercially available cellulose esters when considering possible uses for these materials and when selecting the best material for a particular use.

In determining the density of a cellulose ester, a representative sample must be obtained and, if necessary, converted to a form suitable for the density measurement. Thus, it may be converted to a film or a filament or pressed into a block, or, if none of these is practicable, it may be powdered. Care must be taken to remove completely from the sample all residual solvents, moisture, and air; the latter may be considerable in the case of powders. The most useful methods for determining the density of cellulose esters require immersion of the samples in a liquid. Since cellulose esters dissolve or swell in some of the organic liquids commonly used as immersion media, care should be taken to avoid the use of such liquids, since their use would give erroneous or drifting density values.

The varied and apparently discordant values in the literature for the density of cellulose emphasize the difficulties of measurement. Lauer and Westermann (*9*) tabulated observed densities for cotton which vary from 1.45 to 1.62, depending on the method of measurement. Ranges as great as 0.04 in density are shown for a single method—for example, 1.52 to 1.56 using toluene as the immersion medium. Cellulose is considered to be composed of crystalline and noncrystalline portions, and it is possible that they differ somewhat in density. Furthermore, many chemical treatments convert the native cellulose crystal lattice to that of cellulose hydrate. This change involves an increase in the size of the unit cell (*13*) and a corresponding decrease in density. It is no wonder that, with these possible variations in density of pure cellulose plus variations in methods of measurement, so many different values have been reported.

The density value 1.585 grams per cubic centimeter for standard cotton linters, found by Stamm and Hansen (*19*) using helium as the displacing agent, may be taken as a good representative value for the density of natural cellulose. This compares closely with the value 1.582 grams per cubic centimeter calculated by Lyons (*10*) from the dimensions of Meyer's revised model of the unit cell of cellulose (*14*) and the value of 1.58 reported by Herzog and Jancke (*7*), and is supported by recent comments of Heertjes (*5*).

When cellulose is regenerated from viscose, cuprammonium solution, or cellulose acetate, or is subjected to swelling treatments such as mercerization, it is converted to the cellulose hydrate state having a density of 1.52 ± 0.02. Values within this range are reported by Herzog and Jancke (*7*), Davidson (*2*), Frank and Caro (*4*) and Moll (*15*), and are confirmed by data in this paper.

Data on the densities of various cellulose esters have been reported. Mosenthal (*16*) studied the densities of cellulose nitrates, and Frank and Caro (*4*) worked with alkyl oxalates of cellulose. Wünnenberg, Fischer, and Biltz (*21*) and Heertjes, Coltof, and Waterman (*6*) measured densities of cellulose acetate samples. Sheppard and Newsome (*18*) reported densities of many cellulose esters of the homologous fatty acid series. Malm, Fordyce, and Tanner (*11*) show graphically the variation of density with composition of cellulose acetate, propionate, butyrate, acetate propionate, and acetate butyrate.

METHODS OF MEASUREMENT

The general principles and experimental details of the measurement of the densities of solids are discussed in standard reference books, such as that of Reilly and Rae (*17*) and of Weissberger (*20*). Six of the most important methods used are the volumetric method, use of dilatometer, use of volumenometer, use of pycnometer, method of Archimedes, and flotation method. The latter three methods are widely used because of the simplicity of the apparatus and its general availability. The Archimedes and pycnometer methods are used by the American Society for Testing Materials for determination of specific gravity of plastics (*1*).

METHOD OF ARCHIMEDES. This has been found to be suitable for use with cellulose ester films and filaments. It is less satisfactory for powders than is the flotation method. The Archimedes method involves weighing a body in two media of known densities, usually air and a liquid such as water or carbon tetrachloride. The density of the body can then be calculated from the difference in weights as follows:

$$d = \frac{W_1}{W_1 - W_2} \times D$$

where d = density of the body, grams/cc.
W_1 = weight of the body in air, grams
W_2 = weight of the body in liquid (often negative in sign), grams
D = density of immersion liquid at temperature at which measurement is made, grams/cc.

For very accurate work it may be desirable to apply corrections for the buoyancy of air and for surface tension (*17*).

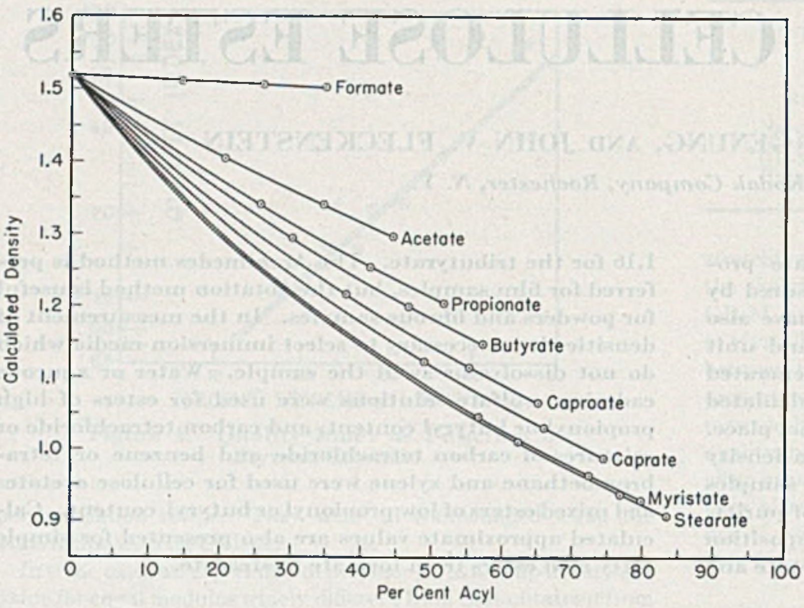

Figure 1. Calculated Densities of Aliphatic Acid Esters of Cellulose

For the measurement of films a suitable sample free from air bubbles is cut into as large a shape as can be manipulated in the glass cylinder used for this purpose, and two holes are punched in the film for hooking it to a suspending wire from the balance arm and for attaching a small sinker or plumb. The film is then dried thoroughly to remove moisture and residual coating solvents, and its weight in air is measured in a closed weighing bottle.

The film is hooked onto the suspending wire from the arm of an analytical balance, the plumb is hooked in the lower hole in the film, they are placed in the cylinder, immersion liquid is added to the required depth, and the weight is then determined as quickly as possible. The film is then removed, and the weight of the wire and plumb in the liquid is determined. The liquid level should be adjusted if necessary so the same amount of wire is immersed as in the determination. The difference between these two weights is the weight of the sample in the liquid, and this value is negative in sign when heavy immersion liquids are used.

When the sample is known to be porous and when greater accuracy is desired, this procedure is varied by placing the plumb, film, and suspending wire in the empty cylinder and fitting the cylinder with a stopper carrying a dropping funnel with stopcock and a connection to a vacuum line. The cylinder is then thoroughly evacuated to remove as much trapped and absorbed air as possible, and the immersion liquid is added through the dropping funnel to cover the sample before air is admitted and the pressure restored. The suspending wire is attached to the balance arm, the liquid level is adjusted to the proper point, and the weighing is made as before.

This method is particularly advantageous because the time of immersion can be kept short. After the measurement the weight can be checked from time to time, and a significant drift in weight may be taken as an indication of undesirable swelling or change. In this way a measure can be conveniently obtained of the suitability of the liquid as an immersion medium for that particular sample.

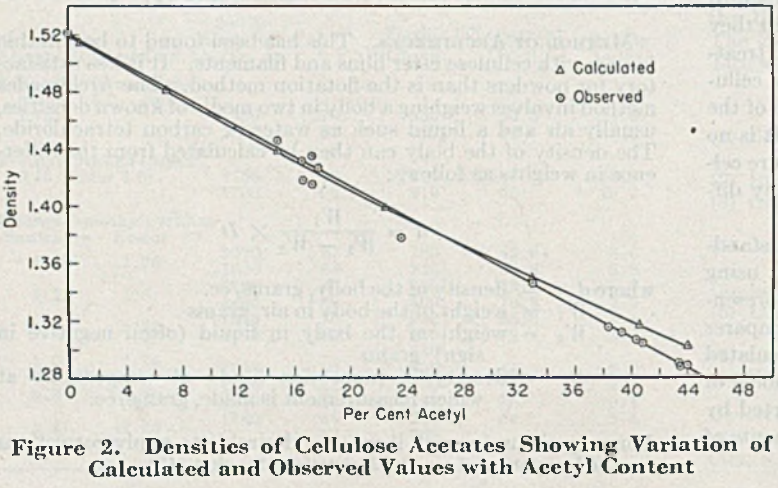

Figure 2. Densities of Cellulose Acetates Showing Variation of Calculated and Observed Values with Acetyl Content

Carbon tetrachloride is a suitable immersion liquid for cellulose acetate and cellulose acetate propionates and acetate butyrates containing up to 25% higher acyl. With esters containing larger amounts of higher acyl, water with 0.1–0.25% of a commercial wetting agent has been used satisfactorily.

The density of the immersion liquid at the temperature of the experiment must be known. It has been found convenient to prepare a density-temperature graph when one medium is to be used frequently.

Filaments are measured as described, except a compact wad is prepared and fastened to the wire and sinker. The evacuation step is essential in this case. Powders may be measured in a similar way using a suitable small container made of fine screen which is suspended from the balance arm. Care should be taken that the powder is of coarser mesh than the screen. The accuracy tends to be poorer in these cases than with film because of difficulties caused by the large surfaces involved and by possible loss of powder through the screen.

Flotation Method. This is easily applicable to small objects including films, filaments, and powders. Pairs of inert liquids, one of lower and one of higher density than the sample, are chosen. The following pairs have been used: concentrated cadmium sulfate solution and water; concentrated calcium chloride solution and water; tetrabromoethane and xylene; carbon tetrachloride and benzene.

The best practice is to place a small amount of the sample on the bottom of an empty cylinder; evacuate as described for the Archimedes method, add a suitable mixture whose density approximates that of the sample to cover the sample, release vacuum, and adjust the mixture so the sample neither floats nor sinks but remains suspended. Sufficient time must be allowed for fibrous samples to come to equilibrium with the suspending medium. Films and granules present no problem, but finely divided powders are difficult to evacuate, and results tend to be low. The density of the suspending medium is then determined at the same temperature using a pycnometer or other suitable means. The observed density is also the density of the sample.

Organic liquid pairs, such as carbon tetrachloride–benzene or tetrabromoethane-xylene, are used for cellulose acetates and for cellulose acetate propionates and acetate butyrates containing less than about 25% propionyl or butyryl. Mixed esters containing more than this amount of propionyl or butyryl are measured using cadmium sulfate– or calcium chloride–water solutions.

This method, which is quite widely applicable, uses simple apparatus and a small sample. It is not so accurate as the Archimedes method because the time of contact between the sample and medium is greater, drifts due to swelling are not easily detected, and close temperature control during manipulation is difficult.

Other Methods. The pycnometer method may be used for powders, films, and filaments. The samples of films and filaments are cut into pieces small enough to be inserted into the pycnometer. The same precautions as to preparation and drying the sample, removal of air by evacuation, choice of immersion medium, control or measurement of temperature, etc., apply as in the other methods. In this case the time of immersion is greater than for the Archimedes method.

The volumetric method is usually unsuitable because the measurement of gross volume is too inaccurate, and no account is taken of the volume of pores and voids.

PREPARATION OF SAMPLE

The measurement of the density of an object involves several sources of error and special precautions, as discussed. When the density of a cellulose ester—for example, a commercial sample of cellulose acetate of 40.4% acetyl content—is to be measured, some new difficulties are added. Either the sample must be powdered and a measurement made which involves the difficul-

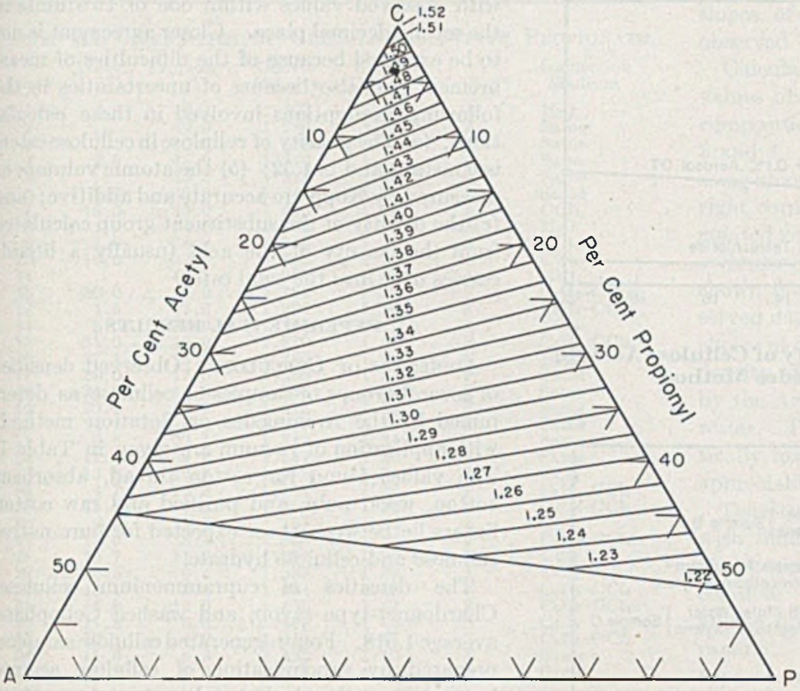

Figure 3. Densities of Cellulose Acetate Propionates

ties of measurement of the volume of a powder, or a film is coated and the difficulty added of completely removing all residual solvent. The density of the film, however, is easier to measure than that of a powder.

Films for this purpose are coated from volatile solvents, such as acetone or methylene chloride plus methyl alcohol. Concentrated solutions are prepared, pressure-filtered, allowed to stand until free from bubbles, poured onto glass plates, and spread into films with a spatula or preferably a special coating knife. The solvents are removed by curing, first at a low temperature to avoid bubble formation and later at a higher temperature (100° C.) to drive off the solvent as completely as possible. The film is stripped from the glass plate, cut and perforated, dried again in an oven to constant weight, and placed in a weighing bottle in a desiccator.

CALCULATION OF DENSITIES

It is often convenient to be able to calculate the density of a cellulose ester, particularly in cases where the material itself is not available and when approximate values are needed immediately. A practical method consists of dividing the unit molecular weight by the unit molecular volume as calculated by the method of Frank and Caro (4). The molecular weight is the weight of the anhydroglucose unit, 162, plus the weight added by the substituent groups, as determined from the composition of the cellulose derivative. An approximate molecular volume is obtained from the densities of cellulose and the component acids, correction being made for the atomic volumes of the elements of water split out during the formation of the ester.

The following calculations illustrate the application to cellulose acetate and to typical mixed esters, such as cellulose acetate propionate and acetate butyrate.

Cellulose Acetate. The number of acetyl groups per glucose unit of cellulose, N_a, may be calculated from the weight per cent acetyl content, a, by the following equation (3):

$$N_a = \frac{3.86a}{102.4 - a} \tag{1}$$

$$\text{Molecular weight} = 162 + 42N_a \tag{2}$$

The molecular volume of the cellulose portion of the ester, 106.6, is found by dividing the unit molecular weight, 162, by the density of cellulose hydrate, 1.52. The atomic volumes of hydrogen and oxygen are taken to be 5.5 and 7.8, respectively, and the volume of hydroxyl is 13.3 (8). The volume of the cellulose portion of the ester is thus $106.6 - 5.5N_a$.

The volume of the acetyl group is the molecular weight of acetic acid, 60.05, divided by its density, 1.049, minus the volume of the hydroxyl group, 13.3, which gives a value of 43.9 for the group CH_3CO. The molecular volume of cellulose acetate is thus,

$$106.6 - 5.5N_a + 43.9N_a = 106.6 + 38.4N_a \tag{3}$$

$$\text{Density of cellulose acetate} = \frac{162 + 42N_a}{106.6 + 38.4N_a} \tag{4}$$

For example, cellulose acetate containing 40.4% acetyl gives

$$N_a = \frac{3.86 \times 40.4}{102.4 - 40.4} = 2.515$$

$$\text{Density} = \frac{162 + 42\ (2.515)}{106.6 + 38.4\ (2.515)} = 1.317$$

Other Simple Esters. Densities of cellulose formate, acetate, propionate, butyrate, caprate, and other higher fatty acid esters of cellulose have been calculated in this manner and are shown in Figure 1.

Cellulose Mixed Esters. The calculation is basically the same as that for cellulose acetate but is more complicated because of the presence of the second acid group.

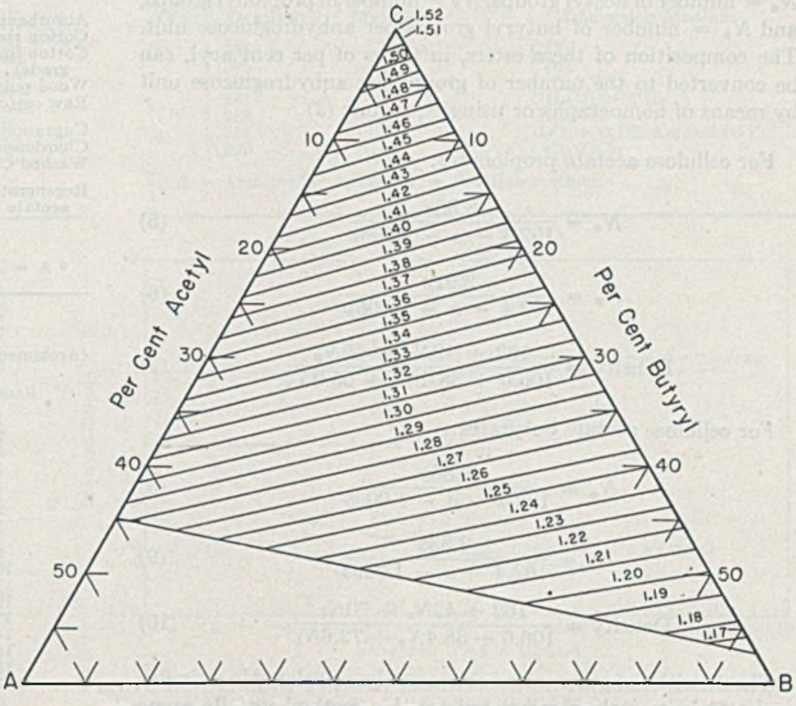

Figure 4. Densities of Cellulose Acetate Butyrates

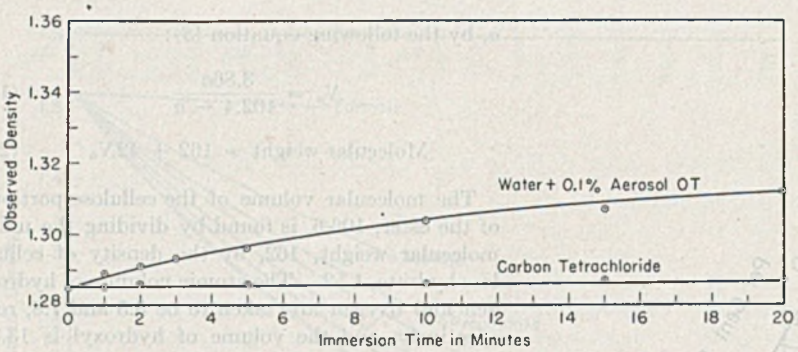

Figure 5. Effect of Time of Immersion on Density of Cellulose Acetate (43.3% Acetyl) as Measured by Archimedes Method

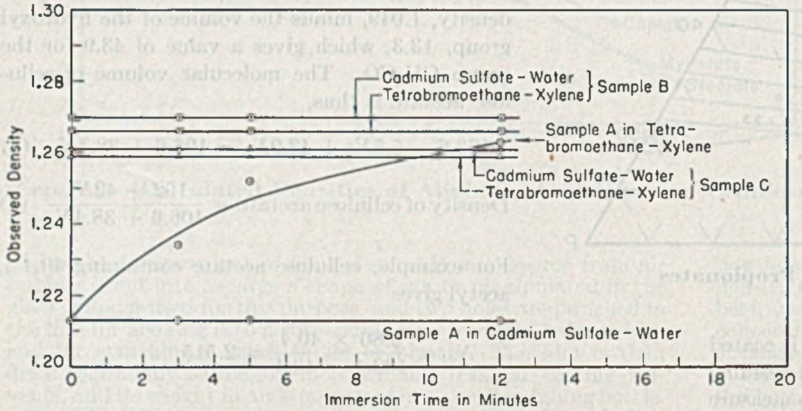

Figure 6. Effect of Time of Immersion on Density of Cellulose Mixed Ester Films as Measured by Flotation Method

Sample	Acetyl, %	Propionyl, %	Butyryl, %
A	14.8	...	35.7
B	31.0	16.0	...
C	30.8	...	16.0

Let a = weight per cent of acetyl in sample, p = weight per cent of propionyl in sample, and b = weight per cent of butyryl in sample.

These values may be determined by analysis (*12*). Then let N_a = number of acetyl groups, N_p = number of propionyl groups, and N_b = number of butyryl groups per anhydroglucose unit. The composition of these esters, in terms of per cent acyl, can be converted to the number of groups per anhydroglucose unit by means of nomographs or using equations (*3*).

For cellulose acetate propionates:

$$N_a = \frac{3.86a}{102.4 - a - 1.006p} \qquad (5)$$

$$N_p = \frac{2.91p}{102.4 - a - 1.006p} \qquad (6)$$

$$\text{Density} = \frac{162 + 42N_a + 56N_p}{106.6 + 38.4N_a + 55.9N_p} \qquad (7)$$

For cellulose acetate butyrates:

$$N_a = \frac{3.86a}{102.4 - a - 1.009b} \qquad (8)$$

$$N_b = \frac{2.33b}{102.4 - a - 1.009b} \qquad (9)$$

$$\text{Density} = \frac{162 + 42N_a + 70N_b}{106.6 + 38.4N_a + 72.6N_b} \qquad (10)$$

The densities of other mixed esters can be calculated in a similar way. Density values calculated by this method usually agree with observed values within one or two units in the second decimal place. Closer agreement is not to be expected because of the difficulties of measurement and also because of uncertainties in the following assumptions involved in these calculations: (*a*) The density of cellulose in cellulose esters is constant and is 1.52; (*b*) the atomic volumes as measured by Kopp are accurate and additive; and (*c*) the density of the substituent group calculated from the density of the acid (usually a liquid) carries over into the solid ester.

EXPERIMENTAL RESULTS

DENSITIES OF CELLULOSE. Observed densities of several groups of samples of cellulose as determined by the Archimedes or flotation methods with application of vacuum are given in Table I. The values found for cotton thread, absorbent cotton, wood pulp, and purified and raw cotton linters lie between those expected for pure native cellulose and cellulose hydrate.

The densities of cuprammonium cellulose, Chardonnet-type rayon, and washed Cellophane average 1.518. Four regenerated cellulose samples, prepared by saponification of cellulose acetate butyrates ranging in butyryl content from 18 to 48%, average 1.520. These results confirm the literature values cited and justify the use of the value 1.52 in the calculation of densities.

DENSITIES OF CELLULOSE ESTERS. Cellulose acetate densities, both observed and calculated, are shown in Table II for samples of varying degrees of hydrolysis. These values have been plotted against acetyl content (Figure 2) and the line for observed densities extrapolated to 1.52 for regenerated cellulose. The values represent a variety of cellulose acetate samples and are not a single hydrolysis series.

TABLE I. DENSITIES OF CELLULOSE

Type	Obsvd. Density	Method[a]	Immersion Medium
Absorbent cotton	1.555	F	C_6H_6–CCl_4
Cotton thread	1.535	A	CCl_4
Cotton linters (acetylation grade)	1.537	F	C_6H_6–CCl_4
Wood pulp (acetylation grade)	1.534	F	Same
Raw cotton linters	1.543	F	Same
Cuprammonium rayon	1.527	A	CCl_4
Chardonnet-type rayon	1.515	A	Same
Washed Cellophane	1.512	A	Same
Regenerated from cellulose acetate butyrate	1.521	F	$C_2H_2Br_4$–$C_6H_4(CH_3)_2$
	1.518	F	Same
	1.523	F	Same
	1.518	F	Same

[a] A = Archimedes method, F = flotation method.

TABLE II. DENSITIES OF CELLULOSE ACETATE

(Archimedes method using carbon tetrachloride was used on all samples)

Sample	Acetyl, %	Obsvd. Density	Calcd. Density
1	44.0	1.288	1.302
2	43.4	1.289	1.304
3	43.3	1.287	1.305
4	40.8	1.304	1.315
5	40.5	1.304	1.316
6	40.3	1.306	1.317
7	39.3	1.311	1.321
8	38.4	1.314	1.325
9	38.3	1.315	1.326
10	33.0	1.346	1.350
11	23.7	1.373	1.394
12	22.6	1.375	1.399
13	17.8	1.426	1.423
14	17.3	1.415	1.426
15	16.8	1.433	1.428
16	16.7	1.417	1.429
17	14.9	1.445	1.438

TABLE III. DENSITIES OF CELLULOSE ACETATE PROPIONATE

Sample	Acetyl, %	Propionyl, %	Obsvd. Density	Calcd. Density	Method[a]	Immersion Medium
1	2.8	48.4	1.203	1.20	A	H_2O
2	..	49.5	1.230	1.22	A	Same
3	..	46.5	1.238	1.23	A	Same
4	2.0	45.0	1.240	1.23	A	Same
5	..	45.3	1.242	1.24	A	Same
6	5.7	39.0	1.244	1.24	A	Same
7	13.0	33.0	1.250	1.25	A	CCl_4
8	..	44.0	1.253	1.25	A	H_2O
9	4.0	38.0	1.262	1.26	A	CCl_4
10	10.0	33.0	1.262	1.26	A	CCl_4
11	..	42.7	1.264	1.25	A	H_2O
12	30.0	17.0	1.264	1.26	F	C_6H_6-CCl_4
13	4.5	37.6	1.266	1.26	F	C_6H_6-CCl_4
14	8.0	32.0	1.269	1.27	A	CCl_4
15	31.0	16.0	1.270	1.27	F	C_6H_6-CCl_4
16	27.1	15.6	1.280	1.28	F	Same
17	28.0	17.0	1.280	1.27	F	Same
18	24.0	15.0	1.286	1.30	F	Same
19	20.0	14.5	1.318	1.32	F	Same
20	14.7	14.3	1.338	1.35	F	Same
21	6.6	22.1	1.342	1.34	F	Same
22	17.6	9.8	1.347	1.36	F	Same
23	13.5	12.7	1.348	1.36	A	CCl_4
24	4.7	19.3	1.361	1.36	F	C_6H_6-CCl_4
25	15.1	8.9	1.363	1.38	F	C_6H_6-CCl_4
26	8.9	19.5	1.367	1.34	A	CCl_4
27	15.0	8.4	1.368	1.38	F	C_6H_6-CCl_4
28	13.7	11.8	1.381	1.37	A	CCl_4
29	15.5	6.4	1.383	1.39	A	CCl_4
30	18.1	3.8	1.384	1.40	F	C_6H_6-CCl_4
31	5.0	12.0	1.406	1.42	F	C_6H_6-CCl_4
32	11.8	5.0	1.408	1.42	A	CCl_4
33	10.1	4.9	1.419	1.43	F	C_6H_6-CCl_4
34	11.6	5.3	1.423	1.42	F	Same
35	11.2	6.0	1.427	1.42	F	Same

[a] A = Archimedes method, *F* = flotation method.

TABLE IV. DENSITIES OF CELLULOSE ACETATE BUTYRATE

Sample	Acetyl, %	Butyryl, %	Obsvd. Density	Calcd. Density	Method[a]	Immersion Medium
1	1.5	56.3	1.172	1.15	A	H_2O
2	2.1	54.0	1.177	1.16	A	Same
3	6.5	46.5	1.183	1.18	A	Same
4	6.4	47.7	1.185	1.17	A	Same
5	6.1	48.3	1.187	1.17	A	Same
6	1.6	50.1	1.188	1.18	A	Same
7	5.7	45.6	1.192	1.19	A	Same
8	6.0	44.0	1.202	1.19	A	Same
9	14.8	35.7	1.209	1.21	A	Same
10	16.1	34.3	1.220	1.21	A	Same
11	7.1	40.5	1.222	1.21	A	Same
12	7.3	38.0	1.223	1.22	A	Same
13	12.0	37.8	1.225	1.20	F	C_6H_6-CCl_4
14	11.0	33.5	1.240	1.23	A	H_2O
15	19.2	27.5	1.241	1.24	F	C_6H_6-CCl_4
16	30.8	16.0	1.263	1.26	F	Same
17	15.5	25.1	1.264	1.27	F	Same
18	31.6	16.4	1.264	1.25	F	Same
19	32.0	15.4	1.268	1.26	F	Same
20	8.8	28.7	1.284	1.27	F	Same
21	33.0	8.0	1.285	1.30	A	CCl_4
22	21.0	17.0	1.287	1.29	A	CCl_4
23	10.0	22.4	1.306	1.31	F	C_6H_6-CCl_4
24	24.8	12.0	1.316	1.31	F	C_6H_6-CCl_4
25	7.5	19.7	1.319	1.33	F	Same
26	17.2	17.0	1.320	1.31	F	Same
27	10.0	14.6	1.340	1.36	F	Same
28	9.8	11.6	1.357	1.37	F	Same
29	5.0	16.2	1.360	1.37	F	Same
30	19.6	2.7	1.387	1.41	A	CCl_4
31	13.2	1.8	1.426	1.44	A	CCl_4

[a] A = Archimedes method, F = flotation method.

Densities observed for cellulose acetate propionates and acetate butyrates of varying higher acyl content and degree of hydrolysis are compared in Tables III and IV with calculated values. The samples are arranged in the order of increasing observed densities, and the methods of measurement and immersion media used are stated.

Figure 3 shows the relation between observed densities and the composition of cellulose acetates, propionates, and acetate propionates; a similar relation for cellulose acetates, butyrates, and acetate butyrates is shown in Figure 4. These figures were prepared graphically using a density of 1.52 for cellulose and observed values taken from Figure 2 to locate the intersections of the density lines with the acetyl scale. The slopes of those lines were established using these points and observed densities for various mixed esters.

Calculated densites are higher by 0.01 to 0.02 unit than the values observed for cellulose acetates and mixed esters whose compositions lie in the lower left corners of the triangles in Figures 3 and 4. The calculated values tend to be lower by about the same amount for mixed esters whose compositions lie in the lower right corners of these figures. In general, the observed and calculated values differ by less than 0.02 gram per cubic centimeter.

STUDY OF METHODS. Immersion media may be varied, as shown in Table V, without giving significant differences in observed densities. However, the effects of time of immersion and choice of medium are important in certain cases (Figure 5). The density of a cellulose acetate film of 43.3% acetyl was measured by the Archimedes method using both carbon tetrachloride and water. The variation of observed density with time was practically insignificant in the case of carbon tetrachloride but was appreciable in the case of water.

Density measurements by the flotation method do not vary with time if the media are properly selected, as shown by the five horizontal lines in Figure 6. Sample *A* (high butyryl cellulose acetate butyrate) immersed in tetrabromoethane-xylene mixtures gives observed density values which increase rapidly. This combination is therefore unsatisfactory for this type of ester. Figure 7 shows that the density observed for a cellulose acetate sample of 33% acetyl remains constant in a carbon tetrachloride-benzene mixture but decreases rapidly when immersed in cadmium sulfate-water mixtures.

These data illustrate the necessity for proper choice of the medium and the desirability of some knowledge of the composition and properties of the sample to be tested.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of James Harper, Mary Alice Pile, and Paul M. Pitts.

TABLE V. DENSITY OF CELLULOSE ACETATE FILM USING VARIOUS IMMERSION MEDIA

(Acetyl, 43.3%; calculated density, 1.305)

Obsvd. Density	Method[a]	Immersion Medium
1.285	A	CCl_4
1.285	A	C_6H_6
1.288	A	$C_6H_4(CH_3)_2$
1.287	A	$CH_3CHOHCH_3$
1.288	A	CH_3OH
1.284	A	H_2O + 0.1% Aerosol (OT)
1.290	F	C_6H_6-CCl_4

[a] A = Archimedes method, F = flotation method.

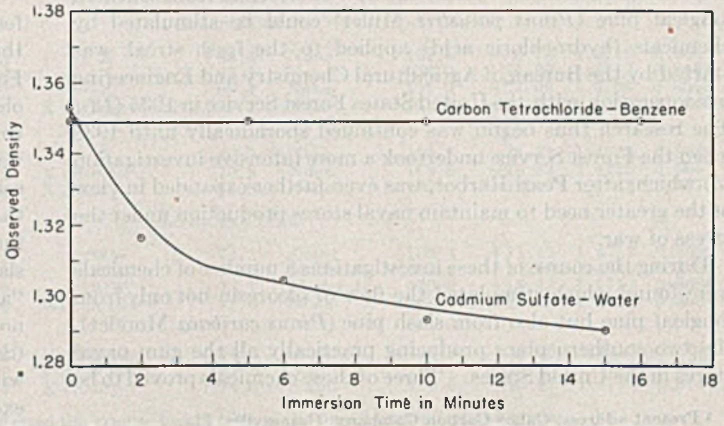

Figure 7. Effect of Time of Immersion on Density of Cellulose Acetate (33.0% Acetyl) as Measured by Flotation Method

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Received October 17, 1946. Presented before the Division of Cellulose Chemistry at the 110th Meeting of the American Chemical Society Chicago, Ill.

Properties of Oleoresins, Rosins, and Turpentines from Chemically Stimulated Slash and Longleaf Pines

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Applications of 25% sodium hydroxide, 24% hydrochloric acid, and 40 or 60% sulfuric acid to slash and longleaf pines affected few of the characteristics of the rosins and turpentines made from the oleoresins produced by the trees, and the oleoresins were in all cases normal with respect to their rosin and turpentine content. The effects on some of the commonly examined physical and chemical properties of the turpentine and rosin are not great when these chemicals are applied to the extent of 0.5 to 1.5 cc. per streak. In the case of turpentine, the properties measured remained well within the limits prescribed by A.S.T.M. specifications for gum turpentine. In the case of rosin, acid number and softening points of all samples were within normal ranges. No difficulty from excessive rosin crystallization was observed. Neither rosin color nor transparency was affected by the sodium hydroxide or hydrochloric acid treatments when glass cups were used. Application of 60% sulfuric acid usually caused a slight darkening of color. Application of 40 or 60% sulfuric acid generally caused some cloudiness or lack of clarity in the rosin. This cloudiness, apparently caused by traces of residual sulfuric acid or water-soluble sulfates, may be avoided by washing the gum during processing or by blending the treated gum with a sufficient amount of untreated gum.

APPLICATION of a chemical reagent to the freshly chipped streak is a promising recent development for increasing yields of gum naval stores. Studies in the use of chemicals to stimulate the flow of oleoresin were initiated almost simultaneously in Germany and Russia (*3, 7*). In the United States an exploratory test to determine whether the flow of oleoresin from southern longleaf pine (*Pinus palustris* Miller) could be stimulated by chemicals (hydrochloric acid) applied to the fresh streak was started by the Bureau of Agricultural Chemistry and Engineering in cooperation with the United States Forest Service in 1935 (*13*). The research thus begun was continued sporadically until 1938 when the Forest Service undertook a more intensive investigation (*5*) which, after Pearl Harbor, was even further expanded in view of the greater need to maintain naval stores production under the stress of war.

During the course of these investigations a number of chemicals were found which stimulated the flow of oleoresin not only from longleaf pine but also from slash pine (*Pinus caribaea* Morelet), the two southern pines producing practically all the gum naval stores in the United States. Three of these chemicals proved to be especially effective: sulfuric acid, hydrochloric acid, and sodium hydroxide (*11*). It then became necessary to determine whether these treatments affected the turpentine and rosin obtained by distillation of the oleoresin and whether these products meet marketing standards.

Previous reports (*1, 4, 8, 9*) in the literature concerning the effect of chemical stimulants on the character and composition of the oleoresin obtained are scanty and sometimes inconsistent. For instance, Sandermann (*8*) found no *l*-pimaric acid in the oleoresin from European *Pinus sylvestris* when the streaks were treated with 25% hydrochloric acid (40 to 48% of *l*-pimaric acid was found in the gum obtained from untreated streaks of this same species of pine). In contrast, Davis and Fleck (*1*) found that pine oleoresin obtained from streaks treated with 10% sulfuric acid showed the presence of 22.6% of *l*-pimaric acid from slash pine and 31.9% from longleaf pine. They concluded that "as far as the 10% sulfuric acid treatment is concerned, little or no change has been effected on the composition of the oleoresin." (Sandermann determined the *l*-pimaric acid content by reaction with maleic anhydride followed by acidimetric titration of the excess maleic anhydride, while Davis and Fleck determined the the *l*-pimaric acid content by reaction with maleic anhydride followed by gravimetric determination of the adduct formed.

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However, Fleck and Palkin (*2*) showed that the volumetric method gives values slightly higher (2 to 4%) than the gravimetric method.)

The present investigation deals with the effect of hydrochloric acid, sulfuric acid, and sodium hydroxide applied to the tree, on the rosin and turpentine contents of the gum and on some of the physical and chemical properties of the turpentine and rosin produced. Experimental work to obtain this information was begun in 1943 and continued through 1944. The investigation was a joint project of the Southern Forest Experiment Station of the United States Forest Service, Lake City, Fla., and the Naval Stores Research Division, Bureau of Agricultural and Industrial Chemistry, Olustee, Fla.

METHODS

In 1943 oleoresin was collected throughout the season (May to November) from slash and longleaf pines in the Osceola National Forest. These trees had not previously been worked. Galvanized iron cups and gutters were used on all trees. Forty untreated or check trees of each species were chipped each week; twenty trees of each species were chipped and treated with 25% sodium hydroxide each week; and twenty trees of each species were chipped and treated with 40% sulfuric acid every other week. The gum from each group of trees was thoroughly mixed after collection and an adequate sample reserved for laboratory distillation.

In 1944 the collection system was modified to obtain gum uncontaminated by metal. Glass cups and wooden gutters were substituted for the galvanized equipment used in 1943, and care was taken that no metal was used at any time during collection or distillation. Fewer trees were used; there were ten slash and fifteen longleaf pines in each treatment group. The trees selected were again in the Osceola National Forest and had not previously been worked. The slash pines were divided into four groups of ten trees each, one an untreated check group and three groups which received chemical treatment weekly, the first with 25% sodium hydroxide, the second with 24% hydrochloric acid, and the third with the 40% sulfuric acid. In addition, one slash and one longleaf pine were selected, and on each tree two faces fitted with glass cups and wooden gutters were chipped weekly. One face on each tree was treated after the weekly chipping with about 0.6 cc. of sulfuric acid, the slash pine receiving the 40% acid and the longleaf the 60%. The second face on each tree was chipped but not treated.

No attempt was made to measure the amount of acid or alkali applied. The treatment used ensured adequate coverage with a spray-type applicator, as recommended by the Forest Service. It is believed that the amount applied to the chipped streaks in 1944 must have been rather consistently in the neighborhood of 0.5 cc. per 8 inches of face width, an amount almost certainly much less than that applied in 1943, which was probably about 1.5 cc. per 8 inches of face width.

Samples of gum weighing 400 grams were distilled in the laboratory as soon as possible after collection by the usual method of steam distillation. Distillation was continued until the distillate contained only 10% of turpentine by volume. At no time during the distillation was the temperature permitted to exceed 160° C. The turpentine and rosin obtained were weighed separately and the yields of each determined on a water-, chip-, and trash-free basis. The weight of trash and chips was obtained by weighing the residue after the rosin had been filtered through flannel. The percentage of moisture was determined by American Society for Testing Materials (A.S.T.M.) Method D95-40. The turpentine samples were stored in glass bottles, and tests for physical constants, density, refractive index, and optical activity were performed as soon as possible, usually within 48 hours. The rosin samples were graded by three persons to reduce the error of personal judgment. All distillations and other determinations were carried out by the same analyst throughout both years. Crystallization tendencies of rosin samples were found by the acetone method of Smith and Palkin (*10*). Softening points were determined by the ring and ball method (A.S.T.M. designation E28-42T).

RESULTS AND DISCUSSION

Some of the characteristics observed during the experiments conducted for the present investigation in the oleoresins obtained from both treated and untreated slash and longleaf pines, and the characteristics observed in the turpentines and rosins obtained from these oleoresins, are summarized in Table I and discussed in this section.

OLEORESINS. It was found that the amounts of turpentine and rosin in the oleoresins from the chemically stimulated trees had increased in proportion to the increase in the yield of oleoresin. Moreover, the ratio of turpentine to rosin in the oleoresin was normal—that is, it showed no significant difference that could be attributed to the chemical stimulation treatment.

No difference was noted in the appearance of the oleoresins from treated and untreated pines, nor were any differences found in behavior during distillation of treated and untreated samples. Fresh oleoresin from trees treated with either 40 or 60% sulfuric acid had a distinct sharp odor, which disappeared, however, as the gum aged.

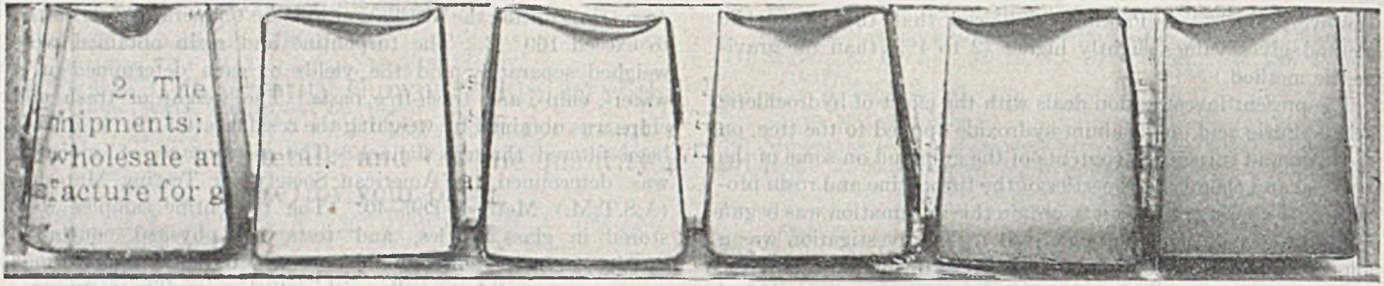
TURPENTINE. Hessenland (*4*) and Sandermann (*9*) were of the opinion that turpentine was unaffected by the use of 25% hydrochloric acid applied to the streaks. In the present investigation, although minor and rather irregular differences in the refractive index and specific gravity of the various turpentines obtained were observed, all values remained well within the limits prescribed by the A.S.T.M. specifications for gum turpentine.

Table I. Seasonal Average Characteristics of Oleoresins, Turpentines, and Rosins from Treated and Untreated Trees, 1943 and 1944

	Oleoresin, %		Rosin				Turpentine		
Treatment	Rosin	Turpentine	Grade[a]	Softening point, °C.	Crystals	Acid No.	α_D^{20}	n_D^{20}	Sp. gr. at 15.5°C
				Slash Pine					
1944									
Untreated	79.2	20.5	X	68.4	None	162.0	−20.78	1.4710	0.8665
25% NaOH	79.9	19.8	X	67.1	None	158.9	−25.89	1.4712	0.8655
24% HCl	79.4	20.2	X	68.4	None	161.0	−23.09	1.4709	0.8659
40% H_2SO_4	79.4	20.8	X slightly cloudy	70.3	None	161.8	−21.91	1.4704	0.8663
1943									
Untreated	79.4	20.6	X	69.8	None	163.7	−14.31	1.4728	0.8669
25% NaOH	78.9	21.2	X off-color	70.2	None	163.8	−16.38	1.4725	0.8661
40% H_2SO_4	79.3	20.6	X cloudy	69.8	None	162.5	−12.43	1.4728	0.8673
				Longleaf Pine					
1944									
Untreated	78.4	21.4	WW	74.1	Slight	169.4	+11.59	1.4712	0.8682
25% NaOH	77.9	21.6	WW	74.1	Moderate	169.4	+11.18	1.4715	0.8682
24% HCl	77.9	21.9	WW	75.1	Moderate	170.2	+13.12	1.4714	0.8680
60% H_2SO_4	78.8	21.4	WG cloudy	77.6	None	168.5	+11.31	1.4710	0.8681
1943									
Untreated	81.1	18.9	H off-color	74.4	Slight	169.0	+16.96	1.4713	0.8691
25% NaOH	81.4	18.7	F off-color	74.5	Slight	167.1	+16.96	1.4710	0.8679
40% H_2SO_4	81.3	18.7	K cloudy	74.8	Slight	169.6	+15.87	1.4713	0.8687

[a] In 1943 galvanized cups affected the grades, but in 1944 glass cups did not affect the grades.

[b] 10-cm. tube.



COURTESY, U. S. FOREST SERVICE

Figure 1. Cloudiness of Rosin with Increasing Amounts of Sulfuric Acid

Figures represent approximate volume of 40% sulfuric acid in milliliters per 8 inches of face width. The asterisk after fifth figure indicates shallow bark chipping; all other samples were obtained by the ordinary method of chipping.

Table II. Zinc and Sulfur Contents of Rosin in Relation to Amount of Sulfuric Acid Applied to Trees^a (*12*)

40% H_2SO_4 per 8-In. Streak, Cc.	Turbidity	% Zinc, Av.	% Water-Sol. Sulfur, Av.
0	None	0.0015	<0.001
1/4	Very slight	0.0029	0.001
1/2	Slight	0.013	0.0015
1	Cloudy	0.0044	0.0075
1 1/2	Opaque	0.0022	0.027

[a] Acknowledgment is made to R. T. O'Connor, Dorothy C. Heinzelmann, and R. H. Robinson of the Southern Regional Research Laboratory, New Orleans, La., for these analyses.

Rosin. In none of the tests conducted during the present investigation in either 1943 and 1944 was any difficulty encountered from excess rosin crystallization following application of any of the three chemicals to slash or longleaf pines. No crystallization was observed in rosin obtained from treated or untreated slash pine. Rosin from untreated longleaf pine occasionally crystallized to a slight extent in the acetone test applied, and this same slight tendency to crystallize was shown in rosin obtained in 1943 from longleaf trees treated with sodium hydroxide or hydrochloric acid. Rosin obtained in 1944 from longleaf trees treated with 25% sodium hydroxide or 24% hydrochloric acid showed a moderate crystallizing tendency, whereas the 60% sulfuric acid treatment caused no crystallization. This virtual lack of crystallization is in contrast to the results obtained by Hessenland (*4*) and Sandermann (*9*) with application of hydrochloric acid to *Pinus sylvestris*, when such extreme crystallization occurred that methods had to be found to reduce the crystallization not only in the rosin but also in the crude oleoresin. Rosin that has a tendency to crystallize is, of course, undesirable for many uses.

For all rosin samples from both years the softening points and acid numbers were well within normal ranges for gum rosin; and no significant differences attributable to chemical treatment were observed in either of these characteristics.

Rosin transparency and color (hence grade) appear to be the characteristics most affected by chemical treatment. Although neither sodium hydroxide nor hydrochloric acid in the concentrations and amounts tested had any effect on the appearance of the rosins, sulfuric acid in certain concentrations affected both transparency (Figure 1) and color.

Both the 40% and 60% concentrations of sulfuric acid caused some cloudiness, or lack of transparency, in the rosin. The cloud was apparent in rosin made from gum collected in either metal or glass cups. The possibility was considered that the cloudiness arose from the presence of zinc sulfates that might have resulted from reaction of the galvanized iron cups with the sulfuric acid applied to the tree, but a series of tests in which the oleoresin was collected in galvanized iron cups showed no correlation between the amount of cloud and the amount of zinc in the rosin. This series did show a definite correlation between the amount of sulfuric acid applied to the tree, the amount of visible cloud in the rosin, and the water-soluble sulfur content of the rosin. Accordingly, it would seem that the cloud-forming material consisted of traces of residual sulfuric acid or water-soluble sulfates (Table II).

Since clarity is a characteristic considered in the grading of rosin, excessive cloudiness in rosin may degrade it. Cloudiness resulting from treatment of the trees with sulfuric acid can be eliminated if the gum is washed before distillation, or it can be reduced sufficiently to avoid degrading if the treated gum is blended with adequate quantities of untreated gum (*12*).

Application of 60% sulfuric acid to longleaf pines almost invariably caused a slight darkening of the color of the rosin. This darkening of color, another factor in grade lowering, did not occur with application of 40% sulfuric acid to either slash or longleaf pines; these results were confirmed by the experiments in which untreated and sulfuric acid–treated faces on the same tree were chipped. With the other chemicals tested no darkening of color was observed.

ACKNOWLEDGMENT

For the supervision of the chipping and gum collection the authors are indebted to A. G. Snow, Jr., of the Southern Forest Experiment Station, Lake City, Fla., for the 1943 season, and to N. C. McConnell of the Naval Stores Station, Olustee, Fla., for the 1944 season. For many helpful suggestions and comments the authors also express appreciation to I. E. Knapp, L. A. Goldblatt, R. V. Lawrence, and G. P. Shingler of the Naval Stores Research Division, Bureau of Agricultural and Industrial Chemistry, United States Department of Agriculture, and to C. E. Ostrom of the United States Forest Service.

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Received June 6, 1946.

Cellulose Intercrystalline Structure

STUDY BY HYDROLYTIC METHODS

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In the hydrolysis of cellulosic fibers with aqueous hydrochloric and sulfuric acids at boiling temperatures, the disordered intercrystalline chain network appears to be attacked first. This inference is drawn from sharp reductions in cuprammonium viscosity and moisture regain coincident with the rapid accumulation of glucose. Simultaneously the fibers are reduced to powdery hydrocellulose. With further hydrolysis glucose continues to form and moisture regain slowly increases, but viscosity remains practically constant. Attack in this stage may be chiefly on lateral crystallite surfaces. Lengths of crystallites calculated from viscosity data range from 280 glucose units for cotton to 110 for high tenacity viscose rayon. Sulfuric acid is much less active than hydrochloric in hydrolyzing cellulose and, after neutralization, does not interfere with the direct volumetric determination of glucose.

STUDIES previously reported from this laboratory showed that the behavior of unsubstituted celluloses during acid hydrolysis is consistent with the concept of these as crystallites interlaced by an intercrystalline cellulose chain network. The intercrystalline cellulose appears to consist of two distinguishable parts, arbitrarily called amorphous and mesomorphous components (*7*, *8*). The amorphous component is probably the most disordered part of the structure; the mesomorphous, the transitional state between most disordered and highly ordered components.

The hydrolysis-oxidation method (*6*) employed in these investigations results in extensive decomposition of samples and so yields a broad insight into hydrolytic behavior, but it has some major disadvantages. The samples are degraded rapidly and severely, and, accordingly, the method lacks precision in these initial stages of the hydrolytic process where important changes appear to occur. The method also affords only indirect estimates of the amounts of cellulose hydrolyzed to glucose, and, finally, it exhibits considerable experimental error (*2*, *7*). Thus, in addition to this method, milder conditions and greater precision are desirable for the study of the readily attacked intercrystalline cellulose.

This paper describes a direct, precise method of determining the course of cellulose breakdown under much milder conditions than have heretofore been utilized. Hydrolysis data obtained by the application of this method are given for a number of different cellulosic materials. The variation of moisture regain and cuprammonium viscosity with progressive mild hydrolysis is also shown. Hydrolysis, viscosity, and regain data for one case of the more severe treatment are included to permit a comparison of results from the two methods.

HYDROLYSIS-OXIDATION METHOD

The hydrolysis-oxidation method consists in digesting the cellulosic material in boiling 2.45 *N* hydrochloric acid–0.6 *M* ferric chloride and determining the extent of hydrolysis from the carbon dioxide evolved. The latter appears to originate principally from glucose and other low-molecular-weight split products of cellulose. In practice, hydrolysis appears to proceed at a rapid initial rate which coincides with an equally rapid fall in moisture regain of the recoverable hydrocelluloses. After about 4 minutes the rate of hydrolysis seems to decrease perceptibly, whereas the regain of the corresponding hydrocelluloses ceases to fall and begins a steady rise. These effects are assumed to indicate the rapid decomposition of the hygroscopic, amorphous fraction and the beginning of the breakdown of mesomorphous material (*7*). The latter apparently hydrolyzes at a steadily decreasing rate for about an hour. Thereafter the rate remains fairly constant for several hours and is assumed to represent hydrolysis of the crystalline component.

Data which typify these effects for acetate grade cotton linters are summarized in Table I. In addition, cuprammonium (cuam) viscosity values determined by the method of Mease (*4*) are also presented. Estimates of degree of polymerization (D.P.) were calculated from viscosities with the equation of Battista (*1*). The hydrolysis data are taken from a previously reported study (*7*), which contains details of preparation and treatment of hydrocelluloses. Moisture regain values represent adsorption at 65% relative humidity.

The effects of hydrolysis with hydrochloric acid–ferric chloride reagent are set forth graphically in Figure 1, which is based on the data of Table I. Moisture regain and cellulose hydrolyzed clearly exhibit the behavior described. Viscosity, however, falls sharply with progressive hydrolysis, reaches a low value, and then remains constant for several hours despite appreciable further decomposition of the linters residue. A similar result was found by Staudinger and Sorkin (*10*), who investigated the effects of acid hydrolysis by viscometric methods and concluded that chain shortening ceases where cellulose molecule fragments reach lengths of from 150 to 200 glucose units.

TABLE I. EFFECT OF SEVERE HYDROLYTIC TREATMENT[a] ON SEVERAL CHARACTERISTICS OF ACETATE-GRADE COTTON LINTERS

Time Treated, Hr.	Calcd. Cellulose Hydrolyzed, % of Dry Wt.[b]	Adsorption Regain at 65% R.H., %	Cuam Viscosity of 0.5% Soln., Cp.	Calcd. Basic[c] D.P.
0	0	6.48	13.76	1760
0.07	3.3	5.31	1.83	274
0.20	5.5	5.46	1.75	248
0.80	8.9	5.68	1.78	259
2.0	12.6	5.86	1.73	242
4.0	17.0	6.25	1.73	242
7.0	21.9	6.40	1.75	248

[a] With boiling 2.45 *N* HCl–0.6 *M* FeCl$_3$ except for the very short time intervals for which boiling 2.45 *N* HCl was used.

[b] Calculated from carbon dioxide evolution (*7*).

[c] In glucose units as found by the equation of Battista (*1*).

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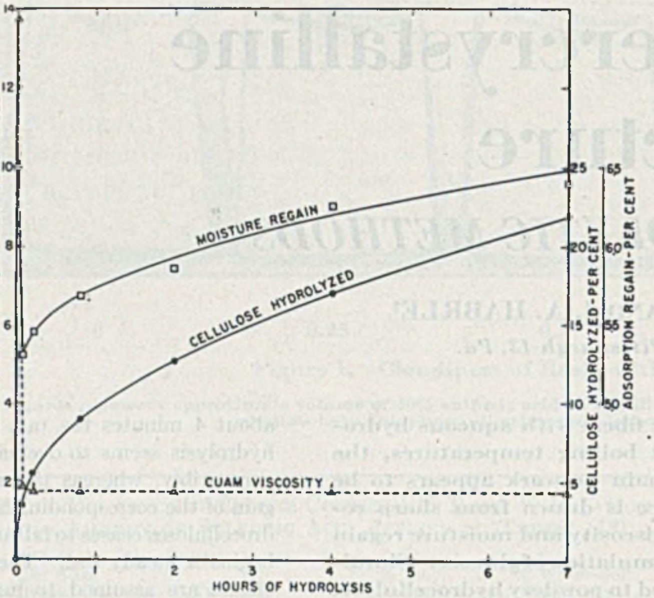

Figure 1. Effects on Cotton Linters of Hydrolysis with 2.45 N HCl–0.6 M $FeCl_3$ as Functions of Time

Percentage hydrolyzed calculated from carbon dioxide yields; regain and viscosity represent recovered hydrocelluloses.

Several conclusions may be drawn from these observations. First, the rapid initial rate of hydrolysis indicates that highly disordered or readily accessible cellulose is attacked, presumably the amorphous component. Secondly, disintegration and removal of this component coincide with a sharp reduction in moisture regain, which suggests that in the linters this component was relatively highly hygroscopic. Thirdly, removal of this component also coincides with a pronounced diminution in viscosity which indicates that the highly disordered regions occur periodically and include a large proportion of the molecules. Fourthly, reversal in trend of regain and leveling off of viscosity after the first few minutes are evidence that chain shortening ceases with the removal of the hygroscopic cellulose. Since decomposition of the cellulose continues and moisture regain begins to rise, chain length remaining constant, it is reasonable to conclude that attack must then be principally on the lateral surfaces of crystallites. This attack would effect a relatively rapid increase in surface area per gram of the hydrocellulose and would perhaps explain the rising moisture regain in the case of moisture-impervious crystallites. [A question has been raised concerning the possible effects on moisture regain data of "humic substance" whose formation under acidic conditions was studied by Philip, Nelson, and Ziifle (*9*). That humic material does not influence present results is probable for two reasons: (*a*) Its accumulation is largely, if not completely, prevented by the oxidizing action of ferric chloride, and (*b*) after the acid treatment the hydrocelluloses were washed with dilute ammonia which dissolves such material. The final hydrocelluloses were pure white (*7*).] Finally, hydrolysis appears to proceed at a decreasing rate for about an hour and thereafter to continue at a fairly constant rate. If the attainment of constant rate represents the slow hydrolysis of dense, homogeneous, crystalline material, then it may be assumed that any mesomorphous or partially ordered cellulose has at this stage been eliminated. Some evidence that constant rate of hydrolysis is attained in about an hour has already been given (*7*), and further evidence is presented later in this report. However, since progressive hydrolysis of the mesomorphous or transitional cellulose has no apparent effect on viscosity and no unique effect on regain, it follows that this partially ordered cellulose is similar to the highly ordered, differing from it only in being more readily hydrolyzed.

Further support for this explanation of moisture regain variation is given by adsorption and desorption data for acetate grade linters and high tenacity viscose rayon (Table II). Each series of progressively hydrolyzed samples was conditioned in parallel at 65% relative humidity. The same samples were used for both adsorption and desorption measurements, drying being effected in vacuo at room temperature over phosphoric anhydride. Viscose rayon data are included because that material is different in regain behavior from natural and modified celluloses. The somewhat erratic results for the rayon samples subjected to prolonged acid treatment may be attributed to the fact that these hydrocelluloses tend to dry to horny transparent lumps.

Table II. Variation of Adsorption and Desorption Moisture Regain at 65% Relative Humidity of Acetate-Grade Linters and Viscose Rayon with Hydrolysis

	Linters			Viscose Rayon		
Time Hydrolyzed, Hr.	Desorption, %	Adsorption, %	Des./Ads. Ratio	Desorption, %	Adsorption, %	Des./Ads. Ratio
0^a	7.67	6.48	1.18	14.2	12.1	1.17
0.07	6.18	5.31	1.16	9.71	8.70	1.12
0.20	6.48	5.46	1.19	9.83	8.63	1.14
0.80	6.80	5.68	1.20	9.90	8.60	1.15
2.0	7.05	5.86	1.20	9.72	8.68	1.12
4.0	7.78	6.25	1.24	10.2	8.90	1.15
7.0	8.73	6.40	1.36	9.96	8.75	1.14

It is apparent that hydrolysis causes an initial sharp reduction in regain in both cases, but, unlike the linters, the viscose rayon fails to exhibit a subsequent reversal in trend. This difference may arise from a relatively high perviousness of the rayon crystallites to moisture as compared to linters crystallites (*5*). The small drop in desorption/adsorption ratio which accompanies the initial reduction in regain suggests that disintegration of the amorphous component lowers slightly the hysteresis effect. Despite this indication of a small change in the amount of capillary condensed moisture as a result of hydrolysis, there seems to be ample reason for assuming that the principal cause of the large regain diminution is the destruction of a highly hygroscopic component of the intact structure. Free cellulosic hydroxyl groups are known to have high affinity for moisture. It is evident, therefore, that the highly hygroscopic regions of the fiber must be unusually rich in free hydroxyls, which would be the case if these regions were highly disordered.

SULFURIC ACID HYDROLYSIS

The preceding experiments show that hydrochloric acid–ferric chloride reagent effects extremely rapid hydrolytic changes at the outset of the process. Less severe conditions of hydrolysis were obviously necessary for the investigation of this region, but lowering the concentration of hydrochloric acid in the reagent would make carbon dioxide data difficult to interpret (*6*). Exploratory work, however, indicated that boiling 2.5 N sulfuric acid caused suitably slow hydrolysis, and this medium was selected for subsequent experiments.

DIRECT DETERMINATION OF GLUCOSE

The method of Hassid (*3*) was found to be entirely satisfactory for the direct determination of glucose both in known glucose solutions and in sulfuric acid hydrolyzates of cellulose. This method consists in treating a dilute glucose solution with excess alkaline ferricyanide and titrating the ferrocyanide produced by the oxidation of glucose with standard ceric sulfate. In the experiments to be described the ceric sulfate was standardized against known glucose controls run in parallel with each series of unknowns.

It was first determined that refluxing with 2.5 N sulfuric acid did not influence the analytical results. Known glucose solutions were boiled under reflux for varying times with 2.5 N sulfuric acid,

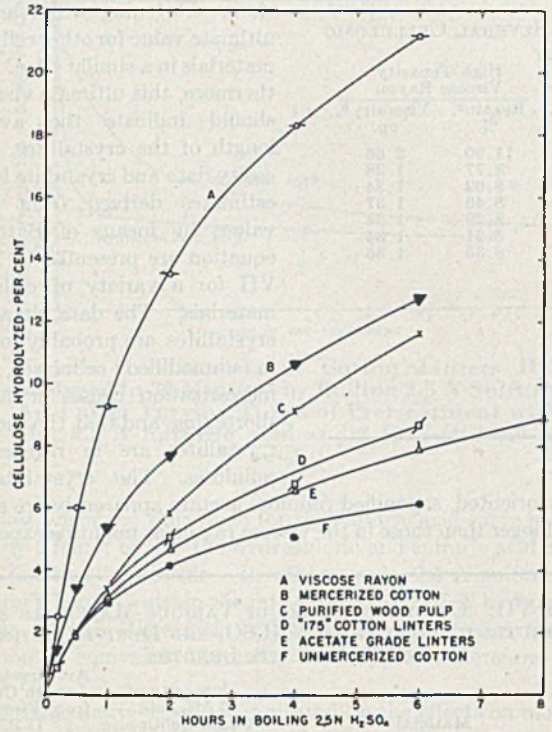

Figure 2. Effect of Time in Boiling 2.5 N Sulfuric Acid on Cellulose Hydrolyzed for Various Cellulosic Materials

neutralized with 5 N sodium hydroxide, and then tested by the Hassid method. The data from a typical experiment are presented in Table III. Neither the acid treatment for periods up to 12 hours nor the subsequent neutralization alters the glucose estimates.

Table III. Glucose Observed after Treatment of 0.2% Solution with Boiling 2.5 N H_2SO_4 and Neutralization

Hours boiled	0	Onset of boiling	2	4	6	12
Glucose found, % of taken	100	98	103	103	103	99

Similar check tests were made on cellobiose, since it is probably a product of cellulose hydrolysis. Aliquots were removed from a known cellobiose solution after varying times of reflux with 2.5 N sulfuric acid, neutralized with 5 N sodium hydroxide, made up to suitable volumes, and assayed for glucose. The apparent yields are shown in Table IV. The data indicate that at least 15 minutes' hydrolysis under these conditions is necessary to convert cellobiose to glucose. However, the error from this source in cellulose hydrolyzates would not be appreciable, especially where the hydrolysis extended over relatively long periods.

Table IV. Apparent Glucose in 0.2% Cellobiose after Treatment with Boiling 2.5 N H_2SO_4 and Neutralization

Hours boiled	0	0.083	0.25	0.50	1.0	2.0	4.0
Apparent glucose, % of theoretical[a]	85	93	97	100	101	100	97

[a] $\frac{360}{342} \times 0.2 = 0.210\%$, glucose concentration at complete hydrolysis.

These experiments indicate that sulfuric acid hydrolysis and volumetric analysis for glucose can be applied in cellulose investigations. A subsequent section of this paper shows that sulfuric acid and hydrochloric acid as used in these experiments have similar hydrolytic effects and appear to differ only in the rate at which the effects are produced. Therefore, it may be assumed that the rapid changes which occur in the early stages of hydrolysis with hydrochloric acid–ferric chloride reagent can be examined more closely by the use of sulfuric acid hydrolysis and volumetric glucose analysis.

PREPARATION OF CELLULOSE HYDROLYZATES

Accurately weighed samples representing approximately 1.5 grams of oven-dry cellulosic material were refluxed for varying lengths of time in about 60 ml. of 2.5 N sulfuric acid and filtered in Alundum crucibles. The insoluble residues were carefully washed with successive small portions of hot water, and the combined filtrate and washings set aside for glucose determinations. The solid residues of hydrocellulose were again washed with hot water, then with dilute ammonia, and finally with more hot water. Thereafter the hydrocelluloses were air-dried and saved for moisture regain and cuprammonium viscosity determinations.

The combined filtrate and washings were cooled and made up to 100 ml., from which a 25-ml. aliquot was transferred to a 50-ml. volumetric flask, neutralized with 5 N sodium hydroxide, and diluted to volume. Glucose was determined in triplicate on 10 ml. portions of the latter solution, and the average so found was corrected to unit weight of dry starting material and converted to cellulose by the factor 0.9.

The air-dried hydrocelluloses representing varying times of sulfuric acid hydrolysis of a given material were conditioned simultaneously at 21° C. and 65% relative humidity to constant weight and then dried in vacuo over phosphoric anhydride at room temperature. After moisture regain was so found, the hydrocelluloses were used for cuprammonium viscosity determinations.

HYDROLYSIS DATA

Cellulose hydrolyzed–time data obtained as described for several typical cellulosic materials are presented graphically in Figure 2. These curves indicate that the three unmodified celluloses—that is, unmercerized lint cotton, acetate-grade linters, and "175" linters (175 seconds viscosity, Hercules system)—are similar in behavior during the first half hour but thereafter become divergent. Purified wood pulp appears initially to hydrolyze like the unmodified celluloses and later to simulate mercerized cotton. Since the mercerized cotton represents some of the unmercerized cotton which had been treated with 25% sodium hydroxide in the absence of tension (*8*), it can readily be seen that mercerization increases the extent of hydrolysis at all stages of the process. The relatively rapid breakdown of high tenacity viscose rayon over the whole range confirms previous results (*5*, *8*). In general, the curves indicate that all the materials may represent molecular ordering ranging from highly disordered and readily accessible to well ordered and less readily hydrolyzed fractions. The absence of transitional irregularities in the curves suggests that all degrees of ordering may coexist in the intact substances.

The variation of moisture regain and cuprammonium viscosity with time of sulfuric acid hydrolysis is shown for a number of cellulosic materials by the data in Table V. The effects of such

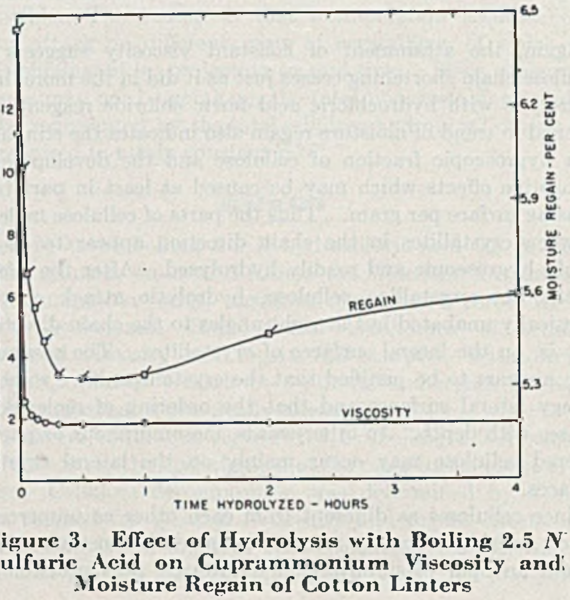

Figure 3. Effect of Hydrolysis with Boiling 2.5 N Sulfuric Acid on Cuprammonium Viscosity and Moisture Regain of Cotton Linters

TABLE V. VARIATION OF ADSORPTION REGAIN AND CUAM VISCOSITY OF SEVERAL CELLULOSIC MATERIALS WITH HYDROLYSIS BY BOILING 2.5 *N* H_2SO_4

Time Hydrolyzed, Hr.	No. 175 Linters		Unmercerized Cotton		Mercerized Cotton		High Tenacity Viscose Rayon	
	Regain[a], %	Viscosity[b], cp.	Regain[a], %	Viscosity[b], cp.	Regain[a], %	Viscosity[b], cp.	Regain[a], %	Viscosity[b], cp.
0	6.33	11.05	6.31	14.5	8.14	12.7	11.90	2.66
0.2	5.23	1.88	5.33	1.92	6.35	1.63	8.77	1.38
0.5	5.19	1.77	5.24	1.81	6.23	1.56	8.62	1.34
1.0	5.20	1.75	5.35	1.79	6.42	1.57	8.46	1.37
2.0	5.35	1.73	5.45	1.72	6.45	1.52	8.29	1.34
4.0	5.47	1.73	5.64	1.74	6.59	1.53	8.21	1.34
6.0	5.44	1.75	5.65	1.77	6.46	1.55	8.35	1.36

	Linen		High Tenacity Saponified Cellulose Acetate		Egyptian Cotton (Malaki)	
0	6.91	6.55	10.3	2.03	6.88	24.7
0.2			8.80	1.41	5.88	1.95
0.5	6.33	1.82	8.45	1.40	5.79	1.86

[a] At 65% R.H., 21° C.

[b] 0.5% solution in cuam.

hydrolysis at the outset of the process are illustrated in greater detail in Figure 3. The data and curves reveal that both regain and viscosity fall sharply at first and then begin to level off. Viscosity appears to reach a low ultimate value in half an hour and thereafter to remain constant. The regain, however, after reaching a minimum value in approximately half an hour, apparently begins a gradual rise. The absence of such a rise in the case of viscose rayon has been noted and has been discussed briefly.

The hydrolysis curves in Figure 2 show that no major change in rate of breakdown occurs in the vicinity of half an hour. Similarly, under the more drastic hydrolysis-oxidation conditions already mentioned, the attainment of constant viscosity and the inversion of the regain trend are not reflected in the cellulose hydrolyzed relation. Simultaneous values of cellulose hydrolyzed by sulfuric acid in half an hour and of moisture regain reduction in the same period are recorded for corresponding samples in Table VI. These data are taken from Figure 2 and Table V. A correlation between these variables is clearly indicated, although the number of samples is not large enough to establish a valid relation.

TABLE VI. MOISTURE REGAIN REDUCTION AND PERCENTAGE OF CELLULOSE HYDROLYZED IN 30 MINUTES BY BOILING 2.5 *N* H_2SO_4

Material	Viscose Rayon	Mercerized Cotton	No. 175 Linters	Unmercerized Cotton
Cellulose hydrolyzed, %	5.70	3.25	2.00	1.80
Regain difference, %	3.28	1.91	1.14	1.07

Again, the attainment of constant viscosity suggests that cellulose chain shortening ceases just as it did in the more drastic hydrolysis with hydrochloric acid–ferric chloride reagent. The reversal in trend of moisture regain also indicates the elimination of a hygroscopic fraction of cellulose and the development of absorptive effects which may be caused at least in part by increasing surface per gram. Thus the parts of cellulose molecules between crystallites in the chain direction appear to be both highly hygroscopic and readily hydrolyzed. After the removal of this intercrystalline cellulose, hydrolytic attack continues practically unabated but at right angles to the chain direction—that is, on the lateral surfaces of crystallites. The assumption then appears to be justified that the crystallites have somewhat spongy lateral surfaces and that the ordering of molecules increases with depth. In other words, mesomorphous or partially ordered cellulose may occur mainly on the lateral crystallite surfaces.

Since celluloses as different from each other as unmercerized cotton and high tenacity viscose rayon reach constant viscosity in half an hour of sulfuric acid hydrolysis, it is probable that chain shortening will reach an ultimate value for other cellulosic materials in a similar time. Furthermore, this ultimate viscosity should indicate the average length of the crystallites. Viscosity data and crystallite length estimates derived from these values by means of Battista's equation are presented in Table VII for a variety of cellulosic materials. The data show that crystallites are probably longest in unmodified celluloses, that mercerization causes crystallite shortening, and that the shortest crystallites are in regenerated celluloses. The crystallites in highly oriented, saponified cellulose acetate apparently are somewhat longer than those in the viscose rayon, as might be expected.

TABLE VII. CUAM VISCOSITIES OF VARIOUS MATERIALS AFTER 30 MINUTES IN BOILING 2.5 *N* H_2SO_4 AND DERIVED ESTIMATES OF CRYSTALLITE LENGTHS

Material	Viscosity of 0.5% Soln., Cuam-Centipoise	Av. Crystallite Length Calcd. from Viscosity, D.P.
Egyptian cotton (Malaki)	1.86	283
Linen	1.82	270
Unmercerized cotton	1.76	253
Acetate-grade cotton-linters	1.75	248
No. 175 linters	1.74	244
Mercerized cotton	1.54	179
High tenacity saponified cellulose acetate	1.40	132
High tenacity viscose rayon	1.34	110

HYDROLYSIS BY SULFURIC AND HYDROCHLORIC ACIDS

It was mentioned that the hydrolytic process appears to be the same for sulfuric and hydrochloric acids, even though sulfuric acid is much less active than hydrochloric of equivalent concentration. The similarity in action of the two acids is shown by the experiments which are now described.

Samples of acetate-grade cotton linters from the batch used for the preceding experiments were treated for varying times with boiling 2.5 *N* sulfuric acid as outlined in the section on preparation of cellulose hydrolyzates. The insoluble residues of hydrocellulose so obtained were carefully washed and dried. Thereafter samples of the hydrocelluloses representing varying amounts of sulfuric acid pretreatment were oven-dried for 2 hours at 105° C., weighed accurately, and refluxed for an additional half hour with 2.5 *N* sulfuric acid. Hydrolyzates were separated from these digests and employed for glucose determinations in accordance with the above procedure. Similarly, solid hydrocellulose residues representing acetate-grade linters which had been treated with boiling hydrochloric acid–ferric chloride reagent for varying times (Table I) were dried, weighed, and hydrolyzed for an additional half hour in 2.5 *N* sulfuric acid. Glucose was also determined in these hydrolyzates and calculated to cellulose.

The cellulose-hydrolyzed data obtained from these two series of hydrocelluloses are presented graphically in Figure 4. The curves represent reaction rate variations with time. In other words, the curves show the relative amounts of cellulose hydrolyzed in comparable half-hour increments after the hours of pretreatment which appear as abscissas. It is apparent that 2.5 *N* hydrochloric acid, as the hydrolytically active constituent of hydrochloric acid–ferric chloride reagent, hydrolyzes the linters at a rapidly decreasing rate which reaches a low and constant value in about an hour. A similar conclusion regarding the effects of hydrochloric acid was reached in a study by the differential method (*7*). The figure also shows that 2.5 *N* sulfuric acid decreases the rate much less rapidly than does hydrochloric of approximately equivalent normality. Nevertheless, the two processes appear to be essentially the same. This fact becomes

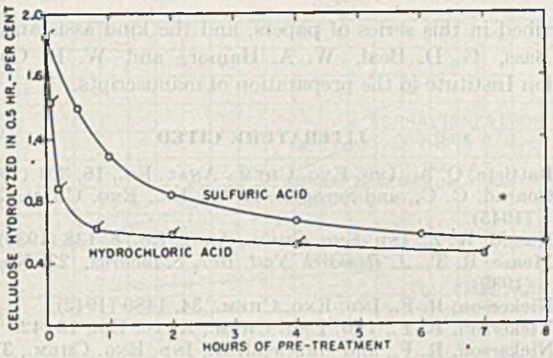

Figure 4. Amounts of Cotton Linters Hydrolyzed in 30 Minutes by Boiling 2.5 *N* Sulfuric Acid after Varying Times of Pretreatment with Hot 2.5 *N* Sulfuric Acid and 2.45 *N* HCl–0.6 *M* $FeCl_3$

manifest when the time scale for the sulfuric acid curve is shortened by a factor of $^1/_6$; the hydrochloric and sulfuric acid curves then practically coincide. In other words, 2.5 *N* sulfuric acid requires 6 hours to attain the rate reached by 2.45 *N* hydrochloric acid in 1 hour. The ratio of hydrolytic activities of the two acids on an equivalent normality basis appears, therefore, to be about 1:6.

The same activity ratio is indicated by the effects on moisture regain produced by the two acids (Figure 5). The moisture regain data were obtained by the procedure given. Corresponding minima in regain are produced by 2.45 *N* hydrochloric acid in approximately 4–5 minutes and by 2.5 *N* sulfuric in about 30 minutes. These results also suggest that the hydrolytic activities of sulfuric and hydrochloric acids are in the ratio of about 1:6. Finally, a comparison of the cuprammonium viscosity data for unmodified cotton celluloses in Tables I and V demonstrates that the constant low value produced by 2.45 *N* hydrochloric acid in 4 minutes agrees favorably with that produced by 2.5 *N* sulfuric in 30 minutes.

DISCUSSION OF RESULTS

The sulfuric acid hydrolysis data presented in Figure 3 indicate that neither regain nor viscosity change in direction so abruptly as might be expected from the hydrolysis-oxidation data in Figure 1. For this reason it is rather difficult to determine precisely the moment or moments at which chain shortening ceases and destruction of highly hygroscopic cellulose is complete. In the cases of both the slow and rapid hydrolysis, moreover, the rate of cellulose decomposition is still relatively fast during these changes. In view of these facts and of the previously given criticisms of the hydrolysis-oxidation method, it is not surprising that the amounts of cellulose hydrolyzed in 30 minutes by sulfuric acid differ considerably from the estimates of amorphous cellulose found by the hydrolysis–oxidation method (*7, 8*).

The data obtained by sulfuric acid hydrolysis and volumetric determination of glucose, and hence of cellulose, appear to be reliable. In addition to the proof already given, it was found for several different materials that the sum of cellulose hydrolyzed to glucose and hydrocellulose recovered did not vary more than 1% from the weight of sample taken. It appears, therefore, that the amounts of amorphous or highly disordered cellulose may be closer to the 30-minute sulfuric values than to the 4-minute hydrolysis-oxidation values.

The inclusion of viscosity measurements in these experiments permitted a clarification of the structure which previously could only be surmised from regain alone. In fact the viscosity behavior is worthy of further emphasis. The curves in Figure 3 indicate that only 2, 3.5, and 6%, respectively, of cotton, mercerized cotton, and viscose rayon are hydrolyzed as the viscosities of these materials are reduced to relatively constant values. This relation suggests that the selective chemical treatment of this small part of the structures, as by etherification or esterification, would effectively stabilize them against degradation, such as by microorganisms. In other words fiber strength and structural continuity are highly dependent on this small percentage.

It is now clear that the full appraisal of celluloses by hydrolysis requires at least two sets of conditions, one relatively mild and one sufficiently severe to extend the breakdown well beyond the point at which the rate appears to become constant. For example, Figure 4 shows that constant rate of hydrolysis is not attained with sulfuric acid in 8 hours; from this it may be assumed that the mesomorphous cellulose is not completely hydrolyzed in that time. The more severe condition, on the other hand, causes too rapid hydrolysis at the outset but yields a better over-all conception of behavior.

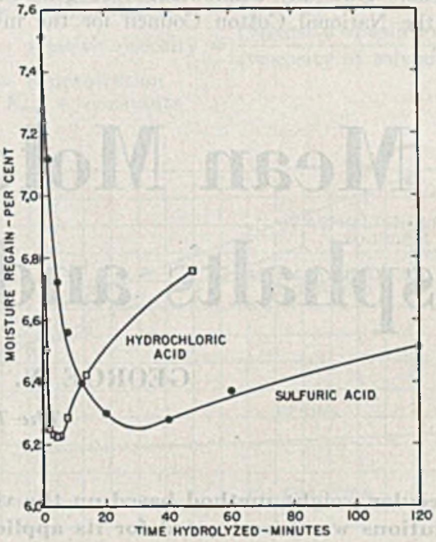

Figure 5. Moisture Regain at 65% Relative Humidity of Linters Hydrocelluloses Recovered after Varying Times of Digestion with Hot 2.5 *N* Sulfuric Acid and 2.45 *N* HCl–0.6 *M* $FeCl_3$

At least one further problem is presented by these results. If, as the viscosity data suggest, hydrolytic attack soon ceases on the ends of crystallites and continues at a decreasing rate on the sides of crystallites, extrapolation of breakdown curves as a means of estimating total noncrystalline cellulose may not be permissible. The reason is that extrapolation assumes concurrent attack on different parts of crystallites, of which one part is eliminated by projection to zero time. Since concurrent processes may not be going on, the total noncrystalline cellulose may be represented by the total cellulose hydrolyzed during the time required to attain constant rate.

SUMMARY

The effects of boiling 2.5 *N* hydrochloric acid–0.6 *M* ferric chloride solution on cotton linters are described in terms of cuprammonium viscosity, moisture regain, and percentage of cellulose hydrolyzed. Rapid initial breakdown of cellulose occurs, and viscosity and regain fall sharply. With further hydrolysis, cellulose breakdown continues and regain increases, but viscosity remains practically constant.

Less severe conditions represented by boiling 2.5 *N* sulfuric acid were used in the investigation of the rapid initial phase of the process. Cellulose decomposition was determined by a volumetric method for glucose. Viscosity and regain effects were obtained for several different cellulosic materials. Results indicate that the two methods supplement each other and permit

adequate coverage of extensive sample breakdown. Under the conditions employed, sulfuric acid appears to be only about one sixth as active in hydrolyzing cellulose as is hydrochloric acid of equivalent concentration.

The data suggest that cellulose molecule sections which interlink the crystallites in the chain direction are attacked first. This part of the structure, highly hygroscopic and probably quite disorganized, represents relatively small percentages of the intact materials. Hydrolytic attack thereafter appears to be limited to lateral crystallite surfaces.

Crystallite length estimates derived from viscosity data range from 280 glucose units for cotton to 110 for high tenacity viscose rayon. Mercerization apparently causes a reduction in crystallite length.

ACKNOWLEDGMENT

The authors gratefully acknowledge the generous provision made by the National Cotton Council for the investigations described in this series of papers, and the kind assistance of L. W. Bass, G. D. Beal, W. A. Hamor, and W. H. Child of Mellon Institute in the preparation of manuscripts.

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Received May 3, 1946.

Mean Molecular Weights of Asphalts and Their Constituents

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The molecular weight method based on the viscosity of dilute solutions was investigated for its applicability to asphalts and their constituents. The two equations proposed by Staudinger for calculating molecular weights from viscosities of solutions were considered. The constants in the equations were evaluated by using cryoscopic molecular weights for the oil and resin fractions from asphalts. The molecular weights of the oils and resins ranged from 370 to 900. Viscosities of benzene solutions were determined at 77° F. in a capillary type viscometer. Modifications of Staudinger's equations are not required for the oil and resin fractions of asphalts on the basis of the present work. Mean molecular weights of 700 to 1800 were obtained by the viscosity method for asphaltenes from asphalts of different sources. Both equations proposed by Staudinger were used to calculate the molecular weights of asphaltenes, and neither appears preferable. Reliable independent data for the molecular weights of asphaltenes are not available to define conclusively the constants in the original and modified forms of Staudinger's equations.

DURING studies in this laboratory on the properties of characteristic components isolated from asphalts—namely, asphaltenes, resins, paraffin oils, naphthene oils, and waxes (*18*), it has been of interest to obtain the mean molecular weights of these fractions. There is general agreement in the literature regarding the order of magnitude of the mean molecular weights of the oil and resin type fractions. However, no such agreement exists for the asphaltenes, probably because of their low solubility, complex molecular structure, tendency to form aggregates, colloidal nature, and the fact that their solutions may depart appreciably from the ideal solution laws. In view of the confusion existing in the literature, some attention has been given to possible methods for clarification in regard to the mean molecular weights of asphaltenes.

Sakhanov and Vassiliev (*14*) reported molecular weights of 5000 to 6000 for asphaltenes determined by the cryoscopic method using benzene. Strieter (*16*) used benzene for the cryoscopic molecular weight determination of asphalts and reported the following values: Trinidad bitumen 1131.8, Bermudez bitumen 620.4, gilsonite bitumen 4251.5. Katz (*7*) employed the cryoscopic method, with camphor and benzene, to obtain the molecular weights of asphaltenes. He obtained values of 4300 to 5600 with benzene and 2219 to 5160 with camphor solutions. He considered the values obtained with benzene too high and attributed inconsistent results to separation of the benzene solution into two phases at the freezing point. Hillman and Barnett (*4*) determined molecular weights of asphalts by the cryoscopic method, using both benzene and naphthalene, and obtained values for asphaltenes from noncracked residua of 2400 and 1660 with the two solvents, respectively. They concluded that the average molecular weight of ill-defined mixtures, such as asphaltenes, cannot be accepted as absolute, since the solutions of these fractions probably depart appreciably from the ideal solution law. Grader (*3*) claimed that camphor as a solvent gives incorrect results even for the oil fractions and preferred naphthalene as a solvent. Pfeiffer and Saal (*13*) measured the molecular weights of asphaltenes by the Langmuir monomolecular film method and reported the following values:

Source of Asphaltenes	Mean Molecular Weight
Mexican, steam-refined	80,000
Mexican, blown	80,000
Venezuelan, steam-refined	110,000
Venezuelan, blown	140,000

Swanson (*17*) carried out diffusion experiments in which the boundary was followed by light absorption, and claimed that the results suggest molecular weight values for asphaltenes at least as high as those obtained by Pfeiffer and Saal. Kirby (*9*) used an isotonic or equal vapor pressure method (*10*) and obtained molecular weights of 1510 for gilsonite (select) and 715 for a Mexican as-

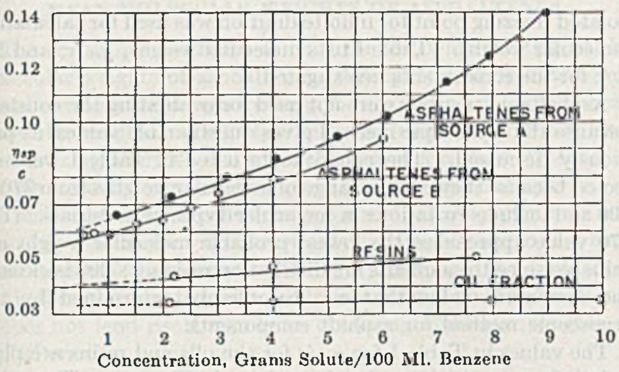

Figure 1. Variation of η_{sp}/c with Change in Concentration

phalt. This implies that the asphaltenes have molecular weights in the range 2000 to 3000, since gilsonite (select) contains 50 to 60% asphaltenes. Molecular weights less than 2000 for asphaltenes were obtained by Mack (*11*), employing viscosities of solutions of asphaltenes.

The published work, then, gives two widely divergent conclusions on the order of magnitude of the molecular weights of asphaltenes. High values of about 100,000 and low values of about 3000 were reported. After the results of other investigators were reviewed, as well as early experiences in this laboratory, it was decided that methods used for determining the molecular weights of high-molecular-weight polymers might apply to asphaltenes. The viscosity method has been discussed extensively in current literature in connection with polymers. This method appeared to have certain advantages if it could be applied to asphalt constituents. Therefore, work was carried out to ascertain the applicability of this method to oils, resins, and asphaltenes from asphalts.

VISCOSITY-MOLECULAR WEIGHT EQUATIONS

The limitations of the viscosity method for molecular weight determinations as set forth by Staudinger (*15*) are: (*a*) products must be members of a polymeric homologous series having a linear structure and a relatively high molecular weight; (*b*) the viscosity measurements must be carried out in a homopolar solvent, as it is only under this condition that the solute molecules are surrounded by a monomolecular layer of solvent molecules; and (*c*) viscosity measurements must be made in dilute solutions to avoid the gel state of the molecules in solutions. Items *b* and *c* are a matter of choice of solvent and concentration, and offer no difficulties with asphalt constituents. Item *a* is the limitation to which asphalt components may not comply, since the nature of the components is still a matter of conjecture. Fuoss (*2*) stated that linear polymers possess a brittle point, a temperature below which the polymers break suddenly under increasing tensile load with no preliminary stretching. Above this brittle point, linear polymers stretch before breaking. Asphalts behave in this manner and may, therefore, comprise a series of compounds having properties resembling those of linear type molecules. Although it is highly improbable that the fractions from asphalts are members of a homologous series, the conventional viscosity–molecular weight equations were used to evaluate the applicability of the viscosity of dilute solutions to asphalt components.

Table I. Data for Evaluation of Constants in Viscosity Equations

Constituent[a]	Mol. Weight	Concn., G./100 Ml. Benzene	Relative Viscosity, η_r	$\frac{\eta_{sp}}{c}$	$\left(\log \frac{\eta_r}{c}\right)10^2$
A (oil fraction)	370	4.086	1.085	0.0208	0.866
B (oil fraction)	460	6.451	1.159	0.0246	0.993
C (oil fraction)	470	5.000	1.134	0.0268	1.092
D (resin fraction)	540	7.152	1.235	0.0329	1.282
E (resin fraction)	550	3.078	1.096	0.0312	1.293
F (oil fraction)	565	3.466	1.107	0.0309	1.272
G (oil fraction)	575	3.760	1.118	0.0314	1.287
H (oil fraction)	590	10.809	1.386	0.0357	1.312
I (oil fraction)	625	2.716	1.089	0.0328	1.362
J (oil fraction)	635	4.752	1.160	0.0337	1.355
K (oil fraction)	710	6.009	1.244	0.0406	1.580
L (resin fraction)	750	5.419	1.239	0.0441	1.718
M (resin fraction)	790	5.125	1.225	0.0439	1.719
N (resin fraction)	900	5.106	1.254	0.0497	1.925

[a] These fractions represent constituents which have been isolated from asphalts; the method of separation will be described in a subsequent paper.

Two equations were proposed by Staudinger to relate viscosity of dilute solutions to the molecular weight of the solutes:

$$M = \eta_{sp}/cK_m \tag{1}$$

$$M = K_{cm} \log \eta_r/C \tag{2}$$

where M = molecular weight
η_{sp} = specific viscosity = $(\eta_r - 1)$
η_r = relative viscosity = $\frac{\text{(viscosity of solution)}}{\text{(viscosity of solvent)}}$
C = concentration
K_m, K_{cm} = constants

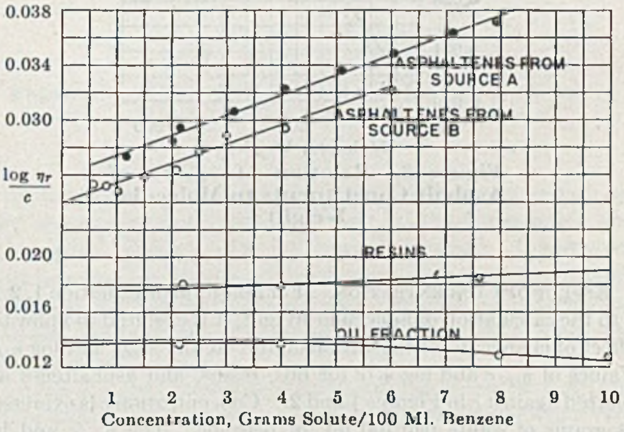

Figure 2. Variation of log η_r/c with Change in Concentration

Huggins (*5*) stated that the use of Staudinger's equations to obtain molecular weights of high polymers is theoretically and experimentally unjustifiable, for most polymer-solvent systems at least. He suggested the equation

$$[\eta] = KM^{\nu} \tag{3}$$

as being more satisfactory for relating intrinsic viscosity of a solution of a polymer to the molecular weight of the polymer:

$$[\eta] = \text{intrinsic viscosity} = \left[\frac{ln_r}{c}\right]_{c=0} = \left[\frac{\eta_{sp}}{c}\right]_{c=0}$$

Equation 3 was also proposed by Mark (*12*) for the calculation of molecular weights of polymers from viscosities of dilute solutions. Flory (*1*) reported that the molecular weights of polyisobutylenes calculated from Staudinger's equations are too low. However, he obtained a straight-line relation by plotting the logarithm of η against the logarithm of the molecular weights (osmotic pressure) of polyisobutylenes for the molecular weight range 6000 to 1,300,000. Thus, Huggins, Mark, and Flory found that a modification of Staudinger's equations was generally suitable for polymers of high molecular weight. Kemp and Peters (*8*) showed that η_{sp}/c varies with molecular weight for some types of materials, and that for these materials log η_r/c is constant over a fairly wide range of molecular weight. In attempting to apply the viscosity method to asphalt constituents, the conventional equations as given here were employed with the following results.

VISCOSITY DETERMINATION. The kinematic viscosities as described in A.S.T.M. Method D445–42T were determined on benzene solutions of the asphalt constituents. The viscosities were measured at 77° ± 0.05° F. in an Ostwald type viscometer having a capillary of 0.6 mm. inside diameter. The time of flow through the capillary ranged from 80 to 120 seconds for solutions having concentrations of 0.5 to 3.0 grams of asphalt constituent per 100 ml. benzene. The viscosity of the benzene was 0.698 centistoke.

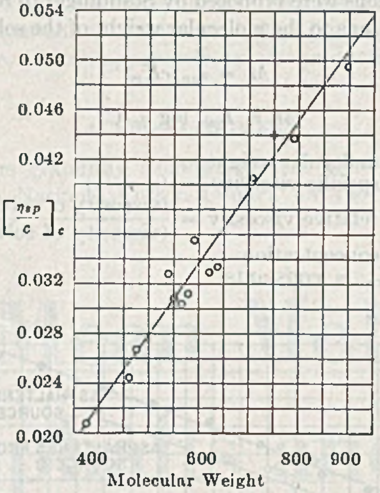

Figure 3. Relation of $[\eta_{sp}/c]_c$ of Asphalt Constituents to Molecular Weight

EFFECT OF CONCENTRATION. For adaption of Equation 1, 2, or 3 to the calculation of molecular weight, it is essential to know the effect of change in concentration on the factors η_{sp}/c and log η_r/c. Values of η_{sp}/c and log η_r/c for oils, resins, and asphaltenes are plotted against c in Figures 1 and 2. Concentration c is expressed as grams of solute per 100 ml. of benzene. The η_{sp}/c and log η_r/c values for an oil fraction from an asphalt tend to change only slightly with increase in concentration. Therefore, finite values of η_{sp}/c and log η_r/c should be as suitable as intrinsic viscosity $[\eta]$ for calculating molecular weights of the oils by the viscosity method. The $[\eta_{sp}/c]_c$ and $[\log \eta_r/c]_c$ values for the resins tend to increase slightly with increase in concentration. Extrapolation of the curves to zero concentration gives the intrinsic viscosity $[\eta]$. For concentrations less than 2 grams per 100 ml., finite values of η_{sp}/c and log η_r/c are within 4% of $[\eta]$. The slopes of the curves for the asphaltenes are greater than those for the resins. For asphaltene concentrations less than 1.0 gram per 100 ml., $[\log \eta_r/c]_c$ is within 5% of $[\log \eta_r/c]_{c=0}$. Finite values of η_{sp}/c at concentrations less than 1.0 gram per 100 ml. are within 10% of $[\eta_{sp}/c]_{c=0}$ values. This would indicate that $[\log \eta_r/c]_c$ is preferable to $[\eta_{sp}/c]_c$; in other words, Equation 2 should give less error than Equation 1 for calculating the molecular weights of asphaltenes from viscosity data.

EVALUATION OF CONSTANTS. To evaluate the constants for a particular homologous series of polymers, molecular weights determined by an independent method on lower members of the series are substituted in the equations. For asphalt constituents the structures are unknown, and the possibility of selecting known members of a homologous series is excluded. The alternative remaining is to use the lower-molecular-weight fractions of asphalt to evaluate the constants in the viscosity–molecular weight equations. The oil and resin fractions from asphalts constitute the lower-molecular-weight members of asphalt components. The molecular weights of these oil and resin fractions were obtained by the cryoscopic method with benzene as solvent. The freezing points were determined at several concentrations, and the extrapolated freezing point for infinite dilution was used for calculating molecular weight. Table I lists molecular weight, η_{sp}/c, and log η_r/c for the constituents investigated.

Asphaltene fractions were not used for evaluating the constant because the cryoscopic method gives questionable values, as previously discussed. The constituents listed in Table I were selected because they cover a range of molecular weights from 370 to 900 and include variations in molecular types of materials. The 370 value approaches the lowest probable molecular weight obtainable since the asphalts are distillation residues; 900 is close to the maximum value that can be reliably determined by the cryoscopic method for asphalt components.

The values in Table I for η_{sp}/c for the oils and resins are plotted against cryoscopic molecular weights in Figure 3. The factor η_{sp}/c is a linear function of the cryoscopic molecular weights of the oils and resins:

$$M = \frac{\eta_{sp}}{0.56 \times 10^{-4} \times c} \tag{4}$$

Figure 4 is a plot of $[\log \eta_r/c]_c$ for the oils and resins against cryoscopic molecular weight. A linear relation expressed by the following equation was obtained:

$$M = 4.48 \times 10^{-4} \frac{\log \eta_r}{c} \tag{5}$$

Both Equations 1 and 2 as given by Staudinger are applicable to the oils and resins investigated. In regard to Equation 3, it has already been explained that for oils and resins finite values of η_{sp}/c or log η_r/c do not deviate appreciably from intrinsic viscosity $[\eta]$. Also, η_{sp}/c and log η_r/x are linear functions of M, and therefore constant ν in Equation 3 is one. Thus, for oils and resins from asphalts, the conventional viscosity–molecular weight equations do not require modification on the basis of the present data.

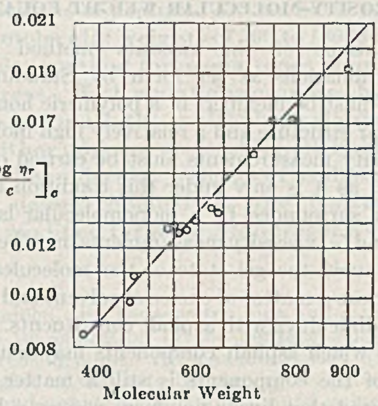

Figure 4. Relation of $[\log \eta_r/c]_c$ of Asphalt Constituents to Molecular Weight

In applying the viscosity method for asphaltenes, Mack (*11*) used the equation,

$$M = \log \eta_r/cK \tag{6}$$

where c was expressed in weight per cent. The value of K was 3.6×10^{-5}, which was determined from the viscosities of naphthalene and diphenyl as solutes in benzene and toluene solutions. His K corresponds to a K_{cm} of 3.0×10^{-4} in Equation 2 in contrast to 4.48×10^{-4} obtained in the present work. The variation in K_{cm} is undoubtedly due to its derivation from the molecular weights of naphthalene and diphenyl in Mack's work, whereas the molecular weights of oils and resins were used in this laboratory.

MEAN MOLECULAR WEIGHTS OF ASPHALTENES

The cryoscopic method was tried for the determination of the molecular weights of asphaltenes. Camphor was used as a solvent because it has a high freezing point constant. The observed molecular weights varied with concentration, as Figure 5 shows. The freezing point lowerings of solutions of less than 1% concentration were difficult to reproduce. For this reason the portion of the molecular weight–concentration curve for concentrations less than 1% was drawn with uncertainty; extrapolation to zero concentration was thus very unreliable. Although the cryoscopic method can be used to give reliable data for oil and resin fractions, it does not lend itself readily to obtaining molecular weights of asphaltenes.

The evaluation of the mean molecular weights of asphaltenes by the viscosity method was attempted with benzene as solvent by means of Equations 3 and 5. Table II gives typical data, and both equations appear equally applicable. Preference is given to Equation 5 in view of statements made by Kemp and Peters (*8*), and discussed in a previous section. Benzene has been a conventional solvent for asphalts and asphalt constituents for many years in testing laboratories. Some colloidal particles are present in benzene solution of asphalts, according to Katz and Beu (*6*). Benzene solutions of asphaltenes show Brownian movement, and some colloidal particles are unquestionably present. Whether the number of these particles is sufficient to discount the viscosity results is uncertain; but dialysis experiments in this laboratory have shown that only minor portions of asphaltenes dispersed in benzene do not pass through a collodion membrane at room temperature. The use of a constant based on the molecular weights of oil and resin fractions was believed justifiable to a certain extent, since asphaltenes are considered to be polymerization and condensation products of the oil and resin fractions. It is obvious from these assumptions that further information on the structure of asphalt components and molecular weights by independent methods are required for acceptance of viscosity molecular weights of asphaltenes.

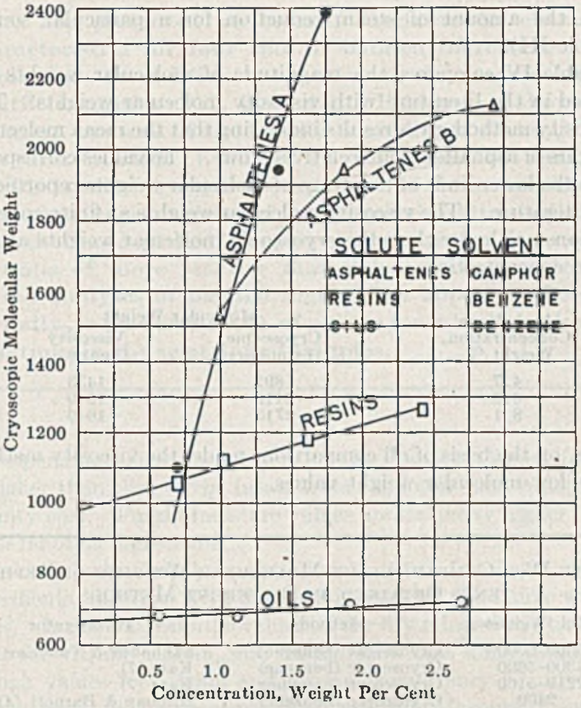

Figure 5. Effect of Concentration on Molecular Weight by Cryoscopic Method

Table II. Typical Viscosity–Molecular Weight Data for Asphaltenes (Series A)

Process of Asphalt Manufacture	Dropping Point of Asphalt[a], ° F.	Concn. of Asphaltenes, G./100 Ml. Benzene	Kinematic Viscosity at 77° F., Centistoke	η_r	Viscosity Mol. Weight	
					Equation 5	Equation 3
......	100	2.00	0.785	1.134	1210	1196
Air-blown	134	1.71	0.776	1.121	1299	1260
	169	1.61	0.777	1.123	1402	1366
	215	3.08	0.883	1.275	1532	1600
Steam-reduced	123	2.12	0.793	1.150	1170	1260
	144	2.02	0.789	1.143	1170	1265
	162	2.14	0.790	1.147	1120	1225

[a] Ball and ring method.

Table III. Viscosity Molecular Weights of Asphaltenes

Series	Source of Asphaltenes	Type of Asphalt	Asphaltenes in Asphalt, %	M.P.[a], of Asphalt, ° F.	Obsvd. Mol. Wt.[b]
A	Mexican	Flux	25.5	100	1210
		Air-blown	28.5	134	1299
		Air-blown	35.2	169	1402
		Air-blown	44.0	215	1532
B	Gulf Coast (Texas)	Residuum	28.8	119	1071
		Air-blown	34.8	145	1254
		Air-blown	40.1	165	1352
		Air-blown	42.4	201	1456
C	Mid-continent	Residuum	8.9	93	1102
		Air-blown	20.9	130	1317
		Air-blown	28.5	165	1442
		Air-blown	37.0	215	1550
D	Gulf Coast (La.)	Residuum	0.9	Soft	1052
		Air-blown	23.5	132	1286
		Air-blown	27.7	169	1451
		Air-blown	33.3	206	1613
E	Mexican	Flux	25.5	100	1210
		Steam-reduced	27.6	123	1170
		Steam-reduced	30.7	144	1170
		Steam-reduced	32.4	162	1120
F	California	Steam-reduced	10.7	96	1070
		Steam-reduced	13.0	119	1031
		Steam-reduced	18.5	136	1010
		Steam-reduced	25.2	159	973
G	Cracked residuum	Steam-reduced	18.0	99	703
		Air-blown	22.4	109	806

[a] Ball and ring.
[b] Calculated by Equation 5.

Equation 5 gives molecular weights for asphaltenes ranging from 700 to 1800. The observed molecular weights of asphaltenes vary with the melting point and source of original asphalt (Table III). With increase in the melting points of a series of asphalts from a particular source, the percentage of asphaltenes increases. The molecular weights of the asphaltenes from air-blown asphalts increase with an increase in the amount of processing or air blowing for a particular source (Figure 6). The molecular weights of the asphaltenes from a series of steam-reduced asphalts do not increase

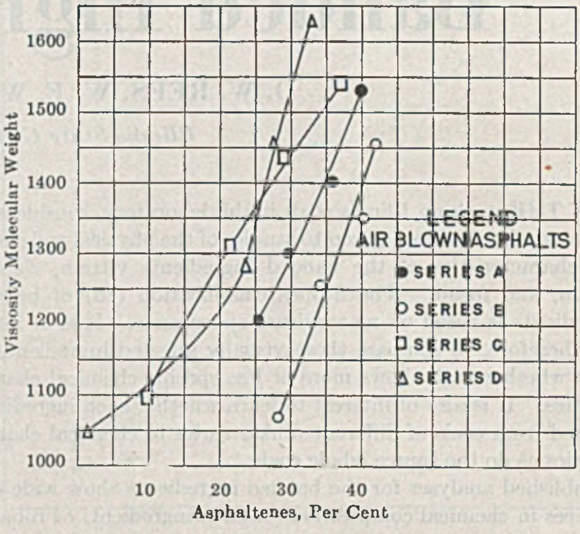

Figure 6. Molecular Weight *vs.* Asphaltene Content in Air-Blown Asphalts

with the amount of steam reduction for a particular source (Table III).

Table IV compares the magnitude of molecular weights reported in the literature with viscosity molecular weights. The viscosity method gives results indicating that the mean molecular weights of asphaltenes are relatively low. The values correspond with the lower limit of the range of molecular weights reported in the literature. The viscosity molecular weights at finite concentrations are lower than the cryoscopic molecular weights at the same concentrations:

Asphaltene Concentration, Weight %	Molecular Weight	
	Cryoscopic (camphor)	Viscosity (benzene)
4.7	1892	1433
6.6	2418	1549
8.1	2713	1649

Thus, on the basis of all comparisons made, the viscosity method gives low molecular weight values.

Table IV. Comparison of Molecular Weights of Asphaltenes Obtained by Different Methods

Mol. Weight	Method	Investigator
5000–6000	Cryoscopic (benzene)	Sakhanov & Vassiliev (*14*)
4300–5600	Cryoscopic (benzene)	Katz (*7*)
2219–5160	Cryoscopic (camphor)	Katz (*7*)
2400	Cryoscopic (benzene)	Hillman & Barnett (*4*)
1660	Cryoscopic (naphthalene)	Hillman & Barnett (*4*)
80,000–140,000	Monomolecular film	Pfeiffer & Saal (*13*)
1800	Viscosity of dilute soln.	Mack (*11*)
700–1800	Viscosity of dilute soln.	Eckert & Weetman

Because of the possibility of agglomerated asphaltenes in benzene solution and the viscosity-molecular weight constant used, the validity of the low molecular weights obtained remains to be confirmed. The development of a solvent in which it is certain that the asphaltenes are completely dissolved would eliminate one disadvantage that can be claimed for benzene solutions. Further developments in electron microscope technique may provide required information on the actual sizes and molecular weights of asphaltenes.

SUMMARY

The viscosity method of measuring molecular weights appears to be satisfactory for the oil and resin fractions from asphalts. The values for η_{sp}/c and log η_r/c for oils and resins do not change appreciably with increase in concentration, but values for asphaltenes show a gradual increase in η_{sp}/c and log η_r/c with increase in concentration. For concentrations of asphaltenes in benzene less than 1.0 gram per 100 ml. benzene, differences between $[\log \eta_r/c]_c$ and $[\log \eta_r/c]_{c\,=\,0}$ are less than 5% of $[\log \eta_r/c]_{c\,=\,0}$. Both equations proposed by Staudinger apparently can be applied to oil and resins from asphalts since $[\eta_{sp}/c]_c$ and $[\log \eta_r/c]_c$ for these constituents are linear functions of the cryoscopic molecular weights. The mean molecular weights of asphaltenes were determined by the viscosity method, using constants based on the molecular weights of the oil and resin fractions. The molecular weights of asphaltenes increase with increase in time of air blowing (as indicated by melting point for asphalts from one source) of the original asphalts.

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Received March 14, 1945.

Chemical Characteristics of Banded Ingredients of Coal

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IN THE work on Illinois coals in this laboratory, considerable attention has been given to studies of the physical and chemical characteristics of the banded ingredients vitrain, clarain, durain, and fusain. The Stopes classification (*15*) of banded ingredients is based on macrovisual appearance. It is of interest, therefore, to compare these visually selected ingredients to learn whether each shows more or less specific chemical characteristics. It is also of interest to learn whether each ingredient, secured from coals of different ranks, varies in chemical characteristics as do the source whole coals.

Published analyses for the banded ingredients show wide differences in chemical composition for each ingredient. Probably the composition of each ingredient, at least of vitrain, clarain, and durain, is influenced by the degree of metamorphosis undergone; but how far this may account for reported differences and how much may be due to variation in the selection of ingredients, source plant materials, etc., is a question. Recently Lowry (*6*), in summarizing chemical information on the banded ingredients, showed clearly the wide differences in reported analyses for each ingredient. Marshall (*7*) attempted to correlate analyses of anthraxylon with type and rank variation in coal seams. Fisher *et al.* (*3*) studied hydrogenation characteristics of the ingredients. Sprunk (*13*) summarized the influence of physical constitution of coal upon its chemical properties. Many other investigators have contributed information on various phases of this problem, but space does not permit a complete summary.

This report presents the results of studies of certain chemical characteristics on four sets of banded ingredients from the three

Data are presented on certain fundamental chemical characteristics for four sets of banded ingredients and whole coals from Illinois representing three ranks—high volatile bituminous A, B, and C. Evidence is shown of variation by rank of the banded ingredients vitrain, clarain, and durain. Evidence of variations by rank of fusains is more erratic. Comparison of characteristics of Hsiao fusains with those of hand-picked fusains indicates that the hand-picked samples contain rather large proportions of more reactive materials. Variations in reported analyses of banded ingredients appear to be due partially to the influence of varying rank, but also to variations in the selection of samples.

ranks of coal—high volatile bituminous A, B, and C—represented in Illinois. The work represents an effort to obtain information on variations of chemical characteristics of ingredients as related to rank of source coals, and in addition to secure information on differences due to variability in visual selection, particularly of the fusains.

TESTS ON COAL SAMPLES

Four sets of samples, including whole coals and banded ingredients from Gallatin, Franklin, Macoupin, and Henry Counties were studied. These represent coals of high volatile bituminous ranks A, B, C, and D, respectively. The whole coals were channel samples, cut down, crushed to pass a 4-mesh sieve, and sealed in sample cans in the mines. The banded-ingredient samples were hand-picked in the mines, the selection being made macroscopically. These samples were crushed to pass a 4-mesh sieve and were sealed in sample cans in the mines. In the laboratory, samples were air-dried, crushed to −20 mesh size in a Braun-type 6 CP pulverizer, and further pulverized to smaller sizes in a ball mill.

Several tests were used to compare chemical characteristics of the banded ingredients. Proximate analysis, calorific value, and total sulfur were determined on −60 mesh samples according to standard A.S.T.M. procedures (*1*). Reactivity index was determined by the C.R.L. reactivity test (*11, 12*). Determinations were made on −40 +60 mesh samples in both oxygen and air, and results were indicated as T_{15} and T_{75}, respectively. Free swelling index tests were made on −60 mesh samples according to a tentative A.S.T.M. method (*2*). Moisture characteristics were determined by the equilibration method described by Stansfield and Gilbart (*14*) and later used in this laboratory (*10*).

Further studies were made on the hand-picked fusains. Fusain determinations were made on these samples by the Hsiao method (*4*). The inert portions (Hsiao fusains) remaining after nitric acid oxidation of the hand-picked fusains were studied for reactivities by the C.R.L. method, and moisture characteristics were studied by the equilibration method. Proximate and ultimate analyses were made according to A.S.T.M. standard methods.

ANALYSES

Proximate analyses, total sulfur, and calorific values for whole coals and hand-picked ingredients are summarized in Table I. In general, analytical values for the vitrains, clarains, and durains vary in the same way as do those for the corresponding whole coals. Moisture and calorific values are of particular interest in considering variations due to rank. As-received moisture values for vitrain, clarain, and durain increase with decrease in rank, as do those for the whole coals. Moisture values for the fusains show an exception in regular increase with decrease of rank of the corresponding source coals; that for the Franklin County fusain is higher than that of the fusain from the lower rank Macoupin County coal. Fusain moisture values are distinctly higher than those for other ingredients.

Calorific values on the moist mineral-matter-free basis, for all ingredients, decrease with decrease in rank of the source whole coals. In general, calorific values on the dry mineral-matter-free basis for vitrain, clarain, and durain show this same trend, although values for vitrain and clarain from Henry County are higher than those for the same ingredients from Macoupin County. This is also true for the corresponding whole coals. Fusain from the Franklin County rank B coal showed the highest calorific value on the dry mineral-matter-free basis. With the exception of the fusain from the Gallatin County rank A coal, calorific values (dry mineral-matter-free) for fusains are higher than for other banded ingredients and whole coals. This is in accord with the findings of Parr, Hopkins, and Mitchell (*8*) in a study of Illinois fusains. However, the work reported by these authors covered fusains from high volatile bituminous B and C coals but not for fusain from high volatile bituminous A.

REACTIVITY AND FREE SWELLING INDICES

Table I gives reactivity indices for the samples studied. The T_{15} and T_{75} values for the whole coals decrease with decrease in

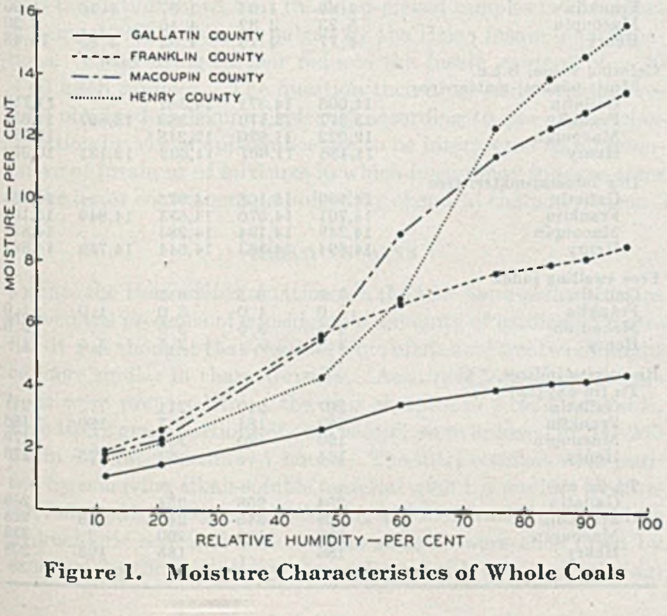

Figure 1. Moisture Characteristics of Whole Coals

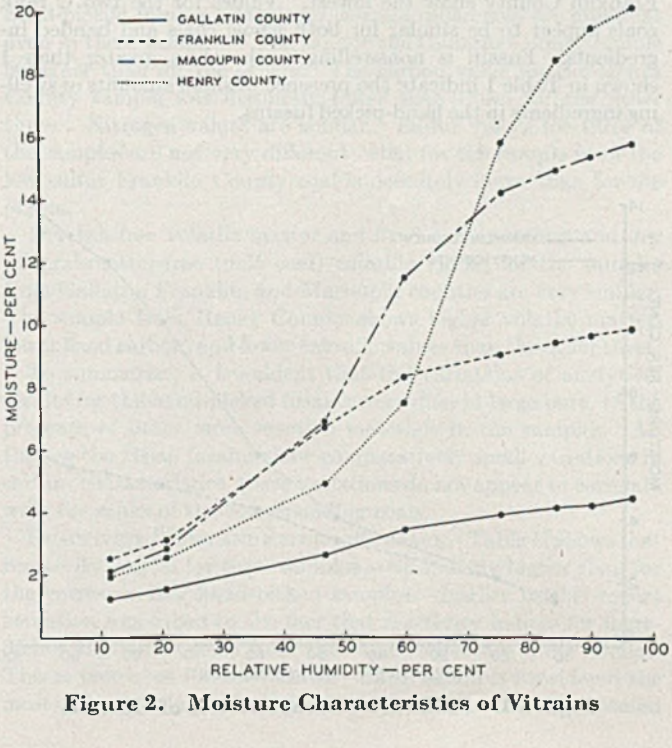

Figure 2. Moisture Characteristics of Vitrains

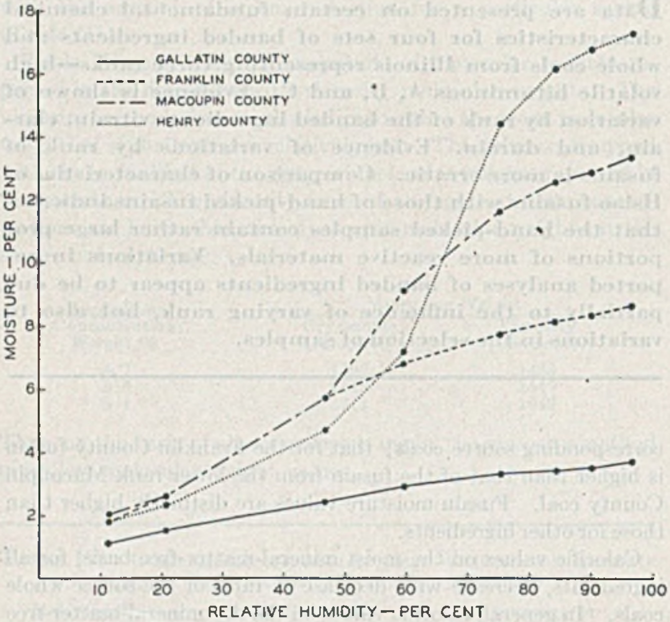

Figure 3. Moisture Characteristics of Clarains

rank. This same trend is exhibited also by the banded ingredients. Reactivity indices for ingredients and whole coals from the same source are similar. Results obtained by the C.R.L. test are probably more nearly a measure of the reactivity of the most reactive portion of mixed samples. Sherman *et al.* (*12*) gave evidence of this. Macroscopically picked ingredients may be mixtures containing portions of various other ingredients as impurities. This may account for the similarity of the values for samples from the same source. The fact that ingredient reactivity indices decrease with decrease in rank of corresponding whole coals is further evidence of variation of ingredients with rank.

Table I also gives free swelling indices for whole coals and banded ingredients. These values do not show progressive decrease with rank as do the reactivity indices. Samples from the highest rank coal from Gallatin County show the highest free swelling indices. Samples from the next highest rank coal from Franklin County show the lowest. Values for the two C rank coals appear to be similar for both whole coals and banded ingredients. Fusain is nonswelling, and values greater than 1 shown in Table I indicate the presence of small amounts of swelling ingredients in the hand-picked fusains.

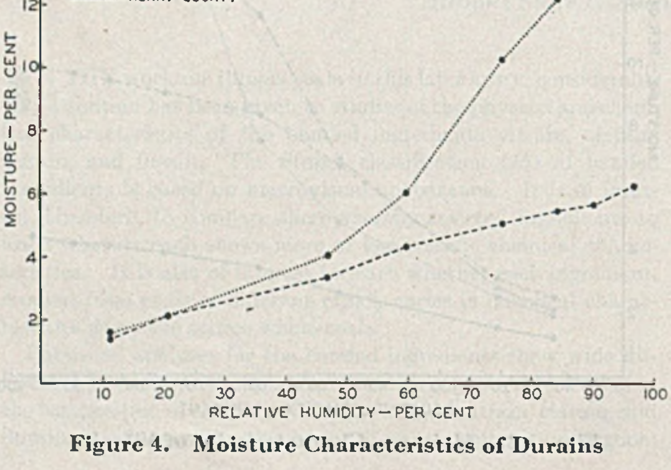

Figure 4. Moisture Characteristics of Durains

MOISTURE CHARACTERISTICS

Figures 1 to 5 show graphically the results obtained. Samples, ground to pass a 14-mesh sieve, were brought to equilibrium at different humidities, and moisture contents were then determined by heating in a vacuum oven at 105° C. for 3 hours. These values were plotted against the corresponding relative humidities. For the four sets of samples studied, the interrelations of moisture-humidity curves are similar. In general, vitrain curves are highest, clarain and whole coal are next, durain is somewhat lower, and fusain is decidedly lower up to high humidities where the curves rise steeply. Comparisons of the moisture-humidity curves for the four whole coals studied, as well as for the corresponding banded ingredients, show wide differences. Curves for vitrains, clarains, and durains have the same general shape and occupy the same relative positions as do curves for the different rank whole coals. The fusain curves (Figure 5) do not occupy the same relative positions.

These comparisons appear to show that moisture characteristics indicate variations by rank in vitrain, clarain, and durain as in the whole coals. Indications of variation by rank of fusains are not clear.

FURTHER STUDIES ON FUSAINS

The question of purity of banded ingredient samples made it desirable to study the characteristics of more carefully purified

Table I. Analyses of Hand-Picked Samples

	Whole Coal	Vitrain	Clarain	Durain	Fusain
Moisture (as-received), %					
Gallatin	5.1	4.4	3.6	...	17.8
Franklin	8.0	9.2	8.0	6.0	21.1
Macoupin	14.0	15.3	13.4	...	20.3
Henry	19.3	17.2	18.2	16.2	25.2
Ash (dry), %					
Gallatin	10.0	8.1	10.3	...	18.9
Franklin	10.3	4.3	4.9	11.4	8.6
Macoupin	11.9	3.4	4.3	...	10.0
Henry	11.0	7.5	11.0	7.5	14.1
Volatile matter (dry, ash-free), %					
Gallatin	43.1	42.8	41.1	...	28.6
Franklin	40.6	34.1	37.3	43.2	15.2
Macoupin	45.0	43.3	47.0	...	19.6
Henry	44.0	41.6	44.9	43.6	26.9
Fixed C (dry, ash-free), %					
Gallatin	56.9	57.2	58.9	...	71.4
Franklin	59.4	65.9	62.7	56.8	84.8
Macoupin	55.0	56.7	53.0	...	80.4
Henry	56.0	58.4	55.1	56.4	73.1
Total S (dry), %					
Gallatin	3.19	2.42	2.74	...	4.26
Franklin	1.69	1.04	1.37	1.16	4.20
Macoupin	5.23	3.32	4.16	...	6.20
Henry	4.77	4.76	4.32	3.85	10.46
Calorific value, B.t.u.					
Moist mineral-matter-free					
Gallatin	14,098	14,371	14,361	...	11,719
Franklin	13,377	13,170	13,386	13,827	11,634
Macoupin	12,022	11,920	12,248	...	11,428
Henry	11,486	11,667	11,633	12,131	10,397
Dry mineral-matter-free					
Gallatin	14,989	15,108	14,975	...	14,985
Franklin	14,701	14,576	14,633	14,849	15,155
Macoupin	14,349	14,194	14,284	...	14,812
Henry	14,694	14,383	14,644	14,739	14,847
Free swelling index					
Gallatin	7.0	6.5	6.5	...	1+
Franklin	3.0	4.0	3.0	1.0	1.0
Macoupin	4.5	3.5	3.5	...	2.0
Henry	4.5	...	3.5	3.5	1+
Reactivity indices, ° C.					
T_{15} (in oxygen)					
Gallatin	207	210	211	...	211
Franklin	182	184	187	180	186
Macoupin	160	160	159	...	179
Henry	164	...	163	175	170
T_{75} (in air)					
Gallatin	254	258	254	...	258
Franklin	229	245	240	218	228
Macoupin	188	190	190	...	222
Henry	186	...	185	193	208

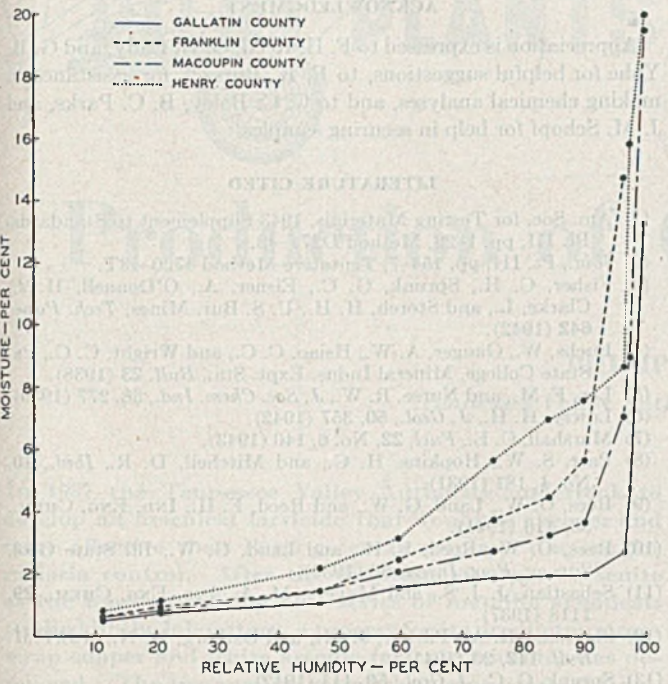

Figure 5. Moisture Characteristics of Hand-Picked Fusains

samples. The relative inertness of fusain to nitric acid (*4*) makes possible its purification, whereas no such means of purification of the other ingredients is available. Therefore further studies were made on the fusains in an effort to learn whether distinct differences in chemical characteristics of the hand-picked fusains were due to the presence of various amounts of other ingredients or to the influence of rank variation of the source coals.

Determinations were made by the Hsiao method (*4*) on the hand-picked fusains. Furthermore, since fusain is quite friable, similar tests were made on the close-sized reactivity samples (−40 +60 mesh) to determine the loss of fusain in sizing between close limits:

County	% Hsiao Fusain in Hand-picked fusains	 −40 +60 mesh fusain
Gallatin	61.5	31.6
Franklin	79.3	46.8
Macoupin	65.0	44.1
Henry	49.0	28.2

This tabulation shows that the hand-picked samples fall far short of being 100% fusain, as judged by the Hsiao fusain determinations. Close sizing further reduces the fusain content of −40 +60 mesh samples. The question then arose as to whether results obtained on samples selected according to the Stopes classification by visual appearance are to be interpreted as representative of fusain or of mixtures in which fusain may in some cases be the lesser constituent as judged by chemical characteristics.

HSIAO FUSAINS

Since the Hsiao determinations on the four hand-picked fusains showed the presence of considerable amounts of oxidizable material, it was thought that residues from nitric acid treatment might be more similar in characteristics. Accordingly, such inert portions were prepared from the four samples of fusain available. Five 10–12 gram portions of each sample were refluxed in 200–240 ml. of 8 *N* nitric acid for 7 hours. The inert residues were purified by removing alkali-soluble material with 1 *N* sodium hydroxide, followed by repeated centrifuging and final washing with dilute hydrochloric acid and water. The samples were then dried by exposure to the laboratory atmosphere (with frequent stirring) for 8 or 9 hours, and then various determinations were made. The nitric acid inert residues prepared as outlined are referred to here as Hsiao fusains.

Table II. Analyses of Hsiao Fusains

County	Hsiao Fusains	Hand-picked Fusains	Hsiao Fusains
	Ash (Dry), %		C (Dry, Ash-Free), %
Gallatin	5.1	18.9	89.64
Franklin	2.3	8.6	89.56
Macoupin	3.8	10.0	89.13
Henry	2.4	14.1	87.62
	Volatile Matter (Dry, Ash-Free), %		H (Dry, Ash-Free), %
Gallatin	13.6	28.6	2.47
Franklin	13.5	15.2	2.44
Macoupin	13.8	19.6	2.57
Henry	14.8	26.9	2.43
	Fixed C (Dry, Ash-Free), %		N (Dry, Ash-Free), %
Gallatin	86.4	71.4	0 68
Franklin	86.5	84.8	0.66
Macoupin	86.2	80.4	0.55
Henry	85.2	73.1	0.87
	Total S (Dry), %		O (Dry, Ash-Free), %
Gallatin	0.42	4.26	6.77
Franklin	0.21	4.20	7.13
Macoupin	0.52	6.20	7.21
Henry	0.46	10.46	8.61
	B.t.u. (Dry Mineral-Matter-Free)		Sp. Surface, Sq. Cm./Gram
Gallatin	14,103	14,985	5490
Franklin	14,076	15,155	4610
Macoupin	14,145	14,812	4170
Henry	13,969	14,847	5310
	T_{15}, ° C.		
Gallatin	285	211	
Franklin	263	180	
Macoupin	243	179	
Henry	266	170	
	T_{75}, ° C.		
Gallatin	326	258	
Franklin	310	228	
Macoupin	319	222	
Henry	313	208	

Analyses. Table II presents the results of proximate, ultimate, total sulfur, and calorific value analyses. Samples available were too small to permit duplicate determinations in most cases. These analyses show much closer agreement than did those for the hand-picked fusains. However, certain differences are apparent even in these samples. The ash for the Gallatin County sample is higher than for the others. The carbon value for the Henry County sample was distinctly lower than those for the other three. Nitrogen values are similar. Sulfur values for three of the samples are not very different; that for the sample from the low sulfur Franklin County coal is definitely lower than for the others.

Dry ash-free volatile matter and fixed carbon values and dry mineral-matter-free (unit coal) calorific values for the samples from Gallatin, Franklin, and Macoupin counties are very similar. The sample from Henry County shows higher volatile matter, lower fixed carbon, and lower calorific values than the other three.

To summarize, it is evident that the variations of analytical results for the hand-picked fusains were due, in large part, to the presence of other more reactive materials in the samples. Although the Hsiao fusains show comparatively small variations in certain characteristics, these variations do not appear to correlate with the ranks of the corresponding coals.

Reactivity Index and Specific Surface. Table II shows that reactivity indices for these samples are decidedly higher than for the corresponding hand-picked samples. Earlier in this report attention was called to the fact that reactivity indices for ingredients and whole coals from the same source are quite similar. This is true even for the fusains. Since fusain is considered the most inert of the ingredients, its reactivity index would be expected

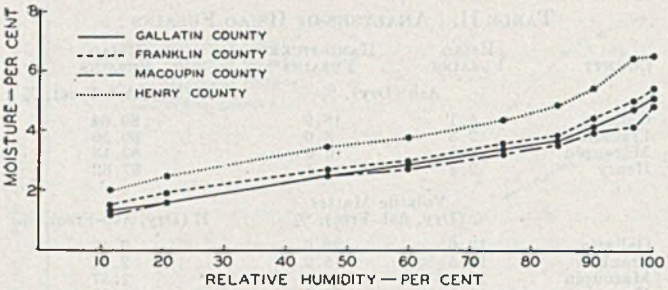

Figure 6. Moisture Characteristics of Hsiao Fusains

to be higher. It was suggested that, since the C.R.L. method probably measures more nearly the reactivity of the most active constituent of a mixture, the values found were representative of the most reactive constituent in mixed samples and not of the particular banded ingredient supposedly being tested. If this were true in the case of the fusains, removal of the more reactive material should have given residues whose reactivity indices were definitely higher. This is exactly what happened in the Hsiao fusains.

Some differences in reactivity indices for the four samples are apparent. T_{15} and T_{75} values are highest for the sample from the highest rank coal. The T_{15} value is lowest for the sample from Macoupin County, and the T_{75} value lowest for the Franklin County sample. No definite correlation with rank is apparent.

It was thought that differences in reactivity indices might be due to differences in specific surface of the samples. Sherman *et al.* (*12*) showed that increasing the specific surface results in lowering reactivity index when studying the same coal. Accordingly, specific surface determinations were made by the Lea and Nurse method (*5*). Table II shows that the sample from Gallatin County with the highest T_{15} and T_{75} values had the highest specific surface; the sample from Macoupin County with the lowest T_{15} value showed the lowest specific surface. Although a study of the relation of surface to reactivity should be made on the same coal, the authors wished to determine whether there might be such a correlation for these samples. As the relation here is the reverse of that to be expected, it seems reasonable to assume that differences in reactivity index for these samples are due to more fundamental causes.

MOISTURE CHARACTERISTICS. Results obtained by the equilibration method are shown graphically in Figure 6. Comparison of Figures 5 and 6 indicates that moisture-humidity curves for the Hsiao fusains are more similar than are the curves for the hand-picked fusains. All samples (Figure 6) show a gradually increasing moisture content with increasing humidity, but there is practically no indication of high moisture take-up at high humidities such as that exhibited by the hand-picked fusains.

At present there is no definite explanation for this difference between the Hsiao and hand-picked fusains. Previous data (*9*) indicate that the differences in moisture characteristics cannot be due to the presence or absence of water-soluble salts. It seems reasonable to suppose that possible changes in porosity or surface characteristics, or both, resulting from nitric acid oxidation might account for the differences in moisture characteristics between hand-picked and Hsiao fusains.

In an attempt to secure further information regarding banded ingredients of Illinois coals, some work has been done with the electron microscope. Through the cooperation of G. L. Clark, of the University of Illinois, electron microscope pictures at various magnifications were made for one set of banded ingredients and for the four Hsiao fusains. This work appears promising but has not progressed far enough to permit definite conclusions to be drawn.

ACKNOWLEDGMENT

Appreciation is expressed to F. H. Reed, G. H. Cady, and G. R. Yohe for helpful suggestions, to F. K. Bursack for assistance in making chemical analyses, and to C. C. Boley, B. C. Parks, and J. M. Schopf for help in securing samples.

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Binary Mixture of *n*-Butane, Isobutane, and 1-Butene with Furfural—Correction

The following corrections should be made in this paper which appeared in June 1947: Page 790, in Table II the second virial coefficient for 1-butene at 125° F. should be −578 ml./gram mole. Page 796, citation (25) should read: Scatchard, G., and Raymond, C. L., *J. Am. Chem. Soc.*, 60, 1278–87 (1938).

T. S. MERTES AND A. P. COLBURN

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Ternary Systems *n*-Butane–1-Butene–Furfural and Isobutane–1-Butene–Furfural—Correction

Errata have been found in this June 1947 paper as follows: Page 798, an incorrect value of x_1 is shown in the sample calculation. The line for γ_1 near the middle of the second column should read:

$$\gamma_1 = \frac{z_1 y_1 P}{x_1 P_1} = \frac{(1.018)(0.4893)(4909)}{(0.1003)(5458)} = 4.46$$

Page 800, a full line of Equation 7 (second column) was omitted. It should read as follows:

$$\begin{aligned} \log \gamma_1 = {} & x_2^2[A_{1-2} + 2x_1(A_{2-1} - A_{1-2})] \\ & + x_3^2[A_{1-3} + 2x_1(A_{3-1} - A_{1-3})] \\ & + x_2x_3[A_{2-1} + A_{1-3} - A_{3-2} + 2x_1(A_{3-1} - A_{1-3}) \\ & + 2x_3(A_{3-2} - A_{2-3}) - C(1 - 2x_1)] \end{aligned}$$

Page 803, in Figure 10 the dotted lines shown for relative volatility of 20 mole % pure isobutane and 20 mole % pure *n*-butane are given only as a guide to trends; they should be used with caution, since it is probable that such concentrations exceed the miscibility limits for these hydrocarbons in furfural.

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PILOT PLANTS

Production of Copper Arsenite

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In 1937 the Tennessee Valley Authority undertook to develop an arsenical larvicide that would be cheaper and more effective than Paris green in airplane dusting for malaria control. After the selection of copper arsenite as the most promising of a series of metallic arsenicals studied in the laboratory, a process for its production from scrap copper and white arsenic (arsenic trioxide) was developed. The two main steps of the process are the dissolution of copper in an ammonium chloride solution and the addition of arsenic trioxide to precipitate copper arsenite. The product is separated by filtration, washed, and spray-dried, and the ammonium chloride solution is recycled. The process was investigated in a pilot plant with a capacity of 600 pounds of copper arsenite per day. Problems incident to continuous steady-state operation not encountered in the laboratory investigation were met and solved. Information on equipment, operation, and recoveries was obtained from which it was estimated that copper arsenite could be produced at a substantially lower cost than Paris green. Pilot plant product was used in airplane dusting tests, which indicated that copper arsenite was superior to Paris green as a larvicide for malaria mosquito control. The present paper describes the study primarily as a pilot plant case history, providing information on such points as historical background; pilot plant design and construction; organization and type of personnel; methods of obtaining, reporting, and utilizing operating and analytical data; and the type of problems encountered. The reasons for carrying out the pilot plant work and the results and benefits of the work are discussed.

AT THE request of the Health and Safety Department of the Tennessee Valley Authority, which is responsible for the Authority's program of malaria control, the Chemical Engineering Department carried out a systematic study on a laboratory scale of the preparation and testing of a series of insoluble arsenites of the common metals. This led to the selection of cupric *m*-arsenite ($CuAs_2O_4$) as the most promising compound and to the development of a process for its production from white arsenic (arsenic trioxide) and scrap copper (*3*). Cupric *m*-arsenite, for convenience called copper arsenite in this work, has been reported in the literature (*2*) but is not produced commercially. It has a theoretical content of 22.9% Cu and 71.4% As_2O_3, compared with 25.1% Cu, 58.6% As_2O_3, and 5.9% $HC_2H_3O_2$ (acetic acid) for Paris green, $(CuOAs_2O_3)_3 \cdot Cu(C_2H_3O_2)_2$. Since copper is a considerably more expensive raw material than arsenic, and since acetic acid is an expensive ingredient of Paris green that is not present in copper arsenite, it appeared that the latter would be cheaper than Paris green if a fairly simple and efficient method for its manufacture could be developed.

A pilot plant for such a process was designed and constructed, and was operated long enough to perfect and prove the process, to produce sufficient material for airplane dusting tests of its effectiveness, and to provide information for a reliable estimate of the cost of production.

The following description of the pilot plant production of copper arsenite is presented not primarily for the sake of its value to the larvicide field but rather with the intention of providing detailed information on the methods used in designing and operating a typical pilot plant, in the hope that such information will be useful to students and teachers of chemical engineering and to engineers engaged in pilot plant work. In accordance with this objective this paper is concerned mainly with such topics as the way in which the design of the pilot plant was related to the basic information provided by the initial laboratory studies and to considerations of space, cost, and operating convenience; the basis for selecting equipment; the type, number, and duties of the operating personnel; the collection and analysis of samples and the use of the analytical results in control of the operation; and the collection of operating data and their tabulation, correlation, and use in operation. From a broader viewpoint an attempt is made to convey somewhat the chronological pattern of a pilot plant investigation; the type of difficulties encountered; the leads followed or rejected; the part played by nontechnical or extraneous considerations; and the interplay of guessing and analysis, of trial and accident, that enters into every investigation.

DECISION TO BUILD PILOT PLANT

Early in the spring of 1939 the laboratory investigation of arsenical larvicides had progressed far enough to indicate that copper arsenite was the most promising of the compounds studied and to demonstrate the technical feasibility of a fairly simple method of preparing it; this method was subsequently patented (*3*). At this stage the status of the project was reviewed, and it appeared desirable to carry the work to a pilot plant scale in order to test the feasibility of the process in engineering equipment, determine suitable equipment and materials of construction for a large scale plant, obtain information for estimating the production cost on a large scale, and provide enough product for field tests. Although the need for the pilot plant work was clear, the information at that time available from the laboratory studies was quite limited, and it would have been desirable to carry these studies further before designing the pilot plant.

However, the timing of the pilot plant, and indeed the entire investigation, was strongly influenced by the fact that the airplane dusting season for malaria control in the Tennessee Valley falls generally from May through September, so that the op-

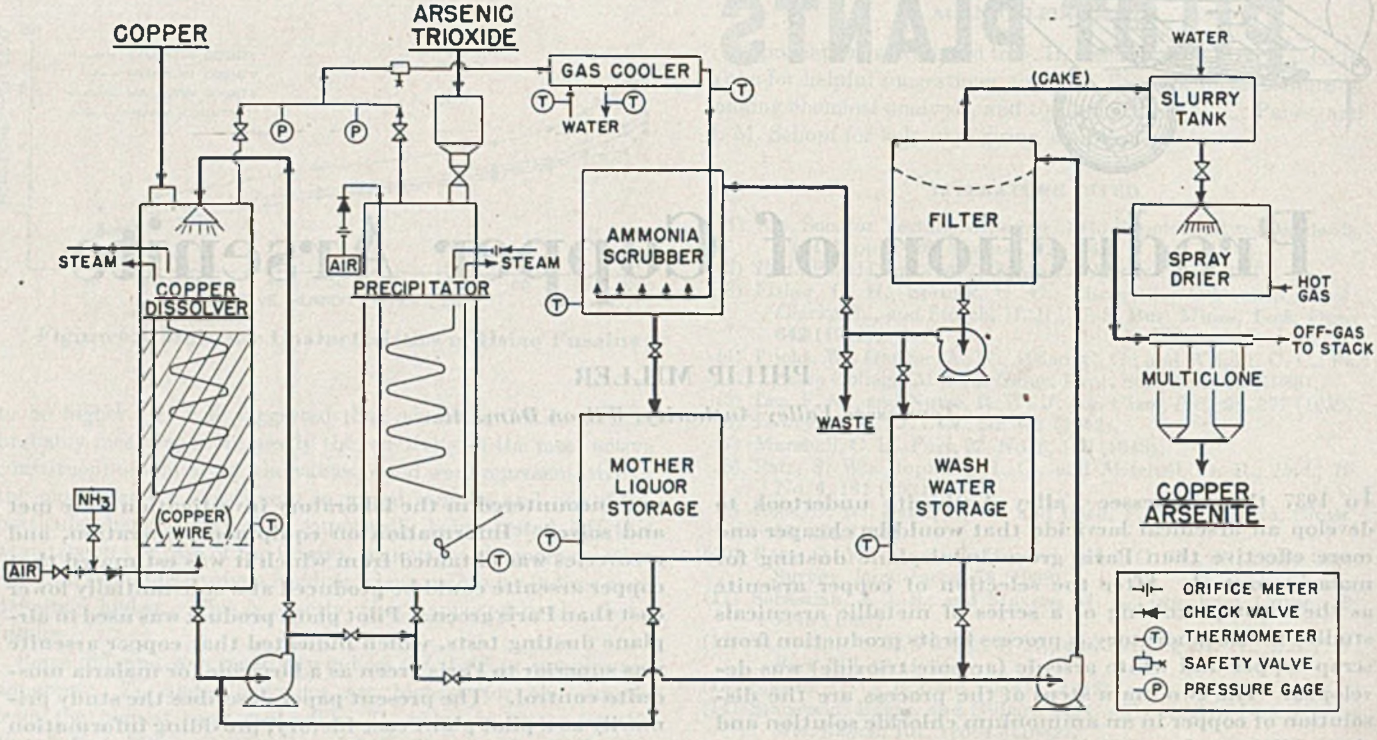


Figure 1. Flow Diagram of Copper Arsenite Pilot Plant

portunity for field testing of larvicides is limited to this part of the year. The choice then had to be made of proceeding immediately to design and construct a pilot plant without the benefit of more thorough chemical studies and of preliminary work in engineering equipment, or of putting off the possibility of a field test of the product for a full year. On March 15 the decision was made to go ahead. The goal was set of having the pilot plant ready for operation by June 15, in order to produce 5 tons of experimental larvicide for airplane testing. The pilot plant process and design were based on the following research results, available on April 1, 1939.

INFORMATION FROM LABORATORY RESEARCH

The process for making copper arsenite that resulted from the small scale studies of the Chemical Research Division consisted essentially of dissolving metallic copper in ammonium chloride solution and reacting the resulting solution with arsenic trioxide to precipitate copper arsenite. These studies had been carried out in glassware with a noncyclic procedure; the laboratory work was continued after April 1 and gave additional results that later proved useful in the operation of the pilot plant, but these were not available in designing the plant. The laboratory work provided the following recommendations and information for design of the pilot plant:

Dissolving Copper. Circulate a batch of 10% ammonium chloride solution at boiling temperature for 1 hour over copper wire with continuous aeration. Use 500 milliliters of solution per kilogram of copper wire. The copper will dissolve at a rate of 18 grams per kilogram per hour.

Precipitating Copper Arsenite. Add 100 grams of arsenic trioxide per liter and agitate at boiling temperature for 1 hour, preferably in a separate vessel, with continuous aeration.

General Information. Ammonia was lost from solution during both steps; a loss of 0.1 gram ammonia per gram copper dissolved was estimated for the dissolving step. From 100 to 250 ml. of water were required for adequate washing of the product from 500 ml. of slurry on a Büchner funnel. The copper wire contained 72% voids. Qualitative corrosion tests of small metal samples in the mother liquor indicated that Duriron was very satisfactory; stainless steel (American Iron and Steel Institute Types 304 and 316) showed some corrosion but probably could be used; lead corroded somewhat more than stainless steel. Of a number of coating materials tested, Tornesit and Pliolite showed promise. Acidproof brick, stoneware, and wood also were suggested.

DESIGN AND CONSTRUCTION

The size of the pilot plant, like the decision to build it, was influenced by the time factor. The need for supplying 5 tons of product by midsummer (although not all of it would be needed at one time) helped to set a lower limit for the plant capacity. The objective of obtaining reliable information for estimating the cost of producing copper arsenite on a large scale was considered in selecting both the desired capacity and the type of equipment to be used. An upper limit for plant size was set by the budget. Weighing these factors and others, a production rate of 25 pounds per hour or 600 pounds per day, which would call for about 3 weeks of good operation for the production of 5 tons, was selected as a figure that left reasonable room for meeting the goal after making allowance for the problems that would be encountered. Rough estimates of equipment sizes confirmed the suitability of this capacity figure.

TVA pilot plants are designed by the Process Development Division, except for the largest and most complex ones; on these help is received from the Chemical Plant Design Division, which carries out the design of the large scale chemical plants and of changes and additions to these plants. In the case of the copper arsenite pilot plant, the design and construction, as well as the operation, were carried out by the group of chemical engineers in the Process Development Division to whom the project was assigned. Drawings were prepared for the pieces of equipment to be constructed in the TVA shops, which included all the major units except the drying equipment. The drafting was done by a junior engineer, who followed sketches and specifications prepared by the project leader but who contributed ideas to the detailed design. Blueprints were submitted to the Research Service Section, which had responsibility for the construction of the equipment in the plant shops and its installation at the pilot plant location. The installation of pumps and piping, wiring, services, and operating platforms was handled more informally. After the major units had been put in position, the field engineer (in this case the same individual who had done the drafting) provided the pipe fitter foreman with a rough piping diagram, from which the detailed arrangement was worked out by the foreman, with the work being closely followed by the field engineer. The wiring, platforms, etc., were handled in much the same manner. The integration of the installation work by the different crafts was done by the Service Section. The entire procedure was flexible and informal, involving consultation and review of plans and drawings by division members not assigned to the project, the collaboration of the Service Section in some phases of the equipment design and plant arrangement, and a continuous check by the field engineer at all stages of construction and installation.

A few dates may serve to make this process more real to the reader, but he is warned that they cannot be taken as typical, even for 1939. Design calculations were started about April 1. Blueprints were submitted two weeks later, and most of the units were in place about May 15. Bricklining of the two reaction vessels was completed May 22. A piping diagram was prepared May 11; pipework was started on May 19 and completed May 29, at which time the pilot plant was ready for trial operation. Orifice calibration was performed May 22 to 25. Procurement of minor pieces of purchased equipment, such as wooden-stave tanks, required three to four weeks from date of preparing specifications. However, the stainless steel spray drier, which was fabricated in California, required four months for procurement and was not placed in use until the latter part of the pilot plant operation.

DESCRIPTION OF PROCESS

As carried out in the pilot plant the main steps of the process (Figure 1) were as follows:

1. A boiling 7.5% solution of ammonium chloride is circulated over scrap copper wire, with simultaneous aeration, to form a solution of copper ammonium chloride.
2. Solid arsenic trioxide is added to the solution, and further heating, aeration, and agitation cause precipitation of copper arsenite.
3. The product is separated from the mother liquor by filtration and washed.
4. The washed product is dried, ground, and packaged.
5. The mother liquor is recycled to the copper extraction step after having been used to scrub ammonia from the gases leaving this step and the precipitation step.

In addition to ammonium chloride, the mother liquor contained varying amounts of copper and arsenic in solution, since the precipitation did not go to completion. The process was batchwise with respect to product and cyclic with respect to mother liquor. An important characteristic of the process was the fact that, in normal operation, the copper concentration of the solution obtained in step 1 varied widely from batch to batch.

The composition and physical condition of the solid material obtained in the precipitation step could vary widely, depending on the composition of solution, the proportion of arsenic added, and the time, temperature, and technique. The desired product was light blue in color and had an ultimate particle size of 2 to 6 microns. Following is a typical analysis of the pilot plant product compared with the theoretical composition of copper arsenite:

	Composition, % by Weight						
	As_2O_3	As_2O_5	CuO	Cl	NH_3	H_2O	Total
Pilot plant product	68.4	1.0	28.3	0.1	0.2	1.1	99.1
Theoretical	71.4	...	28.6	...	...	...	100.0

However, other materials were obtained that ranged in color from bright copper sulfate blue to olive green and contained uncombined arsenic trioxide in amounts up to 30%. These materials were larger in particle size than the normal product and were invariably less effective in larvicidal action. These compounds formed not only in the precipitation step but in the scrubber, copper dissolver, and mother liquor storage tank as well. Consequently, the control of the concentrations of copper and arsenic in the mother liquor at various stages in the cycle constituted the chief problem encountered in the investigation.

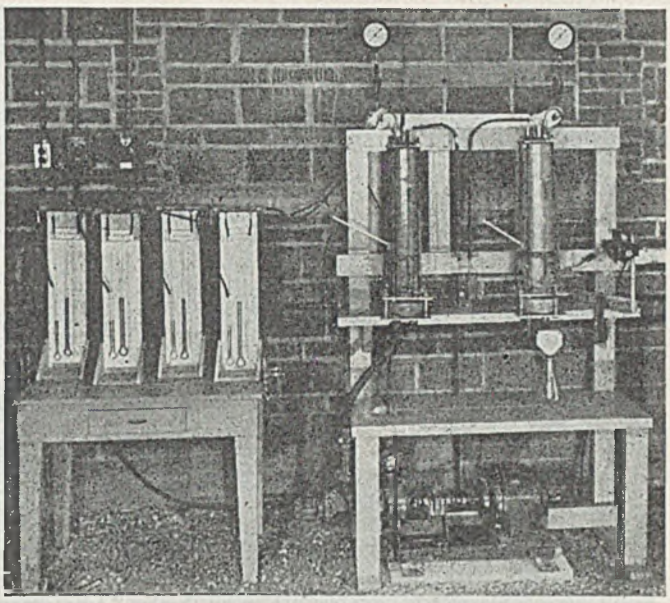


Figure 2. Bench Scale Plant for Copper Arsenite

CHRONOLOGY OF PILOT PLANT WORK

The pilot plant, which had an intended capacity for producing 600 pounds of copper arsenite per 24-hour day by the proposed process, was designed and constructed during the spring of 1939. After intermittent testing, this plant was operated continuously for a month during the summer to produce 3.5 tons of larvicide. A production rate of about 600 pounds per day was obtained initially, but the rate fell rapidly with continued operation to about 200 pounds per day. The decrease was due to the formation and accumulation of insoluble arsenic-copper compounds in the unit for dissolving copper, which cut down the capacity of the unit. Operation of the pilot plant was otherwise quite satisfactory. On the assumption that a means of maintaining the copper-dissolving capacity could be found, it was estimated that copper arsenite could be produced at about half the market price of Paris green in a plant having six times the capacity of the pilot plant. In airplane dusting tests in the field the pilot plant product compared favorably with Paris green, even though measurements indicated that the proportion of the copper arsenite discharged from the airplane actually reaching the designated water surface was smaller than that of Paris green; this was attributed to the smaller particle size of the copper arsenite. Related studies by the TVA Malaria Control Division (*1*) also indicated that the smaller particle size was partly responsible for the superior larvicidal action of the copper arsenite. It therefore was decided to continue the study, concentrating on two objectives: first, to find improvements in the copper dissolving step that would make it possible to maintain steady operation of the plant at full capacity; and second, to determine the factors controlling the particle size of the product.

In the spring of 1940 a study was carried out in a bench scale plant similar in all essentials to the pilot plant but having approximately one hundredth its capacity (Figure 2). A large number of larvicide samples were prepared in this equipment using the cyclic procedure and varying the conditions for the dissolving and precipitation steps over a wide range. During this time rapid methods of analysis for copper and arsenic in the

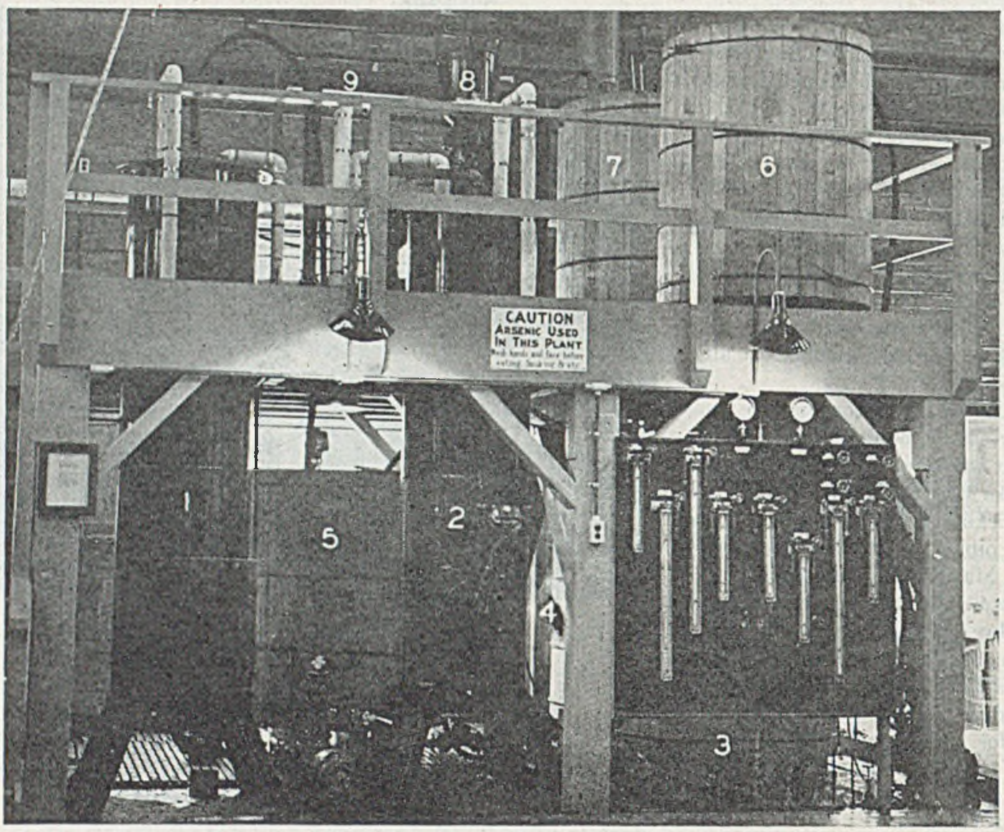


Figure 3. Copper Arsenite Pilot Plant in 1939 with Design Capacity of 600 Pounds per 24 Hours

1. Copper dissolver
2. Precipitator
3. Filter tank
4. Alternate filter tank
5. Mother liquor storage tank
6. Wash water storage tank
7. Scrubber
8. As_2O_3 feed hopper
9. Gas cooler

mother liquor were developed that proved important in the small scale study and in subsequent pilot plant operation. From the correlation of the data obtained in this study, a procedure was devised for controlling the rate of addition of arsenic trioxide to the precipitation step, so as to obtain a uniformly good product and to avoid the precipitation of undesirable compounds at other stages in the mother liquor cycle.

The following summer the pilot plant was operated again, after some equipment changes had been made. After a period of trial operation by the revised procedure based on the small scale work, the plant was operated continuously for 5 days at a sustained production rate averaging more than 500 pounds per day. The product was uniformly good, and steady-state operation substantially free from the effects of undesirable precipitation was adequately demonstrated. The particle size of the product was found to be substantially independent of the conditions maintained in the precipitation or spray-drying operations. The previous cost estimates were confirmed. Laboratory and field tests gave further evidence of the larvicidal value of copper arsenite.

DESCRIPTION OF PILOT PLANT

Following is a description of the pilot plant as initially installed, along with a few of the reasons guiding the selection and design of equipment. Reference is made to subsequent changes in some of the equipment; other changes will be noted in discussing the operation. A diagrammatic flow sheet of the plant is shown in Figure 1. Figure 3 shows a general photographic view of the plant, which was located against one wall of a large, heated building of tile construction, devoted entirely to pilot plant installations.

Copper Dissolver. The copper dissolver consisted of a steel tower lined with Duro acidproof brick, 9 feet high and 18 inches in inside diameter. The dissolver was made tall and narrow rather than short and wide (that is, a tower rather than a tank) to provide adequate liquor depth for effective aeration. Brick-lining was used because it combined corrosion resistance with thermal insulation and also because there was uncertainty regarding the resistance of stainless steel and other metals to the ammonium chloride mother liquor. A bed of copper wire 3.5 to 4 feet deep rested on a perforated stainless steel plate underneath which air was introduced. Ammonia could be introduced from a portable cylinder into the air line. The dissolver was heated by means of a steam coil made of $^3/_4$-inch A.I.S.I. Type 304 stainless steel pipe. The wall was penetrated at points near the bottom and top by two pipe nipples, which, through the use of rubber stoppers, served simultaneously as outlets for a liquid-level gage, for the introduction of thermometers, and for the removal of liquid samples. Recirculated liquor was introduced at the top and distributed over the copper by a stainless steel cone. The copper charge consisted of 1000 pounds of scrap No. 12 cable chopped into 1.5-inch lengths.

Precipitator. The precipitator was a brick-lined tower similar in construction and dimensions to the dissolver. Recirculation was not used in the precipitator, but agitation was provided by a $^1/_4$-horsepower Lightnin mixer introduced at a 45° angle through the side wall. Stainless steel (Type 316) stirrers were used both in the precipitator and storage tank and proved fairly satisfactory, but failed one by one and were replaced with Durimet, which gave much better service. An emergency bronze stirrer installed in the precipitator dissolved completely in a day or two. Arsenic trioxide (technical grade As_2O_3) was introduced through the top of the tower by means of a double-doored hopper, which was closed on top by a hinged flange sealed with a rubber gasket and underneath by a 6-inch quick-opening gate valve. This hopper is seen in Figure 4, which is a view of the upper operating platform.

Gas Cooler and Scrubber. The hot gases leaving the precipitator and dissolver, containing water vapor and ammonia vapor, passed through a common manifold into a shell-and-tube gas cooler. The gases were cooled in order to keep the temperature of the scrubber liquor low enough for good ammonia recovery. Valve arrangements were such that air flow could be arranged in series instead of in parallel through the dissolver and precipitator. The cooled gases passed into a scrubber consisting of an open cypress tank 4 feet in diameter and 4 feet high, filled with filtrate mother liquor, through which the gas was bubbled by means of a distributor made of $^{1}/_{4}$- and $^{1}/_{8}$-inch pipe.

Tanks, Pumps, Etc. The slurry obtained from the precipitator was filtered by gravity through filter cloth stretched across the top of a wooden-stave tank. This tank, like the other tanks shown in Figure 3, was identical with the scrubber tank. Wooden tanks were used because of ready availability, cheapness, and the uncertainty regarding the suitability of stainless steel and other metals. They proved quite satisfactory as long as they were operated at a fairly constant liquid level but leaked badly when the level was raised to a place that had been left dry long enough to shrink the wood.

On the basis of rapid settling obtained in preliminary laboratory tests, it was originally planned to separate the product from the mother liquor by decantation. However, the method proved unsatisfactory in initial pilot plant trials because settling was too rapid; the product settled into a dense cake that could not be effectively reslurried for washing even by vigorous agitation. For the same reason it could not be removed from the settling tank by pump, as planned, but had to be dug out laboriously. The method of separation was then changed to gravity filtration by stretching a cloth across the same tank used for settling, and this was a decided improvement with regard to product recovery, effective washing, and reduction in labor. A further improvement was later made by converting the gravity filter to a suction filter operating essentially like a Büchner funnel.

A wooden tank (Figure 3, No. 5) was provided for the storage of mother liquor to be used in dissolving copper. The tank was equipped with a removable coil, which could be connected to circulate either steam or cooling water, and with a portable Lightnin mixer with a stainless steel stirrer. Two other tanks, 4 and 6, can be seen in Figure 3 but are not shown in the flow diagram. Tank 4 was used alternately with tank 3 as a filter. Tank 6 was used for the storage of wash water that was to be recycled.

Rubber hose was used for the lines handling process solutions, both for its corrosion resistance and to permit use of lines and pumps for more than one purpose. Duriron pumps (1 inch centrifugal), hose connections, and plug cocks, which were available from the storeroom as general pilot plant equipment and had the necessary corrosion resistance, proved satisfactory in spite of occasional breakage resulting from their relative fragility. One pump, by proper valve adjustment, could be arranged to pump liquor from the storage tank to the dissolver, to recirculate liquor in the dissolver, or to transfer solution from the dissolver to the precipitator. A second pump, by means of a movable discharge hose, carried slurry from the precipitator to either filter tank. A third pump removed filtrate from either filter tank to any of the other tanks.

Instrumentation. Air flows and steam flows were measured by means of orifice meters. The air orifices were calibrated against a standard orifice equipped with straightening vanes, and the steam orifices were calibrated by weighing the condensate obtained during a measured period. Steam traps were located ahead of the orifices. Pressures at the inlet and exit of both towers were measured. Steam pressures were measured by 100-pound Bourdon gages, and air pressures were measured by mercury manometers.

Temperatures at the bottom and top of both towers were measured with mercury thermometers inserted through rubber stoppers through the wall. The temperature readings at the lower points were sometimes incorrect because of building up of precipitate about the thermometer bulb, and these readings occasionally were checked by spot measurements of the temperature of the solution as it was pumped from the tower or removed through the sampling lines. Samples were removed through a second opening in the rubber stoppers holding the lower thermometers. These same openings were used to measure the liquid level in the towers by means of glass tubes connected between the upper and lower openings. Temperatures of the water entering and leaving the gas cooler and of the gas leaving the gas cooler were also measured with thermometers inserted into the lines through rubber stoppers.

The liquid level in all five tanks was determined from measuring sticks graduated in half inches, fastened to the inside of the tank. Water flow to the condenser was metered. Arsenic trioxide was weighed on a platform scale to the nearest $^{1}/_{4}$ pound.

Spray Dryer. The product was dried in a Peebles spray dryer with a 5-foot-diameter drying chamber purchased from the Western Precipitation Corporation. This unit has a basket-type atomizer rotating at about 12,000 revolutions per minute. Figure 5 is a photograph of the installed dryer. A Multiclone dust collector, consisting of four 6-inch units in parallel, was used to recover the product. A water spray in the gas outlet stack served to scrub from the gas any dust escaping the Multiclone. The spray dryer was used only in the final week of the 1939 operation and throughout the 1940 campaign. Before the spray dryer was available, the copper arsenite was dried in a tray dryer and ground in a Mosley mill. The spray dryer had a capacity of 150 pounds of dry product per hour. This size of the spray dryer, which was the most expensive single item of equipment, was selected in part on the basis that it would make the unit suitable for use in a plant supplying the full needs of the malaria control program if copper arsenite were adopted for regular use. A spray dryer was decided upon despite its relatively high cost and after such alternatives as a heated pulverizer (kiln mill) had been considered because it combined the function of pulverizer and dryer, and particularly because it carried the material from a water suspension to a packaged product in a single operation in a sealed unit, involving no handling and a minimum of exposure of personnel to the irritating and toxic effects of the powdered product. Its cost was borne equally by the copper arsenite pilot plant and another project in which it was later used.

Hot gases for the drying operation were obtained from the combustion of by-product carbon monoxide gas from phosphorus plant electric furnace operation in an experimental rotary kiln, which was a permanent installation for general use and was

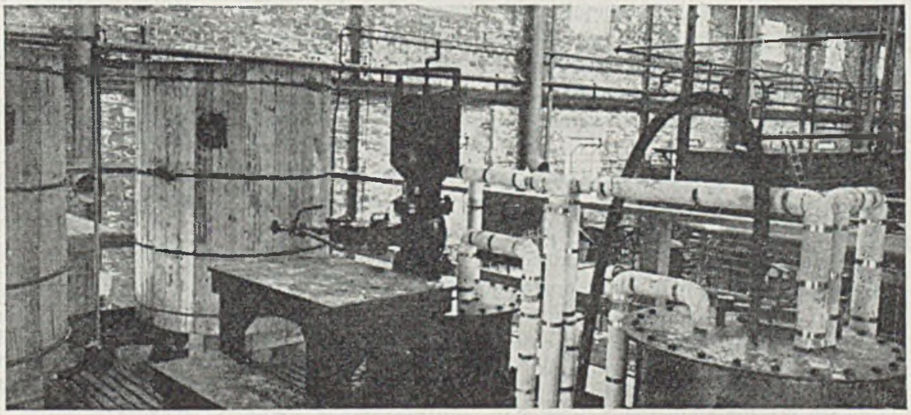


Figure 4. Upper Operating Platform of Copper Arsenite Pilot Plant

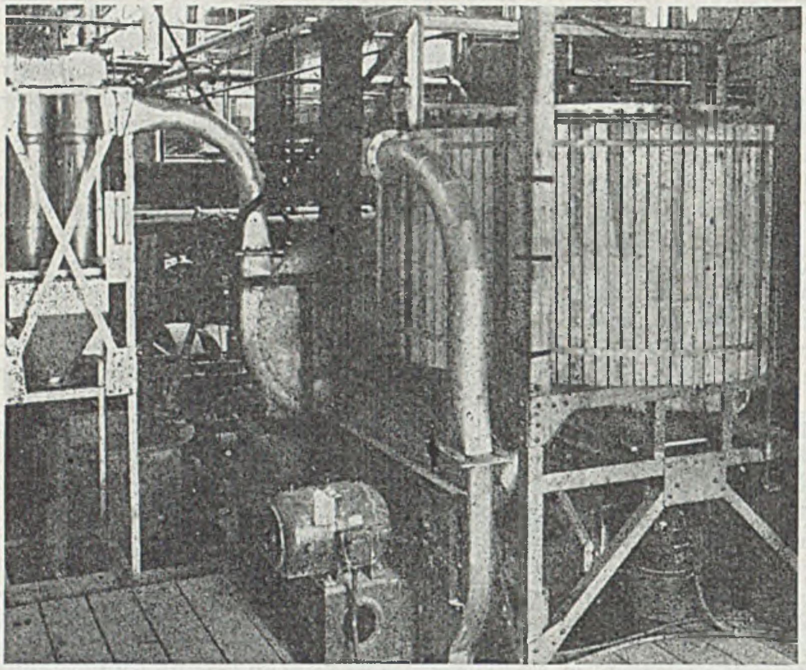


Figure 5. Spray Dryer Used in Copper Arsenite Pilot Plant

located adjacent to the dryer. The slurry to be dried was stored in a lead-lined steel tank and was circulated by a 1-inch Pioneer metal centrifugal pump. The tank was provided with two portable Lightnin mixers ($^{1}/_{4}$ horsepower) to keep the copper arsenite in suspension. The rate of feed was controlled by recirculating the slurry continuously, a small portion being bled into the desiccator through a valve consisting of a 6-inch length of $^{3}/_{4}$-inch rubber tubing that could be constricted with a screw clamp.

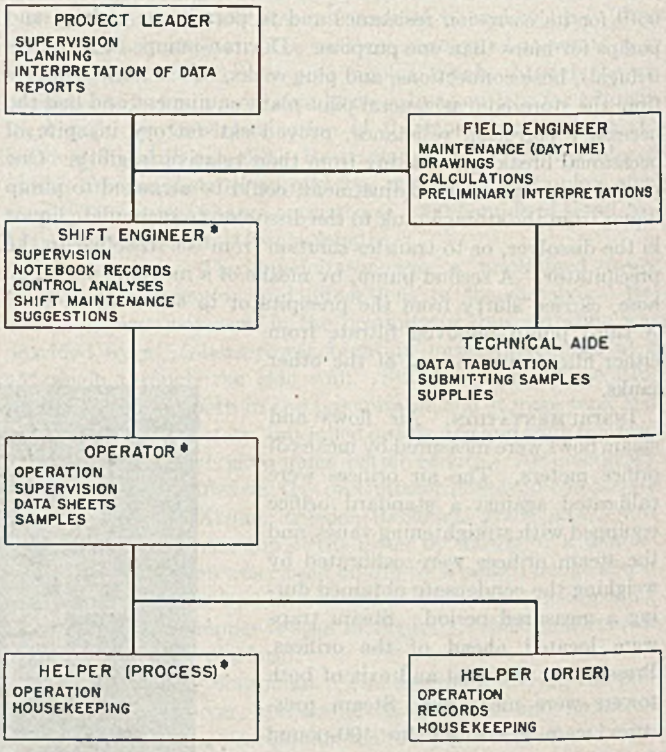
PERSONNEL

Figure 6 is an organizational chart of the personnel, professional and nonprofessional, employed full time in the copper arsenite pilot plant investigation, with a brief indication of their principal duties. Because of the relatively small size of this pilot plant, the number of personnel was probably smaller and the organization simpler than in many cases. The chart represents the period when the pilot plant was being operated continuously on a five-day, three-shift basis. The investigation was the direct responsibility of a project leader. The field engineer acted as general assistant to the project engineer, having been assigned to the project from the start. As previously mentioned, he had assisted in the design, prepared the drawings, and followed the construction. During the regular operation he took care of the maintenance jobs and the equipment changes other than those handled during the night shifts. He prepared drawings for such changes and carried out calculations for the interpretation of results and preparation of reports.

A technical aide (nonprofessional), under the direction of the field engineer, carried out the tabulation and routine calculation of the pilot plant data on a daily basis; once a day he transmitted the samples from the pilot plant to the analytical laboratory, and he secured the various supplies, routine and special, requested by the shift engineer. The shift engineer, who was assigned to the project only during pilot plant operation, was in charge of the operation for an 8-hour shift. In addition to his main job of running the plant successfully, he entered a log of the shift history in a permanent record notebook, saw that the proper records and samples were being taken, and made suggestions as to the improvement of the operation of the process. After the development of rapid methods of analysis of the liquor for arsenic and copper, running these analyses was part of his job. The shift engineer had a B.S. degree in chemical engineering and had one or two years' experience in pilot plant operation and similar work. The field engineer had a similar background with somewhat more experience. The project leader, in addition to such experience, had for the past few years been in charge of development projects of scope similar to the copper arsenite work. The aide was a chemical engineering student in his junior year working for a 3-month period as part of a cooperative training curriculum; such jobs are also held by permanent employees whose qualifications are based on pertinent college training or on high school education plus practical experience.

The plant was operated by a crew (nonprofessional) of two men per shift, whose qualifications consisted of grammar school or high school education and whose previous technical experience was generally confined to several years of service in their current jobs. The head operator's responsibilities included the operation of the plant, periodic recording of data, and securing of samples, plus performance of some of the operating duties. His helper performed most of the operating chores, such as charging the tower with copper, operating the filter, etc., as well as the general task of keeping the area clean. A second helper served on the day shift only to operate the spray dryer and to take the necessary samples and data. The operators were under the administration of the Service Section but were fully subject to the supervision of the shift engineer.

Most of the maintenance work and equipment changes were carried out on the day shift, when craftsmen were available on a full-time basis for pilot plant work by application to the Service



* THREE-SHIFT; OTHERS DAY-SHIFT ONLY

Figure 6. Organization Chart of Full-Time Personnel for Pilot Plant Investigation

Section. For emergency jobs during the night shifts, maintenance men could be had on call from the adjacent full scale plant operations.

A note should be added concerning the supervisory levels above the top block of Figure 6. The project leader held informal discussions of the work progress with his supervisor, the chief of the Process Development Division, at irregular intervals, perhaps once or twice a week. Once a month written progress reports were discussed at a meeting of the project leaders and the division chief, and the program was reviewed in the light of current results and revised if advisable. A formal report to serve as a permanent record of the work was prepared at the conclusion of the 1939 campaign, and another in 1940; these reports included conclusions drawn from the work and recommendations for further work or for utilization of the results. It may be superfluous to mention that these conclusions and recommendations had generally been transmitted by memorandum or otherwise, and acted upon, before the reports themselves had been issued in final form.

PROCEDURE

The operating procedure is illustrated by the following set of actual instructions, which were in effect during the final period of pilot plant operation. (The spray dryer instructions are not included.)

Operating Instructions
Copper Arsenite Pilot Plant, Run P2, June 1940

Most of the following instructions apply to each cycle:

1. At end of reaction period, shut off air, ammonia, and steam to precipitator. Note level. Pump slurry onto filter, having previously started suction. Solution remains in precipitator 60 minutes after first arsenic addition. (Initial precipitate is generally olive-green and gradually turns light blue upon aeration. If sample is still green after 60 minutes, continue aeration and consult supervisor for special instruction.)
2. Transfer solution from dissolver to precipitator. Start air at $\Delta P = 5$ inches mercury, and steam as indicated on board.
3. Transfer 52 gallons ($6^{1}/_{2}$ inches) from tank 7 (scrubber) to dissolver, controlling air flow to precipitator to avoid suction at top of towers. Start air at $\Delta P = 2$ inches water, and steam as indicated, and recirculate.
4. Meanwhile slurry is being filtered. Take 10 gallons of strong wash water from storage tank, heat, and wash cake, adding wash to filtrate. Transfer filtrate to tank 7, removing sample E while pumping. Add 1200 ml. concentrated hydrochloric acid to tank 7. (A and E were used to designate, respectively, samples of liquor from the precipitator and the filtrate.)
5. After solution has been in precipitator 15 minutes, cut air to $\Delta P = 0.3$ inch mercury. Take sample A for analysis. Add 20 pounds arsenic. Start ammonia, adding $^{3}/_{4}$ pound over 60-minute period ($\Delta P = 3.8$ inches oil).
6. Analyze sample A for copper and arsenic. Calculate total arsenic to be used, using curve for $A = 30$ on chart (Figure 7). Add required amount.
7. After collecting three cakes on cloth, wash with 30 gallons of cold water, and transfer filtrate to wash-water storage tank. Wash with 30 gallons additional water and discard filtrate. Remove cake to storage box.

Samples. Take liquid samples A and E from precipitator and filtrate, respectively, once every batch, as indicated in procedure.

Take duplicate samples of mother liquor from tank 7, once every four batches, just before transferring solution to dissolver—that is, before batches 4, 8, 12, etc. (one sample for ammonia and chloride, and one for copper and arsenic).

Determine copper and arsenic in all samples.

Readings. Record both tower levels just before emptying and just after filling.

Note level and time for tank 7 after adding or removing solution.

Record temperature in both towers twice per batch.

Record time and amount of arsenic additions.

Record time of taking samples from tank 7.

Note number of spray dryer batch into which filter cake goes.

Note. Be careful in adding solid arsenic to avoid dusting. Keep barrel on scale and weigh by difference; remove arsenic with scoop from barrel directly to hopper.

Keep wooden plug in tank 7 drain when not pumping out.

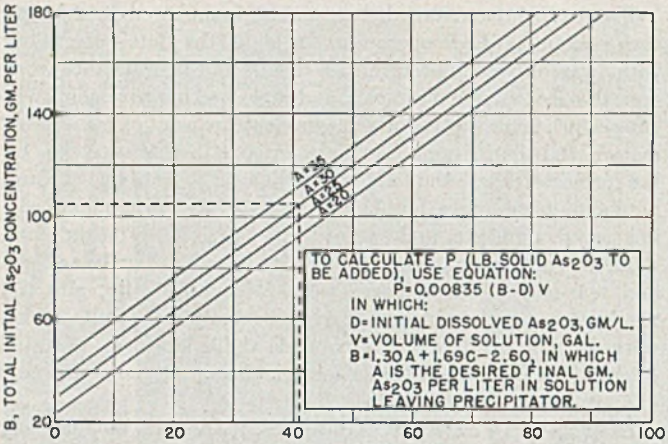
The readings were recorded on standard numbered data sheets, each covering 1 day's operation. A log of the shift's operation, with notes on special occurrences, repairs and maintenance work done or needed, special samples, and suggested improvements was entered in a bound notebook with duplicate tear-out pages. Information and instructions also were entered in this notebook by the project leader and the field engineer. Data sheets and notebook pages were numbered, respectively, with nonrepeating serial numbers and were filed permanently after final reports covering the work had been completed. The data sheets and tear-out notebook pages were picked up daily, and the results were tabulated together with the analytical results, which were received on standard forms from the laboratory. Routine calculations of averages, totals, material balances, etc., were made daily by the engineering aide.

Sampling and Analysis. In the 1939 campaign the following sampling procedure was used: During the preliminary operation on the day shift only, a complete set of liquid samples was taken, which included samples from the dissolver and precipitator at the end of each hourly batch and samples of the filtrate, scrubbing solution, strong wash, and mother liquor at the end of each filtration cycle. During continuous 24-hour operation, in order to keep the analytical load from becoming excessive because of the increased rate of operation, liquid sampling was reduced to samples of every sixth batch from the dissolver, together with samples of the filtrate, scrubber solution, and mother liquor taken at the end of alternate filtration cycles. All solutions were analyzed for copper and arsenic; in addition, the tank solutions were analyzed for ammonia and occasionally for chloride. All analyses for the 1939 pilot plant operation were carried out by the general analytical laboratory, which is set up to handle the analytical work for all the research and development projects, and results generally were available 24 hours after sampling.

The studies carried out in the bench scale plant in the spring of 1940 resulted in a considerable change in the sampling and analysis procedure for the 1940 pilot plant operation. The liquor samples were immediately analyzed by the shift engineer for copper and arsenic by rapid, approximate methods. Copper determination was by a colorimetric method employing the cupric ammonium complex; arsenic determination was by titration with sodium bromate. By dividing the arsenic addition to the precipitator into two steps, the time required for analysis was not lost from the precipitation period. The rapid analytical methods also were used for determining the copper and arsenic contents of the filtrate from each batch. The only solution samples submitted to the analytical laboratory were mother liquor sample taken after every fourth batch and analyzed for copper, arsenic, ammonia, and chloride.

Samples were taken of each product of a given spray dryer operation, which amounted to 200 to 300 pounds. Since riffling or quartering was impractical because of the toxicity of the material, samples were obtained by dipping into the batch at a number of points. The samples were analyzed for copper, arsenic trioxide, arsenic pentoxide, free arsenic trioxide, ammonia, chloride, and moisture. Screen analyses, using screens graded to 325-mesh size, also were made, and these were supplemented by microscopic examination for rough estimates of ultimate particle size.

Portions of these samples were submitted to the Malaria Control Section for pan tests, and the product itself was submitted for field tests. In pan tests the larvicidal efficiency of the material was compared with that of Paris green under laboratory conditions. Equal weights of the two materials, mixed with 9 parts of soapstone in a mortar and pestle, were dusted onto the surface of water contained in shallow pans, each containing substantially the same number of *Anopheles* larvae and maintained at the same constant temperature. The larvae remaining alive at the end of 2, 3, and 4 hours were counted. The ratio of the percentage



TO CALCULATE P (LB. SOLID As_2O_3 TO BE ADDED), USE EQUATION:

$$P = 0.00835\,(B - D)\,V$$

IN WHICH:

D = INITIAL DISSOLVED As_2O_3, GM./L.

V = VOLUME OF SOLUTION, GAL.

B = 1.30A + 1.69C − 2.60, IN WHICH A IS THE DESIRED FINAL GM. As_2O_3 PER LITER IN SOLUTION LEAVING PRECIPITATOR.

Figure 7. Calculation of Solid As_2O_3 Addition to Precipitator

killed by the material being tested to that killed by the Paris green in a 3-hour period was taken as its Paris green coefficient.

Field tests were made under the actual conditions in which larvicide was applied in routine mosquito control operations. Equal amounts of both Paris green and copper arsenite, diluted in the customary manner with 3.5 parts of soapstone, were dusted by airplane over two comparable areas of the reservoir. The number of live *Anopheles* larvae in each area was determined before and after dusting by dipping out samples in a standardized manner at a number of definite locations marked by stakes. The results of the pan and field tests of copper arsenite have been reported by Hinman, Crowell, and Hurlbut (*1*).

NOTES ON OPERATION

In the initial operation of the pilot plant, which started on June 15, 1939, batchwise tests were made intermittently on the day shift during the first 2 months. In the course of this time changes were made gradually in both the equipment and procedure, largely by a trial-and-error process. Both pan tests and field tests were promptly made of the first products and served as a guide in improving the process. Continuous operation started on August 15 and was continued for a month. Noted below are some of the more pertinent observations and changes, both for the equipment and process, that were made during these periods.

Equipment Notes. It became apparent early in the operation that the formation of precipitate in various parts of the system would be a source of operating difficulties. These difficulties were overcome gradually by minor changes in the equipment, and they were virtually eliminated in the 1940 operation through better control of the mother liquor composition as discussed in the next section. The 1/8-inch openings through which air originally was introduced into the dissolver and precipitator clogged almost immediately but were replaced successfully with 1/2-inch openings. The 1.5-inch annular space between the steam coils and the wall of both towers filled solidly with precipitate, creating a dead space, which cut down heat transfer and made it difficult to remove the coils for cleaning. This difficulty was eliminated by using smaller coils, which increased the clearance from 1.5 to 3 inches. The precipitator coils became coated with a hard layer of precipitate, which apparently protected them from corrosion but also cut down the heat transfer capacity to a serious extent. Occasional washing with acid helped somewhat, but the problem was not solved in the pilot plant work. Plugging of the transfer lines at the tees and ells was frequent. Prior to the 1940 operation, permanent cleanout rods working through packing glands were installed at the critical points; this made it easy to keep the lines open.

Several other equipment changes were made prior to the 1940 operation that contributed to both the ease and effectiveness of operation. Conversion of the gravity filter to a suction filter has been mentioned. The mother liquor storage tank was eliminated; instead, all the mother liquor was stored in the scrubber tank. Through this simplified operation it was feasible to operate with two pumps instead of three, and ammonia recovery in the scrubber was improved also. The addition of hydrochloric acid (instead of ammonium chloride) to the mother liquor to replace chloride losses also improved ammonia recovery.

A shortcoming of the pilot plant was the crowded arrangement, particularly the inadequate head room over the filter and storage tanks. The ammonia fumes given off by the hot solution aggravated this difficulty. The conditions above the filter were improved by cutting 1.5 feet off the top of the wooden tank. It was evident that for prolonged operation a system of hoods for fume removal would be desirable.

Another change that was indicated as desirable was the use of oversize pumps and lines to minimize the proportion of time spent unproductively in transferring solutions, and thus increase the over-all production rate of the plant.

The operator controlled the operation of the spray dryer by constant adjustment of the feed rate to keep the temperature of the exit gases in the desired range of 210° to 250° F. In the initial operation slurry was fed by gravity from an overhead tank, the feed rate being adjusted by means of a valve in the feed line. This was unsuccessful because the rapid settling of the copper arsenite particles caused clogging of the valve and wide fluctuation in rate. The problem finally was solved by a feed arrangement in which slurry was constantly recirculated through an overhead line from a vigorously agitated feed tank. Part of the slurry was diverted from this line in an upward direction through a control valve that consisted of an adjustable pinch clamp on a 6-inch length of 1-inch rubber tubing; from this valve the line turned downward to the dryer. Even with this arrangement it was necessary to clean the valve every three or four minutes by a brief injection of tap water through a branch line.

Process Notes. Observations and changes in the process were as follows:

Addition of Air and Ammonia. The proper rate of aeration during the dissolving and precipitating steps was determined by trial. Theoretically, somewhat less than 1.0 cubic foot per minute was needed in the dissolving step, for the oxidation of metallic copper to the cuprous state, but rates up to 10 c.f.m. were tried. At rates above 2 c.f.m. foaming occurred and became increasingly worse with increasing rate. A rate of 1.0 c.f.m. was adopted and prove satisfactory. Analyses of the off-gas, which were made occasionally, agreed roughly with the calculated oxygen consumption. In the precipitation step aeration was needed for oxidation of the cuprous ion to the cupric state, and it was found best to complete the oxidation early in the precipitation period. On the other hand, it was difficult to attain temperatures above 200° F. at high rates of air flow, and it was found that high temperature was essential in the latter part of the period to convert the precipitate from the green color in which it formed initially to the light blue that was characteristic of a good product. These requirements were reconciled by aerating at a rate of 10 c.f.m. for the first 15 minutes, then reducing the rate to 3 c.f.m. for the 60 minutes following the initial arsenic addition.

Although various conflicting theories as to the function of ammonia addition were held at different times, it was finally concluded that its primary function was the obvious one of making up for losses of ammonia from the system. No systematic ammonia addition was provided for initially, but almost at once the need became apparent, and the addition of 3/4 pound per batch to the dissolver was found by trial to balance the losses fairly well in the

1939 operation. During the bench scale studies, it appeared that addition of ammonia to the precipitation step favored this operation; consequently, in the 1940 pilot plant operation ammonia was added to the precipitator instead of the dissolver. Although this proved satisfactory, there was no conclusive evidence that the change was significant.

Both in the bench scale and pilot plant work it was found that the ratio of ammonia to chloride in the mother liquor had no marked effect. However, this ratio was kept much more uniform in 1940 than in 1939 by adding 1 pound of hydrochloric acid (100% basis) to the mother liquor with each batch of filtrate.

Water Balance. One of the problems to be solved in the pilot plant operation was adjusting the water balance in the cyclic part of the process. Water was added to the process chiefly in the form of wash water. It was removed, aside from mechanical losses, as vapor in the gases leaving the scrubber and as moisture in the washed product going to the dryer. In general, input and outgo had to be balanced in order to avoid a cumulative change in the mother liquor concentration. It was obviously desirable to use as much wash water as possible to keep mother liquor loss in the product to a minimum. Practically speaking, the permissible amount of wash water could be increased only by increasing the scrubber temperature to increase the water content of the saturated gases leaving the scrubber. However, such an increase in temperature increased the loss of ammonia vapor in these gases. A fairly satisfactory balance was struck at a scrubber temperature of about 95° F.; however, operation was not prolonged enough to permit an accurate determination of the optimum condition.

An obvious method of improving the water balance is to separate the condensate from the gases leaving the cooler before they pass into the scrubber, and to use this as wash water. This was tried; the separation was accomplished by use of a collecter with a liquid seal. However, the high ammonia content of this condensate made its use as wash water impractical because of ammonia losses and intolerable working conditions around the filter. Washing efficiency was improved by using the available wash water twice in a countercurrent progression and adding the wash solution to the filtrate after its second use. The cake was washed finally with additional water which was discarded; this, of course, did not improve the recovery of mother liquor, but its use proved desirable for the sake of eliminating chlorides from the product as thoroughly as possible in order to minimize corrosion of the spray dryer, which otherwise was appreciable.

Control of Precipitation Step. In the 1939 pilot plant operation the production capacity rapidly decreased with continued operation because of the accumulation of insoluble arsenic-copper compounds in the bed of copper. In addition, the product, while satisfactory, was quite variable in composition and often contained considerable amounts of free arsenic. Temporary improvements were obtained by such methods as removing the copper and cleaning it mechanically, or cleaning it by circulating either fresh ammonium chloride solution or hydrochloric acid through the bed. However, these were makeshift and uneconomical procedures.

It was apparent that the cause for this behavior was the excessive content of dissolved arsenic in the filtrate from precipitator batches and hence in the mother liquor, which led to precipitation of the troublesome compounds when this mother liquor was recycled to the dissolver. This behavior did not become apparent during the first 2 months of operation, which was on a day-shift basis, because when the mother liquor was allowed to cool overnight in the storage tank, considerable precipitation occurred and lowered the concentration of dissolved arsenic in the solution charged to the dissolver. However, with three-shift operation the mother liquor remained hot, little precipitation occurred, and the trouble developed. Cooling the mother liquor was an impractical procedure for steady operation because the precipitates formed in the storage tank were of variable composition and generally had poor larvicidal action, so that they represented an excessive waste.

The copper concentration in the solution before precipitation ranged from 20 to 60 grams per liter; after precipitation the solution contained from 5 to 20 grams of copper per liter and from 50 to 90 grams of arsenic trioxide per liter. At these high concentrations of arsenic, precipitation in the dissolver and other parts of the system could not be avoided. However, there were indications that, if the concentration of arsenic trioxide in the solution leaving the precipitator could be kept below 30 grams per liter, unwanted precipitation could be fairly well eliminated.

In the bench scale studies made the following spring, rapid methods of analysis for copper and arsenic were developed, so that the amount of arsenic added could be based on the actual composition of each batch. The following conditions were then varied in an exploratory manner over the range indicated, in search for a method of controlling the process more effectively:

Condition	Range of Variation	
	Dissolver	Precipitator
Air input, % of normal	100-400	100-133
NH_3 input, % of normal	0-100[a]	0-200
NH_4Cl concentration, %	5-20	5-20
NH_3/Cl mole ratio	0.89-1.22	0.67-1.22
Time, minutes	45-150	45-150
Temperature, ° F.	212	140-212
As_2O_3 concentration, g./l.	0-39	38-184
Cu concentration, g./l.	0-31	6-160
As_2O_3/Cu mole ratio before pptn.	...	0.59-1.96
Repeated pptn.	...	1-2

[a] Based on normal addition to precipitator; no ammonia was normally added to dissolver in bench scale tests.

Obviously, only a limited amount of work could be done on each factor, even though 200 separate precipitations were carried out. The effect of most of these factors was found to be either negligible or too small to account for the pilot plant behavior. Review of the accumulated results of a large number of experiments suggested that the factors most strongly affecting the residual arsenic concentration after precipitation were the initial concentrations of arsenic and copper. However, an attempt to correlate the data for about forty tests made under reasonably uniform conditions on the basis of these two concentrations was unsuccessful. It was then found unexpectedly that, within the range of practical operation, the rate of precipitation was governed solely by the initial copper concentration, and this led to the following simple relation:

$$A = a + bB + cC \qquad (1)$$

where A = residual As_2O_3 concentration (after precipitation), g./l.

B = total initial As_2O_3 present, g./l.

C = initial copper concentration, g./l.

a, b, c = constants

The specific values of a, b, and c depend on operating conditions, such as time and temperature. For the experimental conditions (45-minute reaction period after arsenic addition; temperature, 200° to 212° F.; NH_3/Cl mole ratio nominally 1.0; NH_4Cl concentration, 7.5%; and vigorous agitation) Equation 1 becomes:

$$A = 2.0 + 0.77B - 1.3C \qquad (2)$$

This equation was used for control purposes as follows: A, the arsenic concentration after precipitation, was set at a value shown by experience to give satisfactory steady-state operation with only minor formation of precipitate in the mother liquor storage tank and copper dissolver; 30 grams per liter proved an effective upper limit. Immediate analysis of the copper-rich solution after transfer to the precipitator by the colorimetric method gave a value of C, and B was then calculated from Equation 2. Knowing by analysis the concentration of arsenic trioxide already in solution and the volume of solution, the amount of solid arsenic trioxide to be added to bring the total concentration up to B was determined. Use of this equation was facilitated for routine operation by preparation of the chart shown in Figure 7, in which a series of lines are given for different values taken for A.

The use of this chart proved very effective. In the 1939 operation several rule-of-thumb methods for determining the amount of arsenic addition had been tried, such as making the ratio of arsenic to copper the same as in copper arsenite, or adding a fixed amount of arsenic. They were consistently unsuccessful, and residual As_2O_3 concentrations as high as 70 or 80 grams per liter were frequent. However, with the help of the chart, the residual As_2O_3 concentration averaged 15 grams per liter for the 1940 operation; individual values ranged from 5 to 42 grams per liter, but few exceeded 20. Moreover, the average rate of copper dissolution was as high on the last day of the 5-day run as on the first. In this operation, A was set at 30, but a factor of safety was provided by extending the reaction period from 45 to 60 minutes.

Even with this comparatively steady-state operation the composition of successive batches leaving the dissolver varied widely in a manner inherent in the operation. It was this variation that made a control method essential. Thus the copper concentration before precipitation ranged from 10 to 60 grams per liter, and the required additions of solid arsenic ranged from 20 to 57 pounds. The success of the method is indicated by the fact that, while the mole ratio of As_2O_3 to Cu before precipitation—that is, of C to B on a molal basis—varied from 0.67 to 1.9, the ratio in the corresponding products varied only from 0.94 to 0.99.

Product. The 1940 product was considerably more uniform than that made in 1939, was substantially free from uncombined As_2O_3, and had a smaller particle size. Under the microscope it appeared to consist of ultimate particles 2 to 6 microns in diameter, some of which were combined to form loose agglomerates 10 to 30 microns in size. By comparison, commercial Paris green had a particle-size range of 10 to 50 microns.

The final test run gave an over-all recovery of about 85% of the arsenic and copper as useful product. It appeared that most of the remaining 15% consisted of very fine particles that escaped from the spray dryer Multiclone. Part of this fine material was scrubbed out by the spray water in the exit stack but was not utilized. It would probably be feasible to recover most of this fine material in a bag filter, and this would be particularly desirable, since dusting tests indicated that the larvicidal action increases with decreased particle size. Assuming the recovery of this fine material, material balance figures indicated that, in a steady production of copper arsenite on a moderate scale, it was reasonable to expect 95% recovery of copper and arsenic and a consumption of ammonia and hydrochloric acid not exceeding 2.5 to 3.0 pounds each per 100 pounds of product.

VALUE OF PILOT PLANT WORK

The pilot plant investigation confirmed, in this case on a semicommercial scale, the technical soundness of the process worked out in the laboratory for producing copper arsenite. Further than that, it disclosed that steady-state cyclic operation, such as was necessary for economical commercial production, presented problems not apparent in the laboratory noncyclic experiments, and it then pointed out a practical solution of these problems.

The work led to the development or selection of types of equipment and materials of construction suitable, although not necessarily optimum, for commercial operation, and provided data for the design of a commercial plant. Procedures and techniques for the operation and control of such a plant were developed. Sufficient information was obtained for making reliable investment and production cost estimates. A potential benefit, not utilized in the present case, was the training of supervisory and operating personnel who could have placed a commercial unit into initial operation efficiently. An estimate of the health hazards was obtained, and safe practice was established.

Product was made available in sufficient quantity for adequate field testing. This is always an important function of pilot work. In the present case the comparative field tests disclosed that a much smaller proportion of the copper arsenite than of Paris green reached the designated area of the water surface. This difference, which was not foreseen from laboratory larvicidal tests, was caused by the smaller particle size of the copper arsenite. In spite of the lower efficiency of application of the copper arsenite, its over-all effectiveness was greater than that of Paris green. These results led to a more general study of methods of improving the distribution of larvicide in the field and of the relation of larvicide particle size to effectiveness, which resulted in benefits to the malaria control program.

A final brief comment on the course of the investigation may be made in the light of hindsight. The performance of the pilot plant agreed well with that predicted from the laboratory work in most respects, such as reaction rates, chemical behavior, and product quality. Several comparisons have been indicated in the preceding pages. As a further example, it was found that the average rate for dissolving copper in the final pilot plant run was 13 grams per kilogram per hour, compared with the anticipated figure of 18 grams per kilogram per hour; this difference might reasonably be expected because of channeling and coating of the bed of copper in the pilot plant dissolver.

The chief problem encountered in the pilot plant work not adequately forecast by the small scale research was the cumulative effect of undesirable precipitates formed during steady-state cyclic operation. It might well be argued that if the pilot plant work had been deferred until the bench scale study had been carried out, this problem would have been encountered and worked out more cheaply on the smaller scale. Successful steady-state operation then might well have been achieved in the initial campaign, which under this scheme would not have been undertaken until 1940, and most of the cost of the 1939 pilot plant operation might have been saved. On the other hand, even though steady-state operation was not achieved during the 1939 campaign, it did fulfill its major objective of providing copper arsenite larvicide for field tests.

Thus it appears that the present investigation was carried to the pilot plant scale too soon from the standpoint of the optimum over-all cost of developing the process, but that this was justified by a special circumstance. It probably is true, however, that such special circumstances are more the rule than the exception in pilot plant investigations and are one more reason why there is little danger that process development work will ever be reduced to a dry routine.

ACKNOWLEDGMENT

The work was carried out at the request of the Tennessee Valley Authority Health and Safety Department, and appreciation is expressed to E. L. Bishop and members of his staff for their advice and assistance. The author is indebted to E. R. Rushton, who carried out the initial laboratory investigations and devised the process, for advice and assistance throughout the work. Acknowledgment is made to J. H. Walthall for helpful criticism and advice, and to W. H. Cook, D. O. Myatt, J. C. Barber, A. W. Beinlich, Jr., and other engineers who participated in the pilot plant work.

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RECEIVED April 14, 1947.

October's HEADLINES...

Events of Interest to Chemists, Chemical Engineers, and Executives∼∼*Reviewed by the Editors*

¶ October 1. Levantour Co., Teheran, makes Iranian Government offer to form Iranian oil company with $32,000,000 capital to develop and sell nation's oil to foreign buyers.∼∼Russia and The Netherlands sign chemical pact whereby Soviet zone of Germany will export 40,000 tons potash potassium—15% annual Dutch needs—to The Netherlands in exchange for Dutch superphosphate.∼∼Office of International Trade announces removal of export controls on sodium phosphate, tri- and pyro-, effective Oct. 2.∼∼First German chemical plants declared for reparation to U. S. offered for sale to American industry; offerings include portions of Dynamit A.-G. Geestacht-Krummel, Hamburg, and equipment from Paraxol, Lippoldsberg, to be sold separately[1].∼∼Bakelite Corp. announces operations will begin early in November at Monterey, Mexico, plant for production of plastics molding materials.

¶ October 2. War Assets Administration offers for sale wartime magnesium plant at Marysville, Mich., consisting of 45 buildings.

¶ October 3. Algonquin Chemical Co. plans erection of $1,000,000 sulfuric acid plant at Dubuque, Iowa.

¶ October 4. President's Scientific Research Board submits report, "Administration for Research," asking thorough reorganization of administration of federal scientific research and development activities through following 4 basic policy recommendations: establishment by President of Inter-Departmental Committee on Scientific Research and Development to determine broad policies, authorization of unit in Bureau of Budget to allocate functions and establish relative emphasis among types of research, designation of member of White House staff to maintain scientific liaison for closer cooperation among federal agencies and for collaboration with organizations outside Government, and establishment of National Science Foundation "within administrative framework of Federal Government" to guide federal support of basic research; for implementation of primary recommendations, suggests each federal scientific agency take steps to coordinate its own research and estabish policy and program committee of leading scientists and outside experts to appraise work and advise on policy questions; to improve operations at bureau and laboratory levels, recommends adequate staffs to relieve scientists of burden of administrative detail, and Congressional appropriations for research covering periods of from 3 to 5 years to permit flexibility required in such work; suggests funds be appropriated for broad programs rather than specific projects; 19 recommendations specified to establish "more favorable climate" for scientific minds in federal service; asks utilization of contracts principally for financing applied and developmental studies and placed primarily with industrial laboratories; suggests grants rather than contracts be used for basic research; calls for development by federal agencies of "long-range plans for concentration of research installations in relatively few places," to "produce minimum of disruption[2]."

¶ October 5. P. A. Mattis, formerly of University of Florida, and P. S. Lavik, formerly of Baylor University, have been appointed at Western Reserve University to do research on effects of radioactive substances and of atomic energy on body and living cells under recent $100,000 grant from U. S. Atomic Energy Commission.∼∼Macmillan Petroleum Corp. obtains permits from Italian Government to drill for oil on more than 70,000 acres in Sicily.∼∼Charles Pfizer & Co., Inc., announces completion of negotiations with Emerson Drug Co., Baltimore, Md., for acquisition of subsidiary, Citro Chemical Co., manufacturer of acetanilid, acetophenetidin, and caffeine[3].

¶ October 6. D. E. Lilienthal, chairman USAEC, announces appointment of following 7 to board of consultants "to speed up industrial opportunities" in field of atomic power: J. W. Parker, Detroit Edison Co., chairman; O. E. Buckley, Bell Telephone Laboratories; D. F. Carpenter, Remington Arms Co.; Gustav Egloff, Universal Oil Products Co.; Paul Foote, Gulf Research and Development Co.; R. E. Wilson, Standard Oil Co. (Ind.); and Col. Walker Cisler, Detroit Edison Co., secretary.∼∼Allegheny-Ludlum Steel Corp. announces purchase of Dunkirk, N. Y., steel plant it operated during war from WAA for $1,500,000.∼∼Petroles Mexicanos plans construction of $12,000,000 refinery at Salamanca, Mexico[4].

¶ October 7. American Institute of Mining and Metallurgical Engineers announces award of Anthony F. Lucas Petroleum Gold Medal to W. E. Pratt, former vice president Standard Oil Co. (N. J.), for "distinguished achievement in improving technique and practice of finding and producing petroleum."∼∼Harshaw Chemical Co. purchases Cleveland, Ohio, shipbuilding plant for $385,000; plans to move plant to Gloucester City, N. J., for use as glycerol factory.

¶ October 8. Reconstruction Finance Corp. announces sale of 5,160,000 gal. Cuban ethyl alcohol to U. S. Industrial Chemicals, Inc., Du Pont, and Publicker Industries.∼∼Libbey-Owens-Ford Glass Co. starts limited production of synthetic resins for paint and varnish manufacture at new $9,000,000 chemical plant in Toledo, Ohio[5].∼∼Diamond Alkali Co. plans over $20,000,000 expansion program for new product development and increased production, R. E. Evans, president, announces; firm expects to produce synthetic periclase refractory in 1948[6].

¶ October 9. Department of Agriculture embarks on research plan at Northern Regional Research Laboratory, Peoria, Ill., to improve and retain soybean oil flavor.∼∼Charles Pfizer & Co. develops new penicillin "salt" by combining drug with synthetic, procaine, dissolved in oil, which doubles period of drug effectiveness in human system from 24 to 48 hours.

¶ October 10. AEC reports export rules will be established within 30 days on atomic energy equipment, no longer secret, sought by foreign countries.∼∼U. S. Rubber Co. and Richfield Oil Corp. sign 20-year agreement permitting Richfield to slant drill for oil at rubber company's Los Angeles tire plant site; U. S. Rubber to receive royalties on any oil found[3].

¶ October 12. Stanolind Oil & Gas Co. will operate cycling plant to be built in Texas; estimated daily production 7000 bbl.[3]

¶ October 13. Victor Chemical Works announces construction plans for $1,500,000 phosphorus compounds manufacturing plant at Morrisville, Pa.; changes name of new plastic made of phosphorus and resin from V-Lite to Phoresin to avoid confusion.

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[1] *Chem. Eng. News*, 25, 3157 (Oct. 27, 1947).
[2] *Ibid.*, 3055 (Oct. 20, 1947).
[3] *Ibid.*, 3159 (Oct. 27, 1947).
[4] *Ibid.*, 3158 (Oct. 27, 1947).
[5] *Ibid.*, 3227 (Nov. 3, 1947).
[6] *Ibid.*, 3156 (Oct. 27, 1947).

¶ October 15. Monsanto Chemical Co.'s Springfield, Mass., plastics division announces start of construction on formaldehyde unit for expanded output of plastic resins, to be completed in 1948[6].∼∼Deep Rock Oil Corp. joins recently organized $100,000,000 Co. to engage in Middle East oil operations; 12th independent concern to participate in group organized by Phillips Petroleum Co.∼∼Cities Service Co. forms subsidiary, Cities Service Research and Development Corp., to centralize and expand research and development activities[7].∼∼Sherwin-Williams Co. announces start of operations at Emeryville, Calif., synthetic resin manufacturing unit costing $400,000[8].

¶ October 16. C. A. Thomas, President-elect A.C.S., and vice president Monsanto, suggests petroleum industry set up concrete atomic energy research, development, and application program and seek permission of AEC for undertaking.∼∼Archer-Daniels-Midland Co. will begin construction soon on $1,000,000 flaxseed processing plant at Kenedy, Tex., which will have capacity to maintain year-round crushing of Texas seed crop[9].∼∼Borden Co. acquires Durite Plastics, Inc., thermosetting synthetic resins, molding compounds, and varnishes producer, for stock exchange of $3,000,000.

¶ October 17. Great Britain will soon start production of streptomycin; Distillers Co., which recently bought world's greatest penicillin factory at Speke, near Liverpool, from British Government as part of its $30,000,000 plan to develop industrial wing, will be first producer.

¶ October 19. Resinous Products & Chemical Co. announces development of new water-soluble polymer, Amberlite W-1, compatible with casein, polyvinyl alcohol, carboxy methyl cellulose, and lecithin, and useful to manufacturers of wet strength paper and adhesives as thickener for latex and neoprene; has potentialities for reproduction operations, printing techniques sizing, and various types of paper coatings.

¶ October 20. WAA offers for sale or lease Seagraves, Tex., carbon black plant with annual production capacity of 13,000,000 lb. channel type carbon black; currently operated by Columbian Carbon Co.∼∼Egyptian Salt & Soda Co. plans establishment of caustic soda plant in Alexandria upon receipt of machinery in early 1948 from U. S., Britain, Switzerland, Holland, Belgium, South Africa, and India.∼∼Archer-Daniels-Midland Co. plans additional $6,200,000 expansion and modernization program for 1947–48.

¶ October 21. WAA offers entire inventory of sulfa drugs, valued at $2,500,000, for sale at fixed prices beginning Oct. 27.∼∼Department of Commerce authorizes record export quota of 600,000 grams streptomycin in October due to monthly production record of 1,041,000 grams.∼∼Union Oil Co. (Calif.), which has exclusive concession for oil development in Paraguayan Chaco region, reports exploration will continue, despite failure to find oil through recent $3,000,000 expenditure.∼∼Pan American Chemicals Division, Pan American Refining Corp., announces commercial production of new petroleum drying resin suitable for use in paints, varnishes, printing inks, alkyd enamels, etc.∼∼Phillips Petroleum Co. and Atlantic Refining Co. sign long-term contract for construction of modern propane plant in Philadelphia area, and marketing of product[7].

¶ October 22. Iranian Parliament voids 1946 pact giving Russia exploration rights to oil in northern Iran; Iranian Government agencies plan search instead, and will discuss sale of discoveries to Soviet Union.

¶ October 23. Nobel Prize in Medicine awarded jointly to Carl F. and Gerty T. Cori, Washington University, St. Louis, Mo., for "discovery of process in catalytic metabolism of glycogen" of animal starch; and Bernardo A. Houssay, chief Institute of Biology and Experimental Medicine, Buenos Aires, Argentina, for "discovery of significance of hormone produced by frontal lobe of hypophysis[10]."

¶ October 26. Merck & Co. selected to receive eighth biennial award for chemical engineering achievement, sponsored by *Chemical Engineering*, for pioneering large-scale production of streptomycin and other medicinals[11].∼∼Procter & Gamble plans granule soap drying tower construction in Kansas City, Kan., as part of expansion program.∼∼International Minerals & Chemical Corp. announces plans for construction of $100,000 fertilizer plant at Somerset, Ky., with annual capacity of 12,000 to 15,000 tons mixed fertilizer.

¶ October 27. OIT terminates controls on export of lead arsenate, bone ash, dust and meal, and white and red clover, effective Oct. 24, to all destinations except U. S. military occupied areas, Spain, and Spanish possessions.

¶ October 28. Chinese National Resources Commission announces Chinese infant oil industry is nearing 1947 all-time high goal of 12,000,000 gal. crude oil, 18,000,000 gal. gasoline, and 15,000,000 gal. kerosene, 17,000,000 gal. over highest prewar production.∼∼U. S. crude oil reaches record production of 5,318,415 bbl. daily during week ended Oct. 25, rise of 35,365 bbl. over last week's record of 5,283,050 bbl. daily.∼∼Secretary of Interior Krug says subsidies to keep mines in operation and build up strategic stockpiles may be included in government's minerals program.

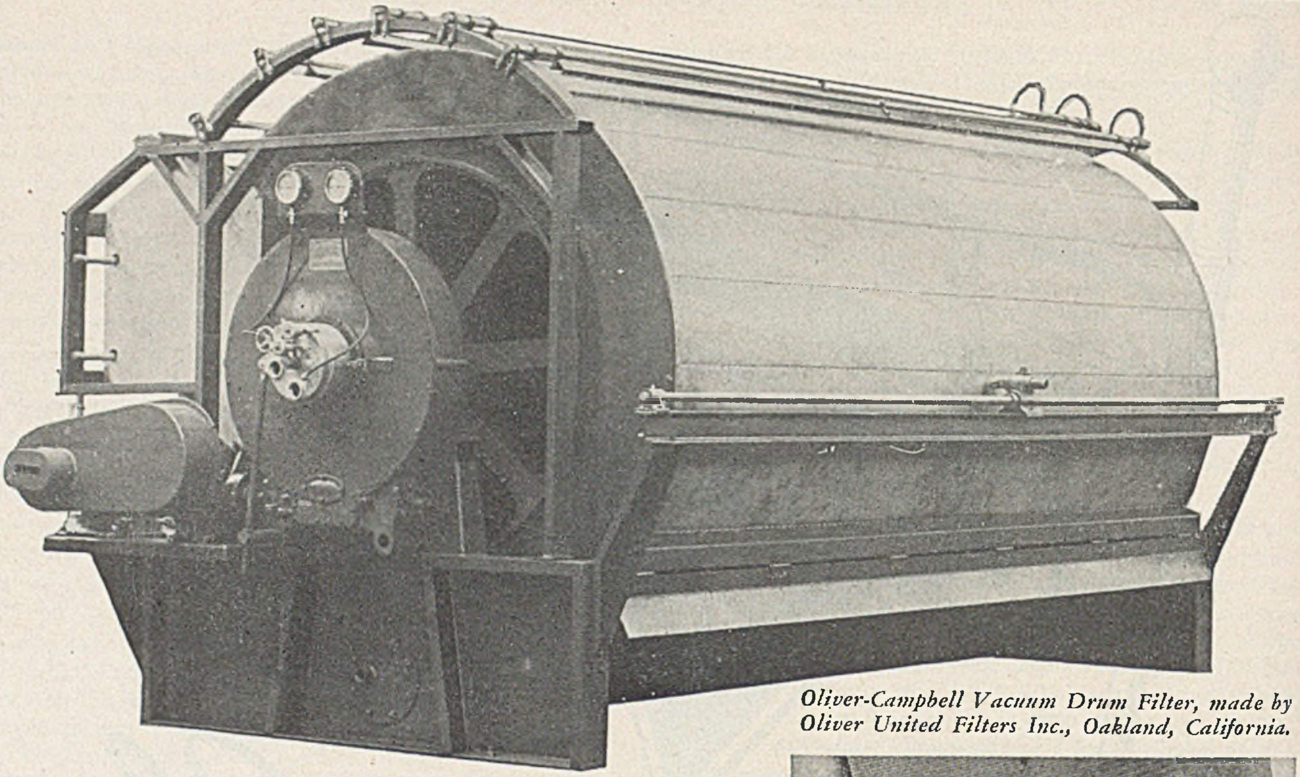
¶ Ocotber 29. Allied Chemical & Dye Corp. grants Columbia University $1200 for continuance of yearly graduate scholarship for advance training in chemical research.∼∼Siamese Government announces agreement to pay British Commonwealth tin mining interests $5,000,000 as restitution for operating profits lost during war.∼∼First oil from Standard Vacuum Petroleum Co.'s Pendopo, South Sumatra, oil fields since war pumped through 80-mile pipeline to Sungei, Gerong, refineries Oct. 25.∼∼Josiah Bridge, U. S. Commercial Co. geologist who surveyed Western Pacific for Navy, says U. S. companies can profitably mine large deposits of high-grade bauxite in Palau Islands; estimates one island has reserve deposit of 50,000,000 tons of ore.∼∼B. F. Goodrich Co. plans establishment in Holland of European selling organization, to be known as Netherlands B. F. Goodrich Co., W. C. Gulick, president Goodrich International, announces.

¶ October 30. Office of Materials Distribution extends to Nov. 15 deadline for export priority assistance to foreign governments placing certified export orders for nitrogenous fertilizer materials.∼∼Dutch chemical sales organization with $945,000 capital will be established in Amsterdam, to promote sales of chemical products, minerals, and ores.∼∼AEC offers provision of funds, buildings, and equipment for completely independent re-establishment of Bar Harbor, Me., cancer research Memorial Laboratory at Brookhaven National Laboratory, Patchogue, L. I.∼∼Sharon Steel Corp. experiments with oxygen process for first time in electric steel furnaces; process speeds up steelmaking in electric furnaces as in open hearths.∼∼Department of Agriculture announces end of sugar controls at midnight Oct. 31.∼∼State Department formally accuses Russia of violating American citizen property rights through seizure last August of British and American-owned oil refinery in Soviet zone of Austria.

¶ October 31. G. C. Lawrence, Canadian atomic scientist, says "production of atomic weapons is beyond Canada's industrial resources."∼∼Rubber Manufacturers Association reports synthetic rubber consumption will pass 500,000 tons this year.∼∼H. J. Kaiser opens aluminum reduction plant at Tacoma, Wash.; closes Permanente Metals Co. magnesium plant near Los Gatos, Calif.

[7] *Chem. Eng. News*, 25, 3224 (Nov. 3, 1947).
[8] *Ibid.*, 3296 (Nov. 10, 1947).
[9] *Ibid.*, 3226 (Nov. 3, 1947).
[10] *Ibid.*, 3228 (Nov. 3, 1947).
[11] *Ibid.*, 3217 (Nov. 3, 1947).


CONOCO

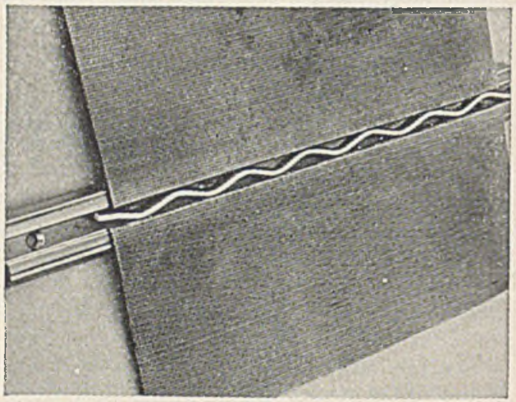


Oliver-Campbell Vacuum Drum Filter, made by Oliver United Filters Inc., Oakland, California.

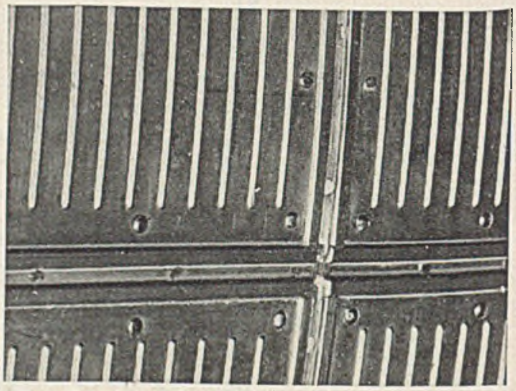
6 types of REVERE METALS in this vacuum drum filter

In the manufacture of this Oliver-Campbell Sugar Cane Mud Filter the following Revere Metals are used: Copper sheet, copper tube, brass sheet, brass discs, brass pipe, and brass extruded shapes. These metals are chosen for three chief reasons: they resist the corrosive action of the filtrate and cake, their mechanical strength is such as to assure durability, and they are quickly and economically fabricated. Use of extruded shapes is particularly interesting from a fabrication standpoint, the rather complicated forms required for the division strip being supplied by Revere in straight lengths that require only cutting and drilling before installation. Similarly, the zig-zag caulking strip that holds the screens is a Revere rectangular extrusion that needs only cutting plus formation of the zigs and zags. The screens, incidentally, are copper sheet, perforated 625 holes to the square inch.

Filtration is an important process, not only in sugar mills, but in a great many industries, such as chemicals, petroleum, coal, paper, cement, mining and refining, breweries, sewage disposal. Often both filtrates and sludges are corrosive, and thus it is that Revere Copper and copper alloys find many important applications. These metals are available in many different alloys and forms, resistant to a wide range of corrosive media. The Revere Technical Advisory Service will gladly collaborate with you in studying the problem of corrosion in your plant equipment or product.



Section showing method of locking copper screen into the extruded division strip by means of a zig-zag brass caulking strip.



Detail of formed or "bumped" brass screen support. The division strips are extruded brass sections.

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TCC UNIT CHARGES 8 DIFFERENT STOCKS ON 8 SUCCESSIVE DAYS!

The remarkable flexibility of the T C C process is well illustrated by the following record from the daily log sheets of a T C C plant:

Date	CHARGE TO T C C PLANT CONTAINED:			
	Full Crude	*Reduced Crude*	*Virgin Gas Oil*	*Kerosene*
June 7	—	—	100%	—
8	—	—	75%	25%
9	—	—	—	100%
10	25%	50%	25%	—
11	70%	—	30%	—
12	50%	—	30%	20%
13	50%	30%	—	20%
14	50%	50%	—	—

Only a Houdry-licensed catalytic cracking unit could possibly accommodate such frequent changes of charge stock without shutdown, and consequent considerable (and costly) loss of production. In the case of the T C C unit reported above, no major reduction in throughput, or in output of catalytic gasoline, resulted from the daily and drastic variations in feed charge.

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HOUDRY CATALYTIC PROCESSES

Equipment and Design

The work of a general maintenance man is important to all companies, particularly small ones, but it is seldom recognized as deserving of praise.

by Charles Owen Brown

We have been told that, on the campus of a western university a statue has been erected to the memory of a student. Contrary to the first impression one might form, this statue is not a memorial to a war hero but to just an average student. This has always appealed to us as a most praiseworthy tribute. The dedication message explains the aims of the donor by recalling the thousands of students who complete their four years on the campus without once making a varsity team but, nevertheless, faithfully and loyally give their time to support the scrubs each year. They strive for top honors but accept the intermediate grades with dignity, knowing they have done their very best. Recognition is due them.

There are similar men in all small chemical plants. In larger organizations each function of plant operations is provided with one man, if not several men, of special training and experience needed for their daily job or assignment. They handle carefully standardized tasks and, by repetition, become highly skilled and efficient. In smaller plants jobs are not so definitized, and there are usually one or two workers who must handle every breakdown and emergency to keep the plant running in good order. These men must know all the tricks in a dozen different packing problems, and the use and misuse of many gasket materials; they must be able to solder a heavy copper still or the hairspring in an instrument. These men seldom get a good word in the front office; more often they are asked by phone to work all night on some repair. Whenever equipment goes sour for any reason, these men must devise corrective measures, find the materials, and make a quick repair with the available tools. These men are, of course, the general maintenance men.

Usually a man able to fill this position is not a young man. It requires many years of patient effort to learn how to wipe or burn a lead joint, modify a bucket conveyer so it will handle a wet plastic solid, adjust the liquid distributor head in the top of some absorption tower, clean and adjust a steam trap, reface the seating surface in a large gate valve, or mend a poidometer. This program is about the average schedule for the general maintenance man in any small chemical plant. Such a man is priceless, but, strange to relate, often some younger man in operations is given praise and credit for an unusually large month's production. It is a situation something like that of a man in the line of a football team. The backfield and quarterback thrill the crowds with an end run, or by a slow dancing fadeback followed by a 10- or 15-second scrutiny of the field and players, then the launching of a long spiraling forward pass to some teammate. That is, it happens in this manner, provided the men in the line hold off the opposing players for 15 or 20 seconds without a break-through, and it is rare indeed if the linemen receive proper acclaim from the crowd. A wonderful production record can be made if all equipment functions at top capacity for the month, but the credit seldom goes to the maintenance man. Such men as these are rare now, notwithstanding high wages, and may disappear altogether.

Experience

In large chemical companies a lack of such a general craftsman is felt much less keenly than in the smaller companies. With the present conglomeration of union rules, regulations, and directives, it is difficult for large plants to use such a man and keep the shop open. The small chemical business is dependent on men with this wide experience. Likewise, when technical knowledge is exported, and chemical plants are constructed and put into operation in foreign countries, it is highly essential to have two or more of these experienced, all-around maintenance men to teach as well as repair. Experience has shown that nationals abroad learn to repair and adjust many kinds of equipment much more quickly than they learn to detect what needs repairing or adjusting, and when. This latter side of maintenance requires judgment, whereas the actual repair can be fairly well completed by going through a set of motions, parrotlike. The harder part of the task is to teach foreign operators to anticipate trouble and avoid it. Too often, a novice who could make a repair or adjustment creditably will permit a machine to run in bad order until something breaks, so that the repair becomes serious or perhaps impossible.

This month's column was written while the author was on a consulting mission in southern India, at Alwaye in Tranvacore. In a brief letter accompanying the manuscript, he made the following comments about conditions in India which may be of interest to our readers, and which doubtless inspired the column that appears on these pages:

"It is hot here, if anyone should ask you—I am melting. Food is very short, but I have not suffered. The rice harvest is a long way off, but stocks on hand vary from 10 days to 3 weeks in the various provinces. The Indians are not lazy, and it is remarkable what long hours at hard work they can give on a few ounces of rice a day. They do everything the hard way, and by hand. They are very suspicious and will not be satisfied with a Dominion status many years. One must not forget that two great new nations have been created, in point of numbers at least. Pakistan has 75 million and India 325 million people."

Equipment and Design

Another characteristic feature of maintenance work in the large unionized shops, where the maintenance force will contain fifteen to twenty-five separate crafts, is the large proportion of spare parts used. Of course, a considerable proportion of the new parts used were wasted; they were not actually needed, but it was easier to throw away the dirty, fouled-up part than to clean it, carefully measure it, and determine if it was defective or worn. A new part would work well, and its use would save a great deal of thinking. The old type of millwright mechanic would be shocked at the amount of replacement material and parts used by large staffs handling repairs today.

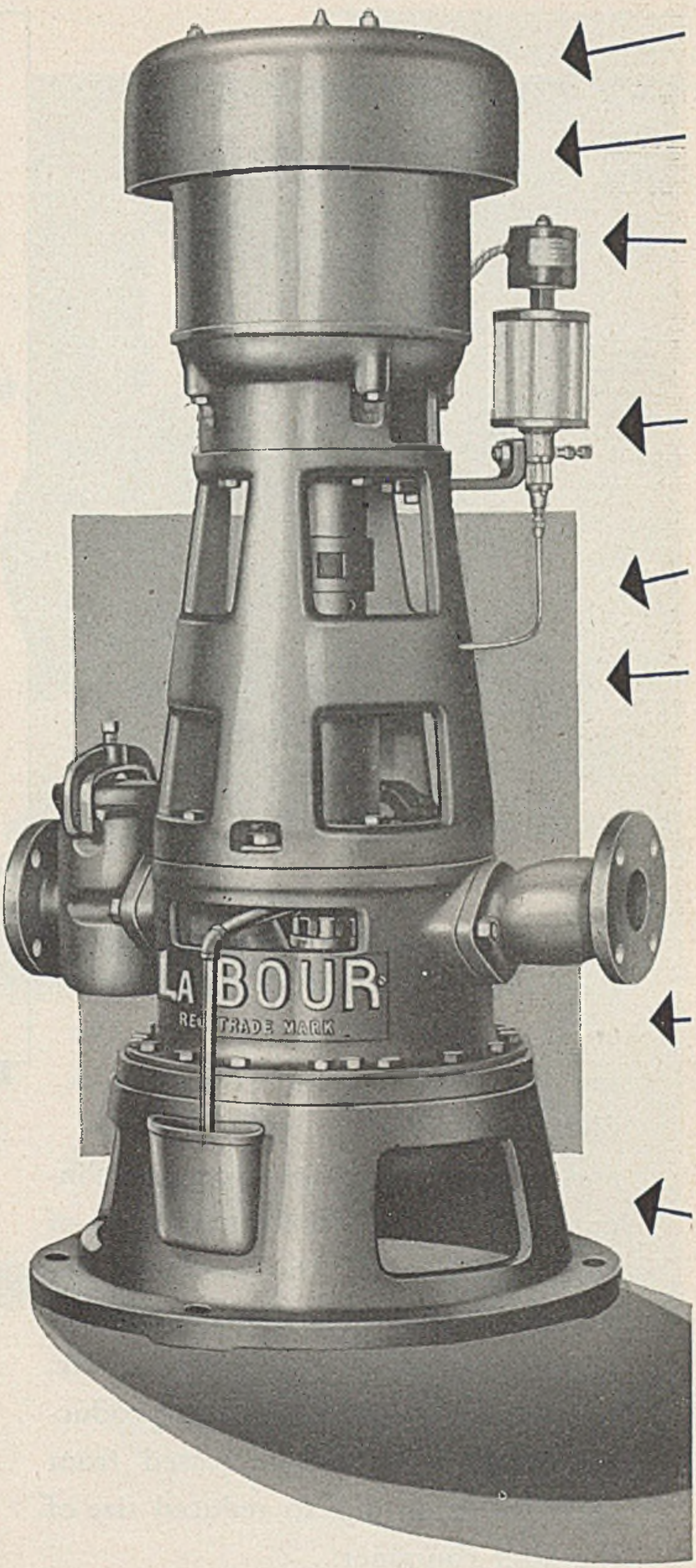
Repair the old

Maintenance work usually suggests repairing a plant which has been operating for some time. There are very peculiar, and sometimes tragic, problems involved in getting a new plant and even new equipment into operation for the first time. The following examples from our experience are not exaggerated. They are noted in some detail in the belief that personnel starting up new equipment will be forewarned, and that equipment manufacturers may improve the distressing or even disastrous condition in which new equipment is sometimes supplied to a cash customer.

Check the new

The worst maintenance problem in starting new equipment, especially a high speed, moving machine, is dirt or foreign matter, which most often consists of steel turnings from the fabrication of the machine itself. Recently a group of chemical engineers was starting a horizontal continuous centrifuge handling ammonium sulfate crystals. The feed ran smoothly, and a stream of moist crystals dropped into the dryer for a few minutes, then almost stopped to an anemic dribble. The rise of level in the feed tank located the trouble in the centrifuge, which was opened. The feed ports were found clogged with a mat of shiny, spiral stainless steel turnings. One of the engineers said the manufacturer must have imported a supply of turnings from Boston; so large an amount completely clogging all the feed ports could not have come from finishing one machine. This unnecessary trouble occurred on the second machine to a lesser extent, and caused a considerable total loss and expense. A large steam turbine was once put in operation and performed smoothly enough except for a musical, rhythmical kettledrum effect in the casing. When the workers realized something was "loose," the turbine was stopped and opened, and three nuts and one washer, similar to those used to bolt the casing together, were removed. A careful inspection did not disclose any real damage, and when the machine was closed and operated again it had lost its night-club characteristics. Welded equipment often has "icicles" of weld metal attached to the inside of the weld, which are jarred loose and become free once the machine is operated, and can usually be found in the first valve or other tight place in the stream flow.

Some peculiar maintenance troubles cannot be attributed to the manufacturer. The tube ends of a condenser were found clogged with three large carp. The three fish almost filled the end cap. They must have come into the end space as very small fish and grown on the food in the flowing water. An evaporator body once yielded two burlap sacks and fifty feet of rubber hose. There can be no doubt that it pays well to clean equipment of all foreign material, then close it tightly and keep it clean. The maintenance man can play his part here also in keeping the plant in tip-top operating condition.



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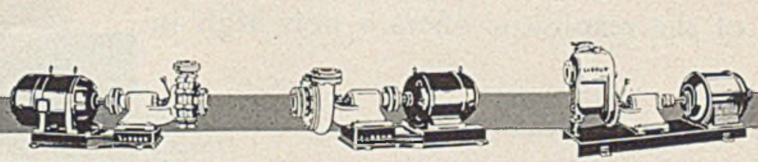

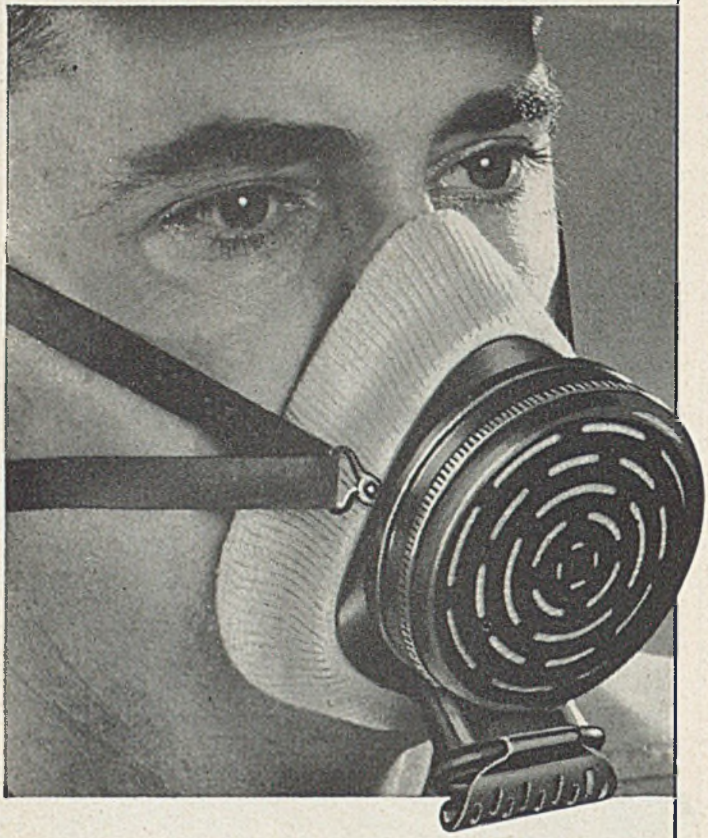

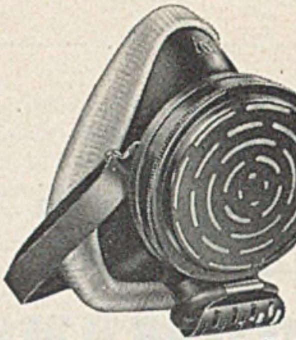

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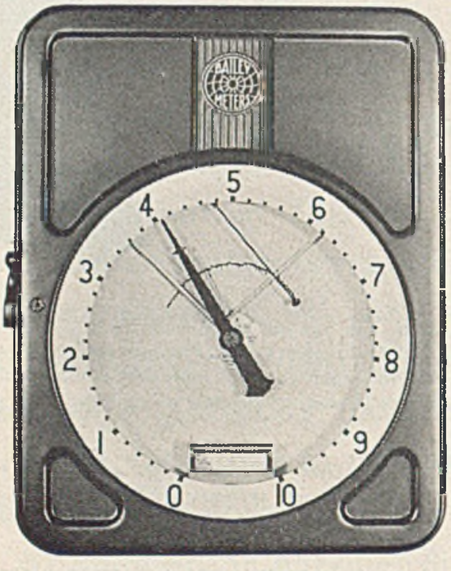

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Instrumentation

Technical papers, educational lectures, plant trips, and instrument exhibits make a worth-while program for the second annual meeting of Instrument Society of America.

by Ralph H. Munch

THE Instrument Society of America held its second annual exhibit and conference at the Stevens Hotel in Chicago the week of September 8. To those interested in instrumentation, this is the most important event of the year. It brings together the mathematicians who develop the theory of automatic control, the laboratory workers and design engineers who develop new instruments, those who manufacture them, those who design the plants which use them, those who install them, and those who keep them in operation, as well as the executives in charge of the plants. Each of these groups benefits by a meeting with the others, where points of view and problems are exchanged.

The fact that there were over 7000 registrants demonstrates that these meetings fill a real need. The activities of the American Instrument Society included an exhibit, technical sessions, educational lectures, plant trips, and, not the least important, individual discussions. The usefulness of the conference was increased by the fact that the Industrial Instrument and Regulators Division of the American Society of Mechanical Engineers met concurrently.

This year's exhibit was even more complete than last year's. Approximately 140 exhibitors displayed their newest and most interesting instruments. A few examples will suffice to indicate the character of the exhibit. The Bailey Meter Company presented its new area meter for metering fluid flow. The theme of its exhibit was that from a few standard components an almost infinite number of control systems can be built. The Brown Instrument Company featured, among other exhibits, the new Elect-O-Vane electronic unit designed to provide electric control action for recording thermometers. The Consolidated Engineering Corporation booth demonstrated its new mass spectrometer-type leak detector. The Foxboro Company exhibited its new electronic recording-controlling potentiometer for use with thermocouples, and showed how its electronic resistance recorder-controller could be used to measure humidity, strain, temperature, electrolytic conductivity, and pressure. The Leeds & Northrup Company prominently displayed the Speedomax G line of electronic potentiometers, including a double range indicator as well as round chart and strip chart recorders equipped for control. Almost every type of instrument used in industrial measurement and control was exhibited by manufacturers. In addition, several government agencies exhibited instruments they had designed. These included the Bureau of Standards, the Naval Ordnance Laboratory, the Office of the Chief of Ordnance of the United States Army, and the Weather Bureau of the United States Department of Commerce. Nowhere else could one get so much first-hand information on new instruments and what they can do as at this exhibit.

One of the features of the meeting was a series of lectures on the basic principles of instrumentation. These were designed to give the instrument maintenance man a better understanding of the principles underlying the work he does. The series covered the following subjects:

Fundamental Electrical Indicating Instrument Mechanisms
Instrument Accessories and Auxiliary Devices
Recorders and Integrating Devices
Electronic Test Equipment
Pressure and Thermal Systems
ABC's of Automatic Control
Flow and Liquid Level
Electrical Temperature Measurements

All these lectures were given by men who are authorities in their fields.

Twenty-one excellent papers were presented before the technical sessions of the Society. These covered the following subjects:

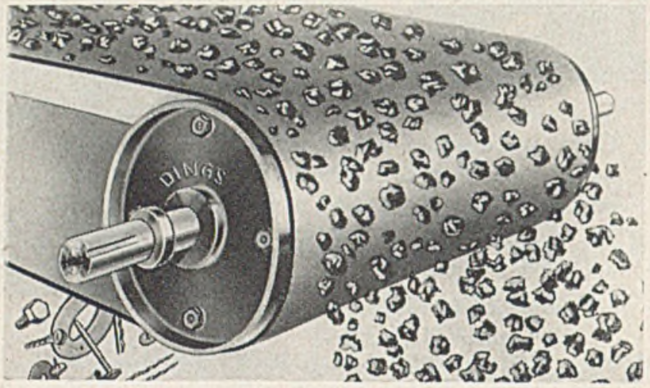
Quality Control
Industrial Use and Measurement of Radioactive Materials
Measurement and Control of Chemical Concentration
Automatic Control and Servomechanisms
Plant Practices
Process Control
New Instruments

In the space available here we cannot cover more than a few of the papers.

Papers presented

The session on Industrial Use and Measurement of Radioactive Materials began with an excellent review of the fundamentals of radioactivity by G. J. Overbeck of Northwestern University. R. D. Evans of Massachusetts Institute of Technology spoke on the application of radioactive indicators to industrial problems. The speaker gave a very interesting account of these uses, but the listener could not help being a little disappointed that the techniques described had not proved to be more useful in industrial practice. This session was completed by a paper on instruments for measurement of tracer radiation by F. R. Shonka of the Argonne National Laboratory.

Because it is difficult to calculate the behavior of an automatic control system even if all its parameters are known, most industrial control systems are designed by trial and error methods. Donald Campbell of Massachusetts Institute of Technology described the simplified method which he has developed for calculating the performance of a control system



before the Symposium on Automatic Control and Servomechanisms. This method, based on frequency response data for the system, uses graphical methods and shortens the necessary calculations greatly.

Porter Hart of The Dow Chemical Company described the sea water–bromine process chemical control system at the session on Process Control. This is an excellent example of a modern continuous process which could not be operated efficiently without automatic control. He describes the automatic controls for pH and oxidation potential, the sea-water salinity recorder, the controls used to proportion the sulfur dioxide to the bromine so that neither will be wasted, the controls for the sulfur burner, and the controls for the bromine steaming-out towers. Those who work in this field will realize that the process control system which he described is a masterpiece of automatic control engineering.

Manufacturers' literature

The Brown Instrument Company has just released two new catalogs which not only describe a wide variety of instruments but give basic information on the fundamentals of measurement and control. The first of these is Catalog 2221 entitled "Differential Controllers for Flow and Liquid Level." After a brief discussion of the basic principles involved in measuring flow by measuring the pressure drop across an orifice, this booklet describes in detail the construction of Brown differential flowmeters. Excellent diagrams make the discussion easy to follow. It describes next the application of various types of control mechanism to these meters and gives information on pneumatic transmission of data from the point of measurement to central control rooms. Then follow descriptions of alarm systems, ratio controllers, and remote index setting systems. Discussions of various types of mechanical and electrical flowmeter bodies, an area flowmeter body, and accessories for use with these instruments complete the booklet.

Catalog 8905 covers "Air-Operated Controllers for Temperature, Pressure, Flow, Liquid Level, and Humidity." It begins with a discussion of the advantages of automatic control and of some of the factors which affect the controllability of a process. Then, after defining certain automatic control terms, it describes the principles of operation of the various types of Brown control instruments. The desirable characteristics of control valves and the need for valve positioners are pointed out. Copies of these catalogs can be obtained from the Brown Instrument Company, Wayne and Roberts Avenues, Philadelphia 44, Pa.

Leeds & Northrup Company, 4934 Stenton Avenue, Philadelphia 44, Pa., has added to its line of instruments a new air-fuel ratio controller. Complete Leeds & Northrup temperature and combustion control systems for large industrial furnaces now include this controller. Like the Micromax pyrometers and furnace pressure controllers with which it operates, this controller employs electric-motored valve drives. It is a balance-type instrument designed with ample flexibility to meet any operating conditions. The air-fuel ratio can easily be adjusted manually for operation with fuels of various B.t.u. contents. As fuel flow changes, the instrument maintains air-fuel ratio constant at the desired control point; it can also provide automatic variation of ratio, increasing or decreasing the percentage of air at reduced flows. The manufacturers will send further information on request.

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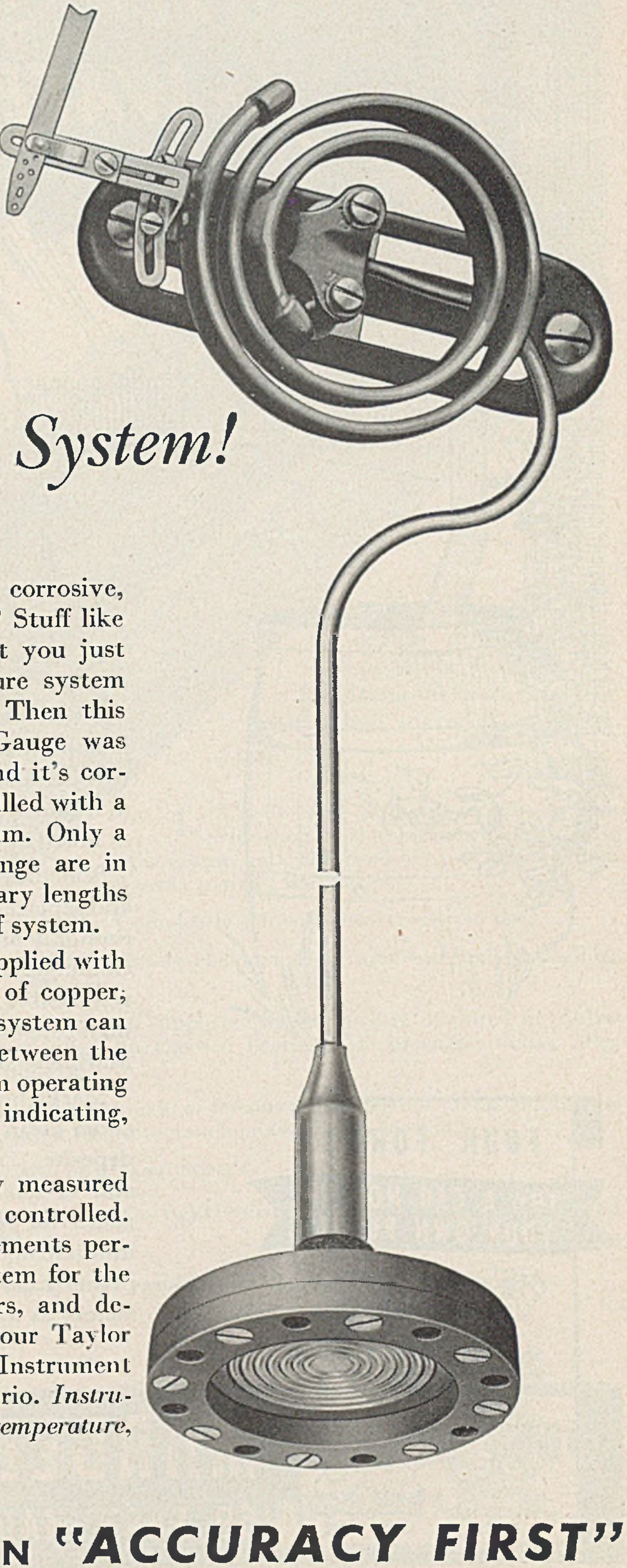

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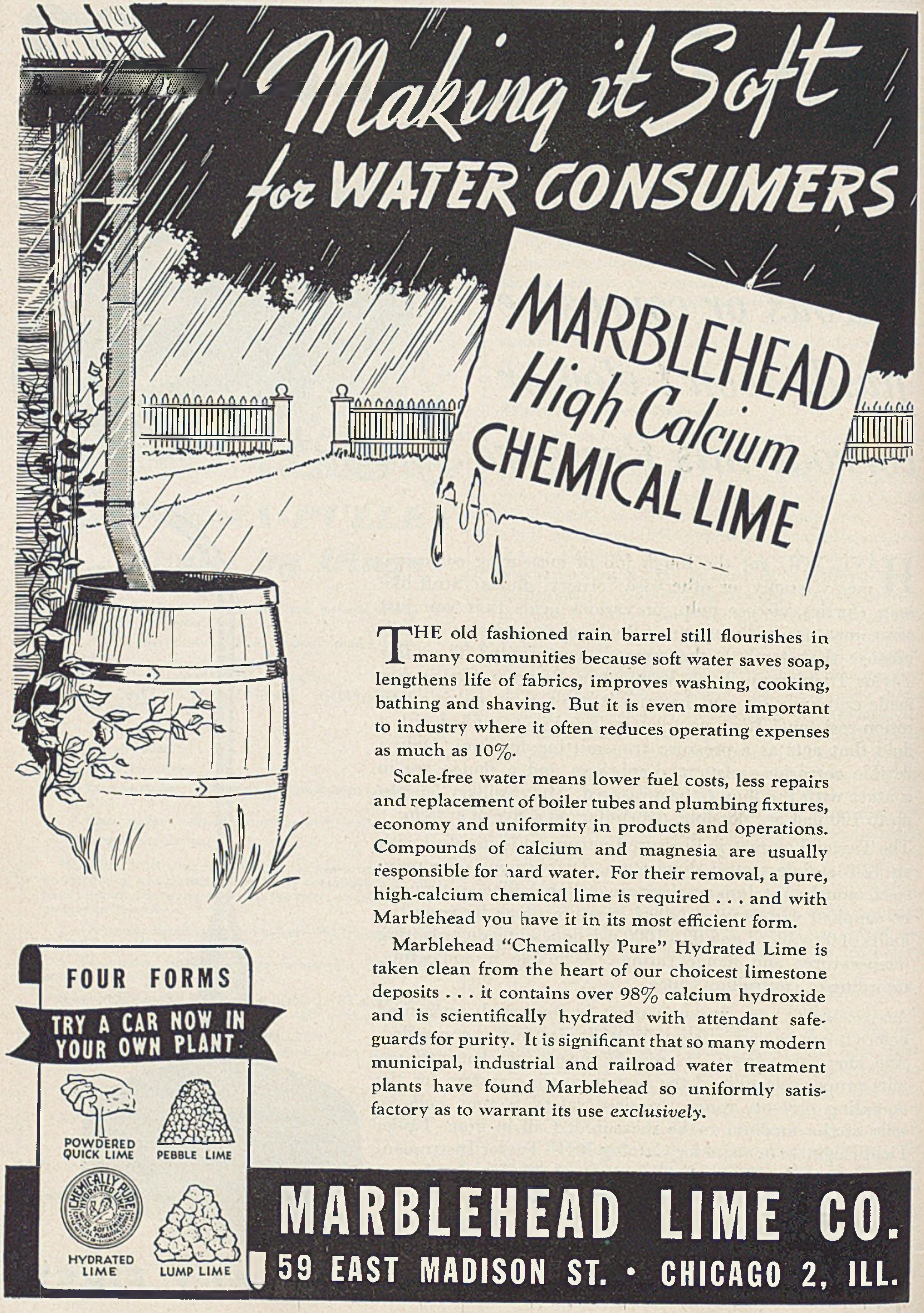

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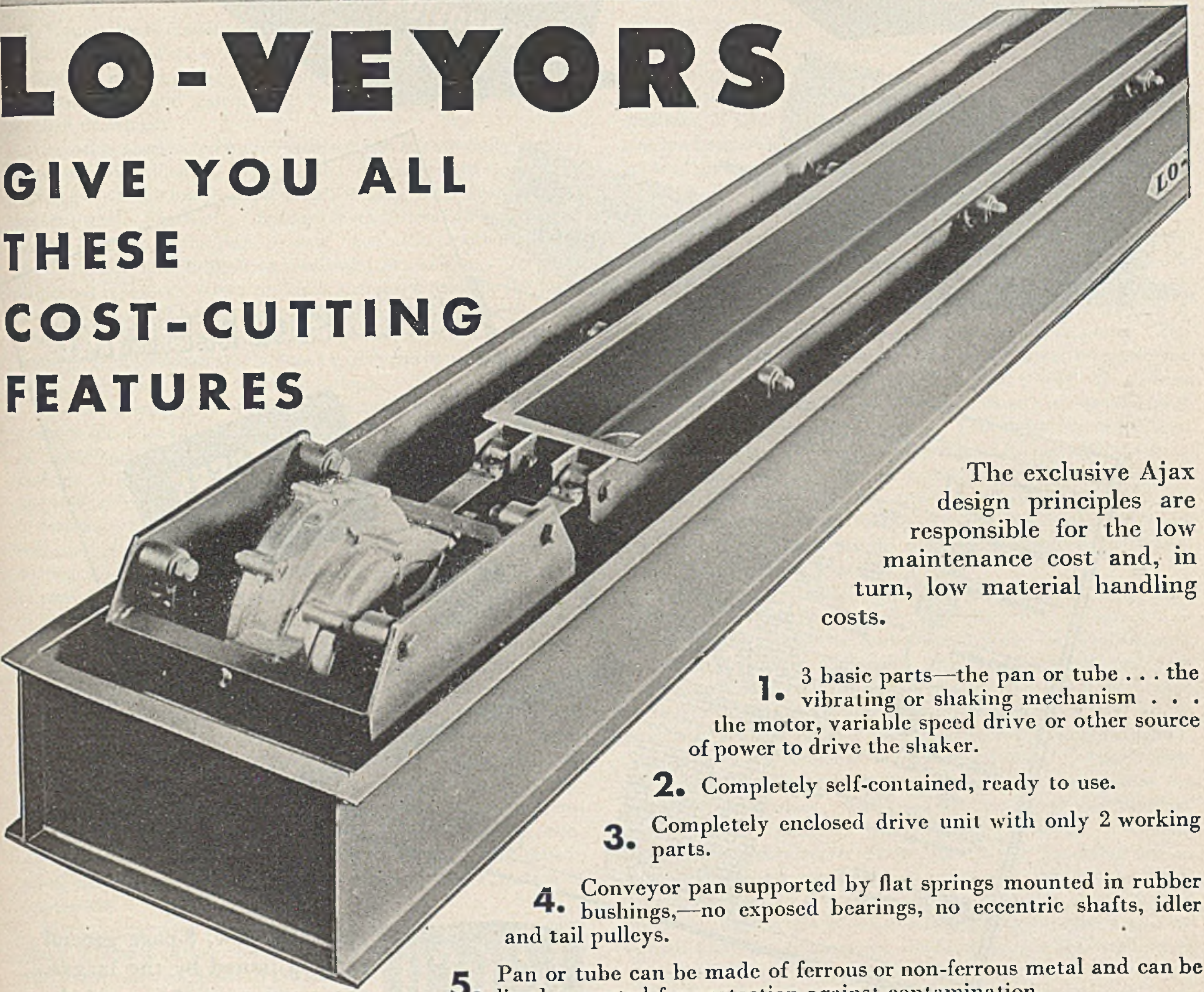
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Corrosion

Stress corrosion is described in this month's column as one of eight visual forms of corrosion.

by Mars G. Fontana

Corrosion is classified into eight forms according to the appearance of the corroded metal. Uniform attack or general corrosion, intergranular corrosion, pitting, dezincification, erosion-corrosion, and galvanic or two-metal corrosion were described previously.

Corrosion accelerated by internal stresses or externally applied stresses is described by the general term stress corrosion. The stresses are sometimes complex, but, in general, tension stresses are required. Internal or residual stresses are often produced during forming of the part, by heat treatment or other means; an example is locked-in stress resulting from welding. In practically all instances, stress corrosion manifests itself in the form of cracks. Accordingly, this phenomenon is also designated stress-corrosion cracking, although the word cracking is superfluous. If the stresses are fluctuating or cyclic in nature, the failure is often described as corrosion fatigue.

Two of the earliest recognized instances of stress corrosion, and perhaps the most widely known, are the so-called season cracking of brass cartridge cases and caustic embrittlement of steam boilers. Many brass cartridge cases failed during World War I, and difficulties were also experienced in the last war. A number of locomotive boilers failed because of stress corrosion. Stress corrosion of metals and alloys has been the subject of many investigations, but no completely accepted mechanism for this form of corrosion has been proposed to date.

In general, stress corrosion for a given material depends upon three factors—namely, the stress, the concentration and nature of the corrosive environment, and the temperature. If one of these factors, such as high stress or high temperature, is present in a high degree the other two factors could be mild in nature. For example, highly stressed brass parts sometimes crack when exposed to ordinary atmospheric conditions. The presence of ammonia or amines in the atmosphere greatly accelerates these failures. In fact, ammonia- and amine-containing atmospheres are used as tests for susceptibility of brasses to stress corrosion. As another example, the tendency for steel to crack in caustic solutions increases with either temperature or concentration of the caustic.

In many cases of stress-corrosion failures, the attack occurs along localized paths. For example, the metal may show no visible corrosion adjacent to the crack. These paths of localized attack are sometimes areas of lower corrosion resistance than the surrounding portions of the metal. In these cases the corrosion is electrochemical in nature with the attacked area anodic and the surrounding metal cathodic; thus a corrosion cell is set up similar to that which takes place in the cells described in galvanic or two-metal corrosion. Once localized attack in the form of a pit, crack, or crevice begins, the effect is accelerated because these areas serve as stress raisers.

Numerous types of stress-corrosion specimens for testing purposes have been devised. Perhaps the most common is the horseshoe type of specimen, wherein the bent specimen is stressed by taking up on a through bolt. Simple beam specimens, cold-worked specimens, and wedge-shaped static cantilever specimens are also used. In connection with a particular problem concerning a shell and tube heat exchanger, the writer once used tubular specimens made by expanding short pieces of tubing in a split mandrel in order to simulate the rolling of tubes in a tube sheet. The holes were several degrees oversize to permit variation in the amount of cold work in the metal. In this problem the Admiralty brass tubes had failed at or near the tube sheets because of over-rolling of the tubes.

One of the most interesting cases of stress corrosion of steel in the writer's experience involved stresses induced in the metal because of severe thermal gradients across the 2-inch wall of a large autoclave. These vessels contained a molten sodium-lead alloy, and they were heated or cooled by Dowtherm in the jacket of the autoclave. Decreasing the temperature of the Dowtherm during the cooling cycle from 200° to 100° C. in order to decrease the total time per batch, and thus increase production, resulted in rapid failure of the autoclaves and shutdown of the plant. The change in the Dowtherm temperature in the jacket increased the temperature drop across the wall from 110° to 154° C. Calculations showed that a ΔT of 154° C. induced a stress of 39,000 pounds per square inch in the metal. This high stress at the temperature of the operation readily accounted for the rapid cracking of the autoclave. The deepest cracks occurred adjacent to the welds of the vessel, but deep cracks were also observed in the parent plate far removed from the welds. Figure 1 shows one of the cracks in the parent metal. This crack started at the surface and is approximately 1 inch deep.

It is well known that the so-called aging steels are somewhat susceptible to stress corrosion. Precipitation of compounds in steel and other alloys often contributes to stress-corrosion failures. Mixed acids (sulfuric and nitric), nitrates, and caustic are often the chief offenders as far as steel is concerned. Large steel tanks erected in the field by welding developed bad leaks and large cracks after only a few months of service when handling mixed acid.

A refrigeration condenser cooled by good quality inland river water failed by cracking, with the cracks starting inside the Admiralty brass tubes. The cause of this stress-corrosion failure was difficult to find, but it was finally attributed to a small amount of organic matter which deposited on the surface of the tubes. Since this condenser operated only during the warm months, it was shut down for several months each year. Apparently the organic matter decomposed during shutdown with resultant formation of ammonia or amines, which were destructive to the alloy from the standpoint of stress corrosion.

Figure 2 shows cracks in a bronze Bourdon tube handling Dowtherm at approximately 650° F.

Copper itself is quite immune to stress corrosion. Although generalizations are often undesirable, it can be stated that the addition of zinc to copper to form brasses increases the susceptibility to stress corrosion, and this tendency increases with the zinc content of the alloy.

The aluminum materials, such as 2S and 3S, most widely used in chemical equipment give little difficulty from the standpoint of stress corrosion. The picture is quite different for the very high strength aluminum alloys. In fact, it

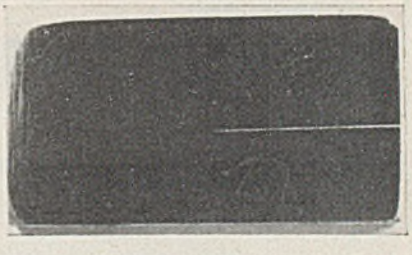

Figure 1. Stress-Corrosion Crack in 2-Inch Steel Wall of Autoclave

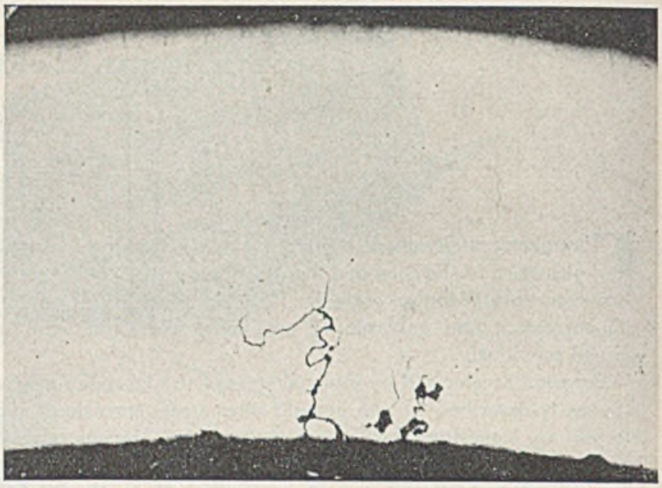

Figure 2. Cross Section of Bourdon Tube Wall Showing Cracks (× 100)

could be stated that the biggest obstacle in the way of further increasing the strength of aluminum alloys is the susceptibility of these materials to stress corrosion.

Stainless steels, which are widely used in chemical plants for corrosion resistance, generally do not fail because of stress corrosion except under certain conditions, such as in the presence of strong chloride solutions at high temperatures. Concentrated boiling magnesium chloride solutions are apparently most harmful. Barium chloride has caused cracking in evaporator tubes. In one case cast 18-8 rolls made by pressing trunnions into the ends of tubes cracked in the stressed ends of the rolls. These rolls were subjected to a dilute sodium sulfide solution made from a good grade of process water which had a more or less normal or low chloride content. This problem was solved by threading the trunnions and tubes.

Stress-corrosion failures of nickel and its alloys are uncommon in the chemical plant. The few cases that have been encountered involved strong caustic at high temperatures.

Prevention

Perhaps the most common method used for combating stress corrosion consists of stress-relieving heat treatments. Internal or residual stresses in the metal or equipment can be greatly minimized by heating at an elevated temperature. For example, it is common practice to stress-relieve welded steel equipment by heating in the range of 1100° to 1200° F. when it is desired to minimize locked-in stresses caused by welding. The failures of nickel tubes in caustic service could be prevented by stress-relief anneals in the temperature range 1000° to 1600° F.

Another effective preventative method involves, of course, the proper selection of alloys. 18-8SMo, for example, is superior to 18-8S for resistance to stress corrosion. A red brass (15% zinc or less) should be more resistant than an ordinary 70-30 brass. The selection of materials for a given application should be a balance between the probability of stress-corrosion failure and, of course, cost of the material; in other words, the economics of the installation must be considered.

A protective metallic or nonmetallic coating is often beneficial. For example, the high strength aluminum alloys are often clad with relatively pure aluminum for better resistance to stress corrosion. Organic paints which prevent the corrosion medium from reaching the metal or alloy are sometimes used.

Design of the equipment is also important. Sharp corners or fillets, which would act as stress raisers, and the application of high applied stresses should be avoided. In some cases the use of corrosion inhibitors are beneficial. In general, the use of more corrosion resistant materials and changes which decrease the corrosiveness of the environment are helpful.

Another Unique

STAINLESS STEEL CASTING

by COOPER ALLOY

This unusual casting, produced for the FOSTER WHEELER CORPORATION, was cast in both Stainless Steel and Monel and is the impeller for a 42" mixed flow condenser circulating pump having a capacity of 28,750 gallons per minute. The casting illustrated is a product of Cooper's 25 years of Stainless Steel "know-how" and indicates the flexibility of Cooper facilities to produce Stainless Steel castings from one ounce to two tons in weight.

Just off the Press

The behind-the-scenes story of Cooper and 25 years of pioneering in Stainless Steel Castings . . . taking you on a tour of Cooper's facilities and detailing the production methods employed in Stainless Steel Castings. We will be glad to forward a copy upon request.

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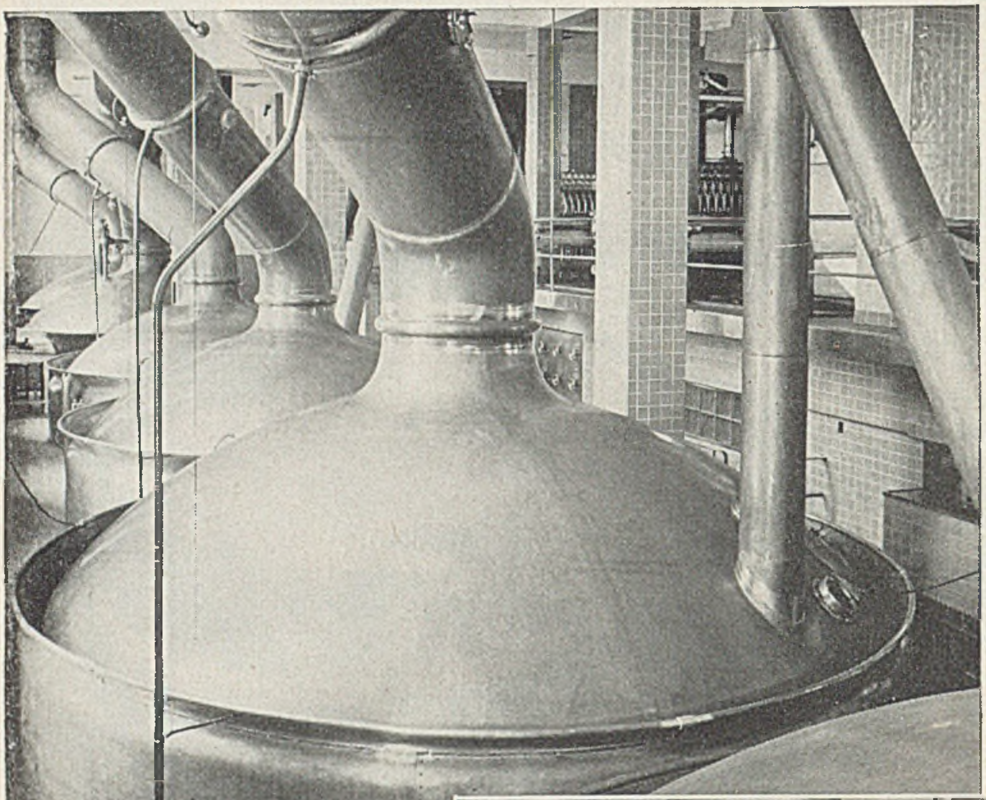
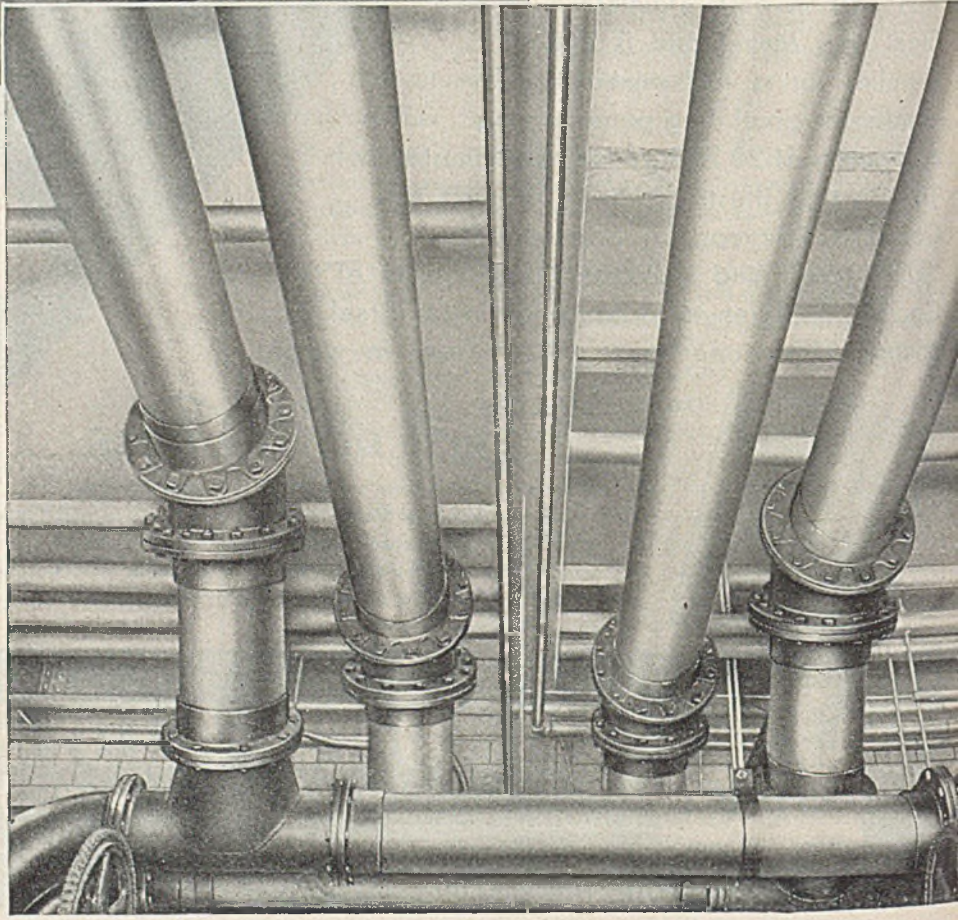


QUALITY—PROTECT COPPER BREW KETT

Battery of 6 Copper Brew Kettle built at the George Keller Copp Works, Brooklyn, N. Y. for one nation's foremost breweries. Each barrel-capacity kettle is 16′ 6″ in diameter and 14′ high. Sides and domed covers are ¼″ thick, dish bottoms are ½″ thick. Copper been used extensively in the brewing and distilling industrie for over a hundred years.



SMOOTH—INTERIOR COPPER PIPELINES

These 8″ copper pipelines feed pulp stock to the wood beaters of a large U. S. paper mill. Copper tubes are used in pulp and paper mills to convey stock and white water, and for water supply lines. Because of their freedom from rust-clogging and the fact that their smooth interiors offer lower resistance to flow, copper tubes may often be of a size smaller than ferrous pipe for the same service.

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Copper is widely used for heat exchangers, pipelines, stills and many types of processing vessels.

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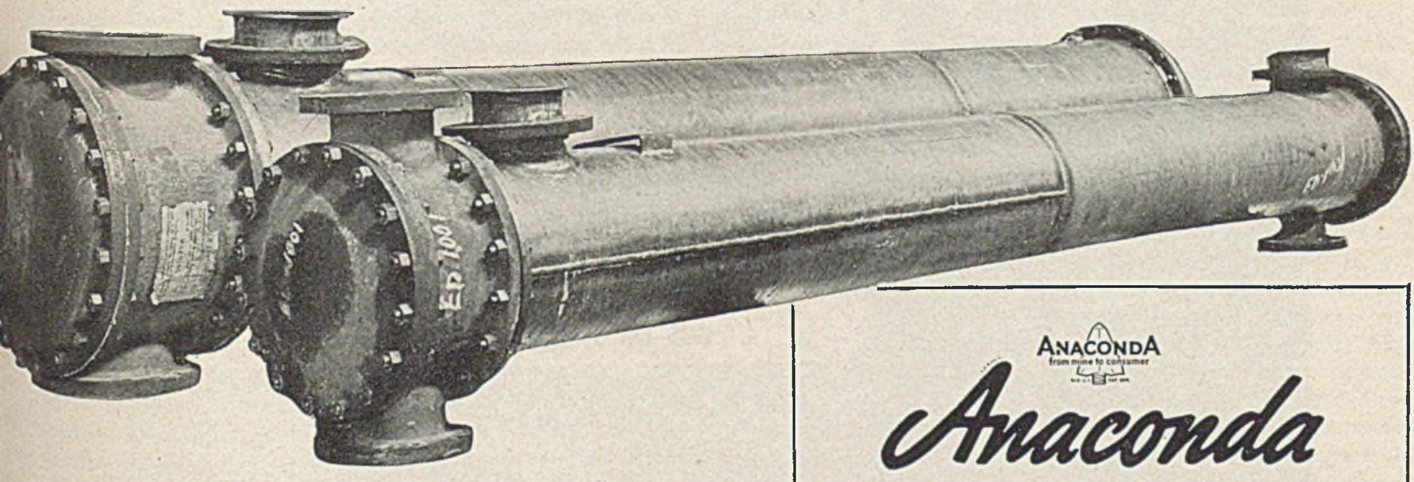
For information on the special uses of Anaconda Metals, write for publications B-28 (Anaconda Copper and Copper Alloys) and B-2 (Anaconda Tubes and Plates for Condensers and Heat Exchangers).

*Reg. U. S. Pat. Off. 4720S



EASILY WELDED EVERDUR* SHELLS

Shells for these Whitlock Type V Heat Exchangers were fabricated from 3/16″ Everdur Copper-Silicon Alloy plates and welded with rod of similar composition (providing excellent examples of the smooth, even welds made without flux by the inert-gas-shielded arc welding method). Everdur Alloys combine exceptionally high strength and ready workability, and are ideally suited for use under many corrosive conditions.

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Plant Management

The reasons why chemical workers often resent changes recommended by industrial engineers should be made clear to production executives.

by Walter von Pechmann

Many workers in the chemical industry regard the industrial engineer as an efficiency expert who is out to increase production at the expense of labor. This way of thinking leads to strained employer-employee relations and makes the industrial engineer's job unduly difficult. Chemical manufacturers who realize this frequently try to explain the principles of industrial engineering to workers before an industrial engineer begins working in a department. This action, however, does not always produce the expected results, because persons assigned the task of explaining industrial engineering sometimes cannot put themselves in the position of the average worker; they either assume too high a level of education on the part of their listeners or talk too much about phases of industrial engineering which are of no interest to the average man in the plant. There is no reason why chemical workers cannot be convinced that industrial engineering is a necessary and intricate part of modern manufacturing. All that is needed is an explanation in every-day language of the aim of industrial engineering and the techniques it employs to bring about improvements. Employees must be convinced that both management and labor benefit by sound industrial engineering.

The prerequisite for any attempt at convincing another person is sincerity. Over- and understatements, covering weak points by using big words, or writing formulas which nobody can understand may prevent embarrassing questions, but will never make workers appreciative of industrial engineering.

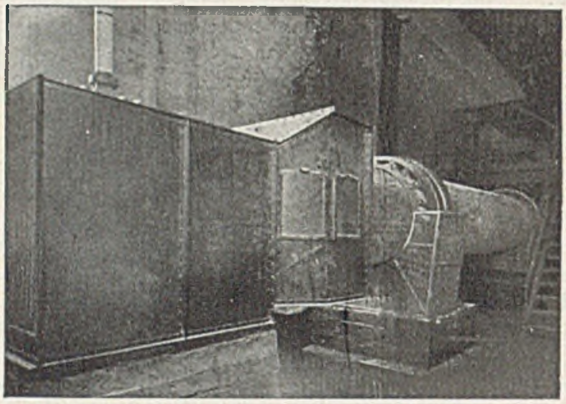
Before a lecture is planned, all factors of resistance likely to be encountered should be considered. It must be realized that an employee's reason for refusing to accept a change is often prejudice and not lack of technical knowledge. A chemical worker cannot be forced to accept an industrial engineer's outlook simply by being confronted with figures and facts which cannot be disputed. Selling industrial engineering calls for patience, tact, and, above all, a thorough understanding of the worker's way of thinking. Here are some of the reasons why employees frequently refuse to accept new methods: (*a*) resentment toward abolishing established practices; (*b*) insisting upon doing the work by the worker's own method; (*c*) the belief that industrial engineering is based on theory rather than practice; (*d*) the fear that industrial engineering will take away the opportunity for personal accomplishment; and (*e*) underestimating benefits of the change.

The desire to retain the status quo, even when common sense shows that a newly suggested working method is easier and more efficient, is frequently attributed to lack of intelligence. This is not always true. The very same industrial engineer or chemist who cannot understand why his suggestions are not willingly accepted may not, for instance, change his method of shaving even though he knows it is quite inefficient. In some instances employees try to cover up feelings of inferiority, jealousy, and prejudice under the guise of habit. The real reason, however, may be that they feel ashamed for not having thought of a better way to do their daily tasks, or that they are afraid they might not be able to handle the new job. Occasionally chemical workers refuse to give up their method of working because they feel that they had a part in establishing the routine and therefore believe that it is their duty to defend it. In some instances chemical workers take advantage of the weak points of a method and resent losing unauthorized privileges. A common objection to change is the erroneous assumption that new methods mean harder work.

Employees sometimes refuse to accept changes for sentimental reasons. The writer recalls one instance where an emulsion maker stubbornly tried to block any attempts on the part of his supervisors to replace his worn-out equipment. After he had been accused of deliberately trying to hold up production, he finally broke down and admitted that he would feel as if he were losing an old friend if his unit were taken away from him. Objections of this nature cannot be laughed off. Often they are byproducts of extreme loyalty, thrift, or a feeling of being part of an organization. The wise executive or industrial engineer will not try to force his ideas upon employees on the strength of authority; he will carefully analyze the real reason for an employee's refusal to accept a change willingly, and will try to eliminate the trouble at its source before taking any disciplinary action.

Production executives and industrial engineers frequently do not know what to say when confronted with the statement that everybody does his work best when allowed to do it in his own way. This applies especially when employees try to prove their point by mentioning, for example, that a left-handed person is often incapable of performing a right-handed operation efficiently. In such a situation the chemist or industrial engineer should point out that the dexterity of the individual is not a factor to be considered when new standards for job performances are set up. All operations must be laid out to allow the average employee to be trained quickly; operations not performed according to a certain pattern lead to variations in the quality of the product and make supervision extremely difficult. Any reasonable employee will see management's point of view in this respect.

It is common belief among workers in the chemical industry that industrial engineering is something intangible and purely theoretical. This impression is often created by industrial engineers who take time studies without telling workers why they are made. Flow of work charts, tendency curves, and statistical information, occasionally observed by employees, often seem to indicate that industrial engineering has little to do with practical work. A great number of workers in the chemical industry believe that methods which originate from a study made by the industrial engineering department work out on paper but cannot be put into practice. If trust in the industrial engineer's ability is to be achieved, it is essential that the average employee consider him a practical man who can talk the men's language and who has a genuine understanding of the chemical workers' problems. It is up to the individual engineer to establish this reputation; it is not alone management's job to create conditions which will allow the industrial engineer to work with ease by building up employees' morale. Often methods are worked out only to the point of establishing a new principle, with the assumption that the practical execution of the method will take care of itself in time. This approach seldom produces results and does more harm than is generally realized; workers attribute failure in put-



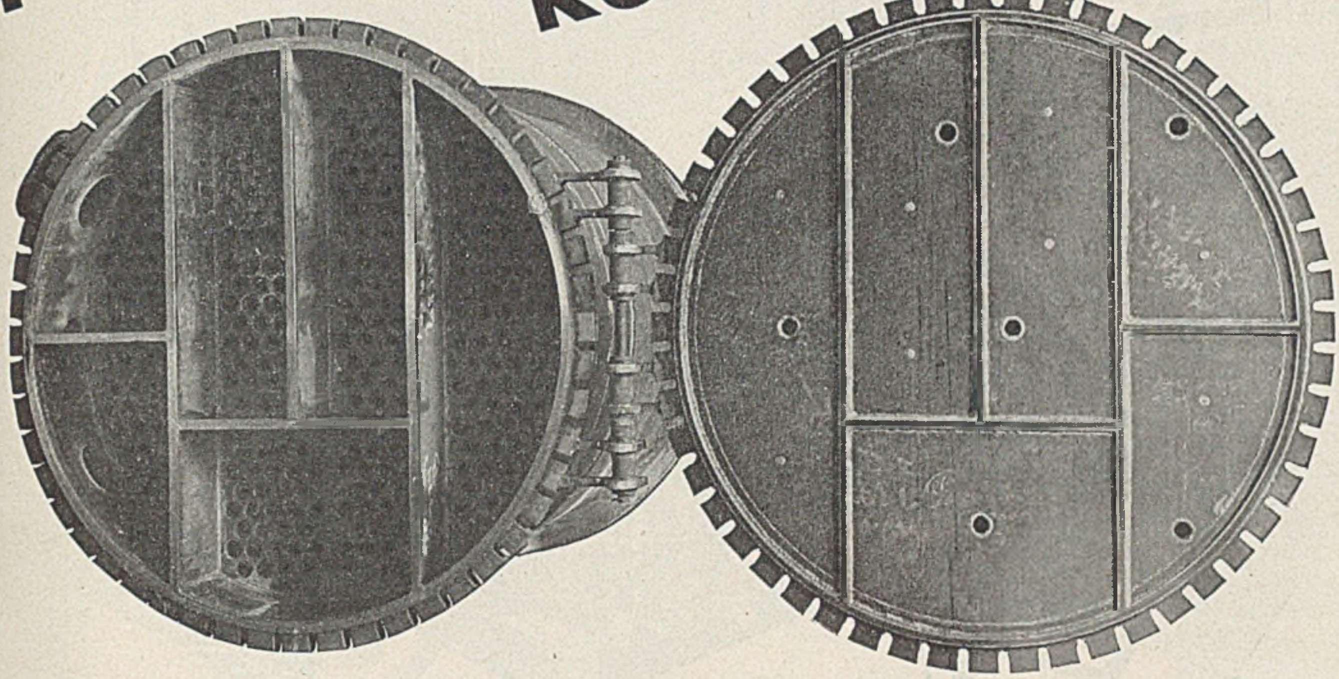
ting a new method into practice to "theoretical" managing. After a few such failures, workers may become convinced that industrial engineering has no useful place in the chemical industry.

There are several ways an industrial engineer can convince chemical workers that industrial engineering is a practical science. It can be pointed out, for example, that anyone who works on the improvement of a job is doing industrial engineering work. The industrial engineer's job may be pictured as a study of the various ways in which people perform tasks, and the selection of that one which is found to produce the most at the least inconvenience to workers. Graphs and charts can be explained as a means of studying numerical findings accumulated in the factory with the assistance of men who have the know-how. It is not always necessary to cover the entire subject and to be 100% correct. It is often better to put a point across than to refrain from explaining simply because there may be times when the explanation may not be entirely correct. Furthermore, it is not necessary to give an academic account of the workings of industrial engineering. Discussing a practical example frequently produces better results than going into details about principles. It is to be assumed that the person who talks to the workers practices what he preaches and that he does not display an attitude of "I know all." He must be capable of listening to foolish advice without letting anyone know that he is annoyed, and must occasionally accept the workers' belief that he cannot do his own thinking.

The inexperienced industrial engineer often thinks that the chemical worker measures his accomplishments merely in terms of output. He believes that employees are paid to perform a job according to a layout established by him and approved by management. He therefore does not think a chemical worker can possibly contribute toward the successful installation of a method by any means other than doing what he is told to do. The chemical worker, however, knows that no method can be worked out in such detail as to allow him to become a mechanical tool in the execution of a production setup. He feels entitled to point out minor flaws in a new method, to use his own judgment occasionally, and to make minor improvements. To deny him these privileges would be foolish; it would kill initiative and create ill will. It is the industrial engineer's job to lay out a method in such a manner that the individual way of working can be retained, as long as that way does not violate the principles of sound industrial engineering. It is sometimes advisable to let the men work out minor problems for themselves in order to avoid the impression that industrial engineering eliminates opportunities for individual accomplishment or tries to make machines out of men.

Everybody recognizes that faster work increases output. To visualize the improvements which can be made by changing flow of work or work layouts, however, it is frequently necessary to have industrial engineering training. Consequently it is not surprising that chemical workers often display little enthusiasm if the industrial engineer tries to increase output by rearranging the work of a department. The conventional method of convincing employees of an improvement is to take a time study and to show the workers how much time can be "saved" if the new method is accepted. Industrial engineers often cannot understand why workers react strangely when shown the findings of a time study. It took the writer years to find out the reason. The word "saved" implies to them that something has been wasted, and the employees instinctly feel that they have done something foolish which is now going to be brought to light and corrected. The logic of this thinking is open to dispute; nevertheless, this is the way many workers feel, and the industrial engineer should recognize the fact. It is recommended that better ways of doing things be presented as an accomplishment. Instead of saying, for example, "We save ten seconds on this operation," one could say "Do you realize that you are making 300 bottles more a day?"

Pass the salt... keep the heat



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● When engineers at Leader Iron Works of Decatur, Ill., looked over the order for this job they agreed with their customer: he had ordered Monel* installed in these heat exchangers using brine-soured process steam.

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For technical Bulletin T-5, Engineering Properties of Monel—packed with pertinent details, physical contents, data on Monel's resistance to salts, etc.,—write to

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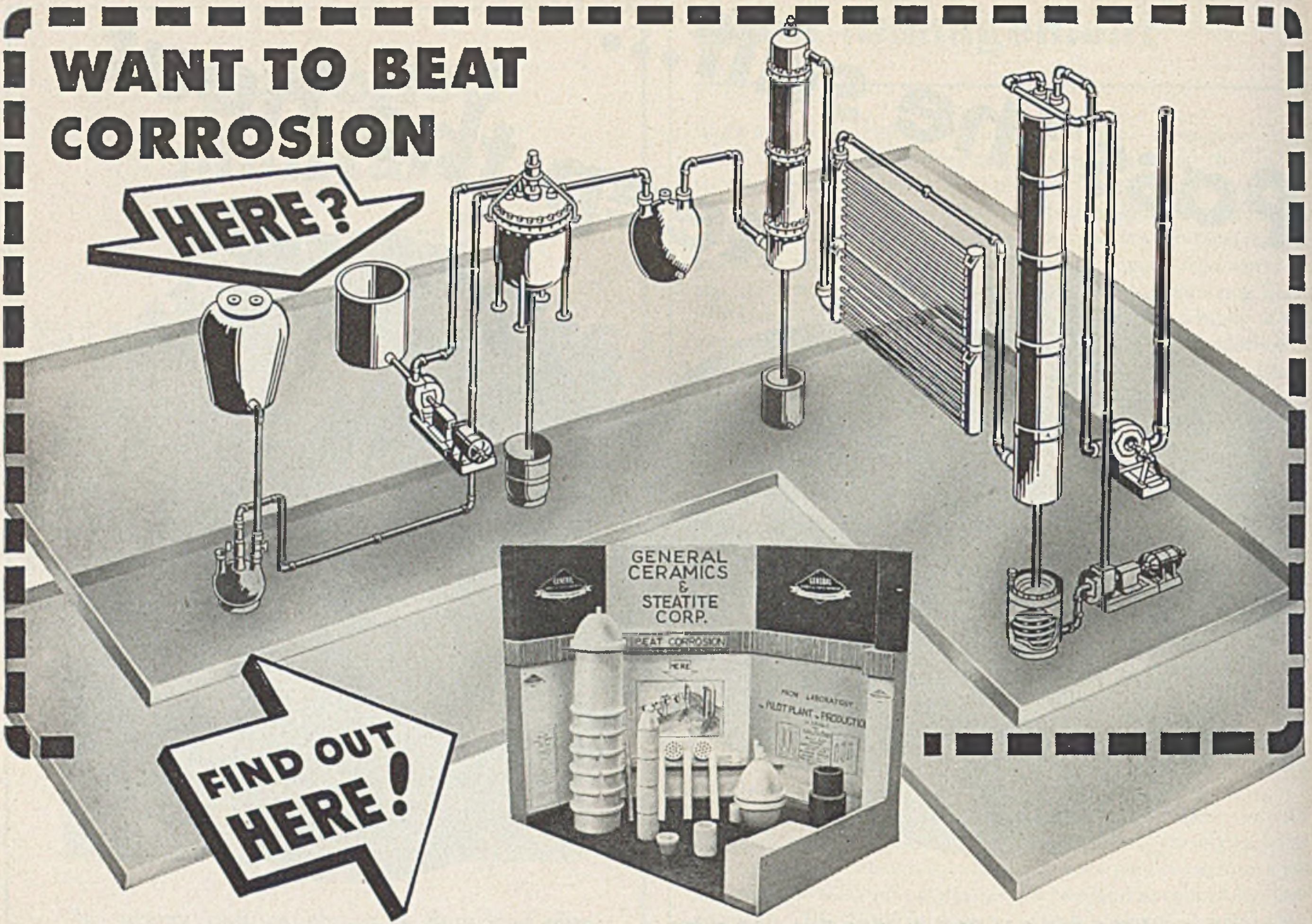

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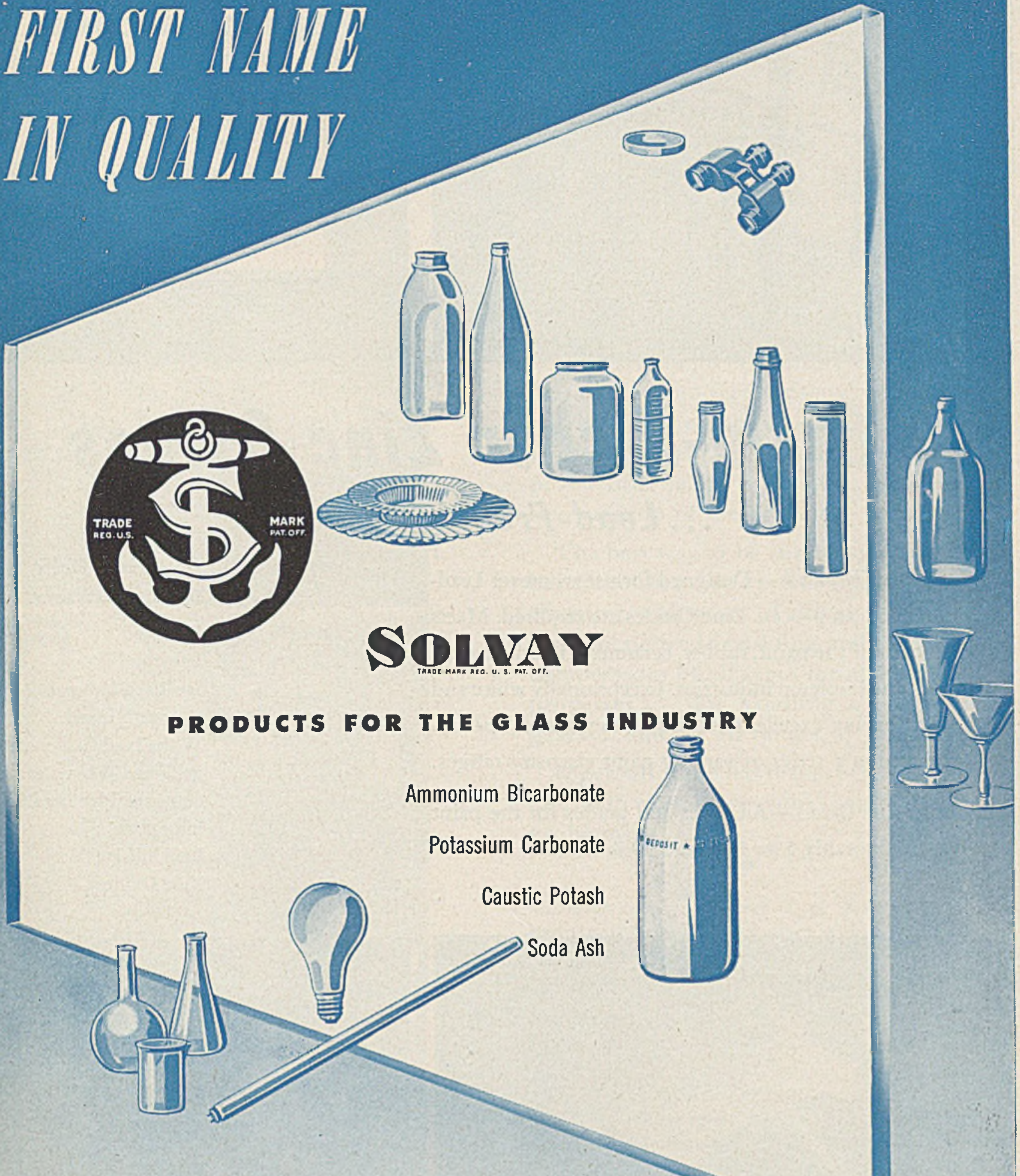


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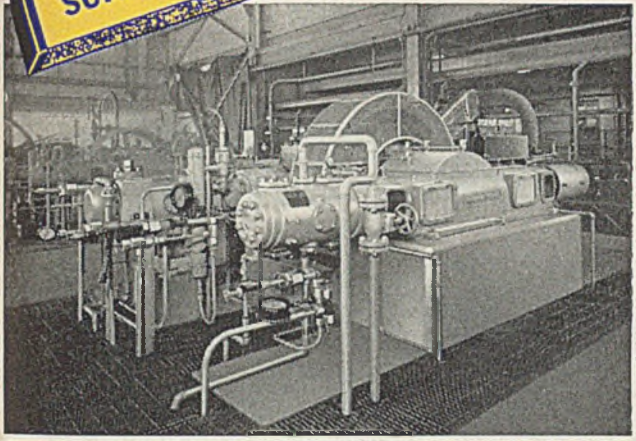
the Yardstick for Process Compressors



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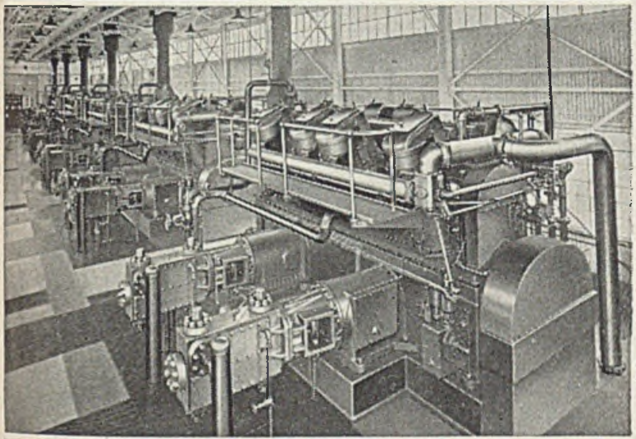

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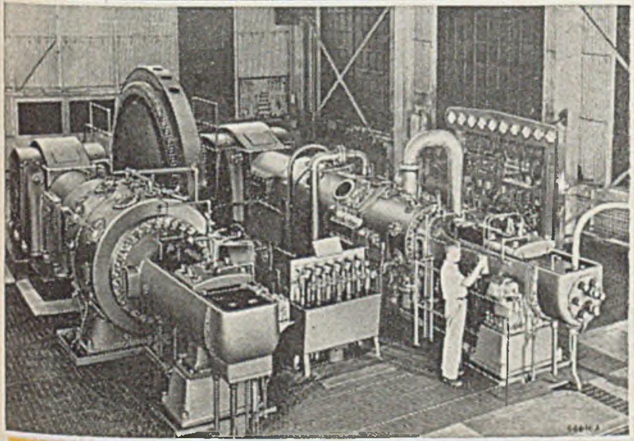

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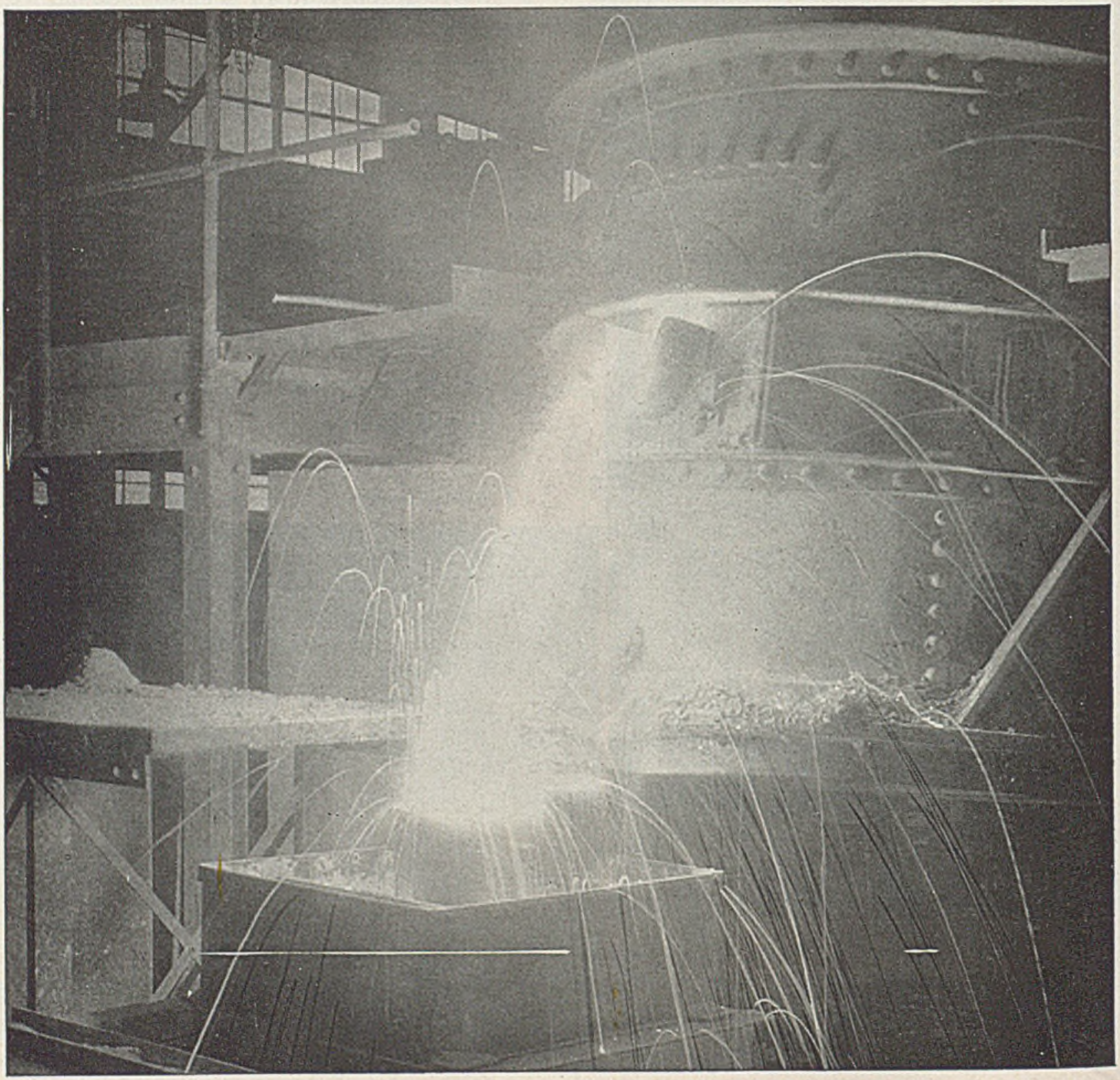
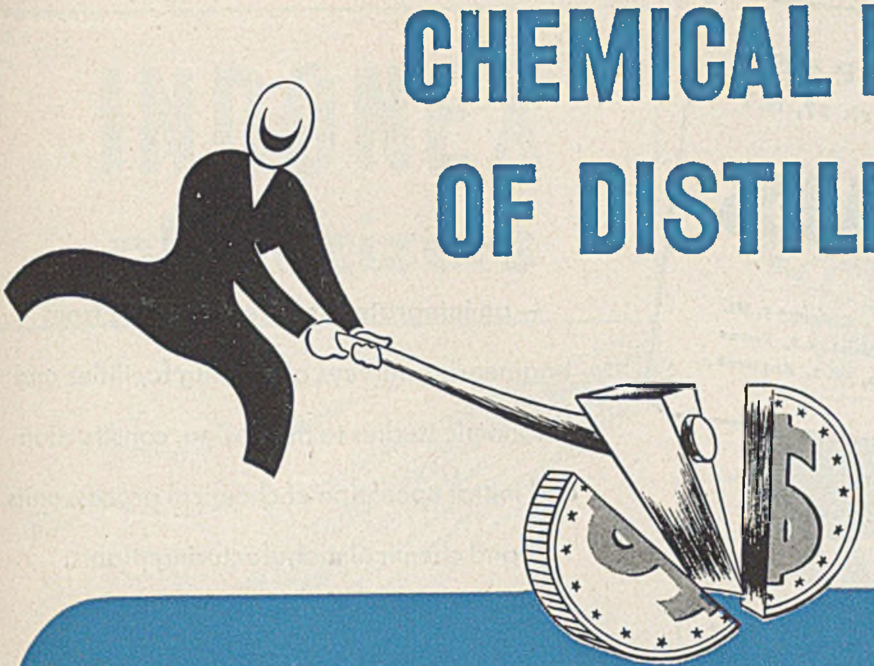


CHEMICAL EQUIVALENT OF DISTILLED WATER



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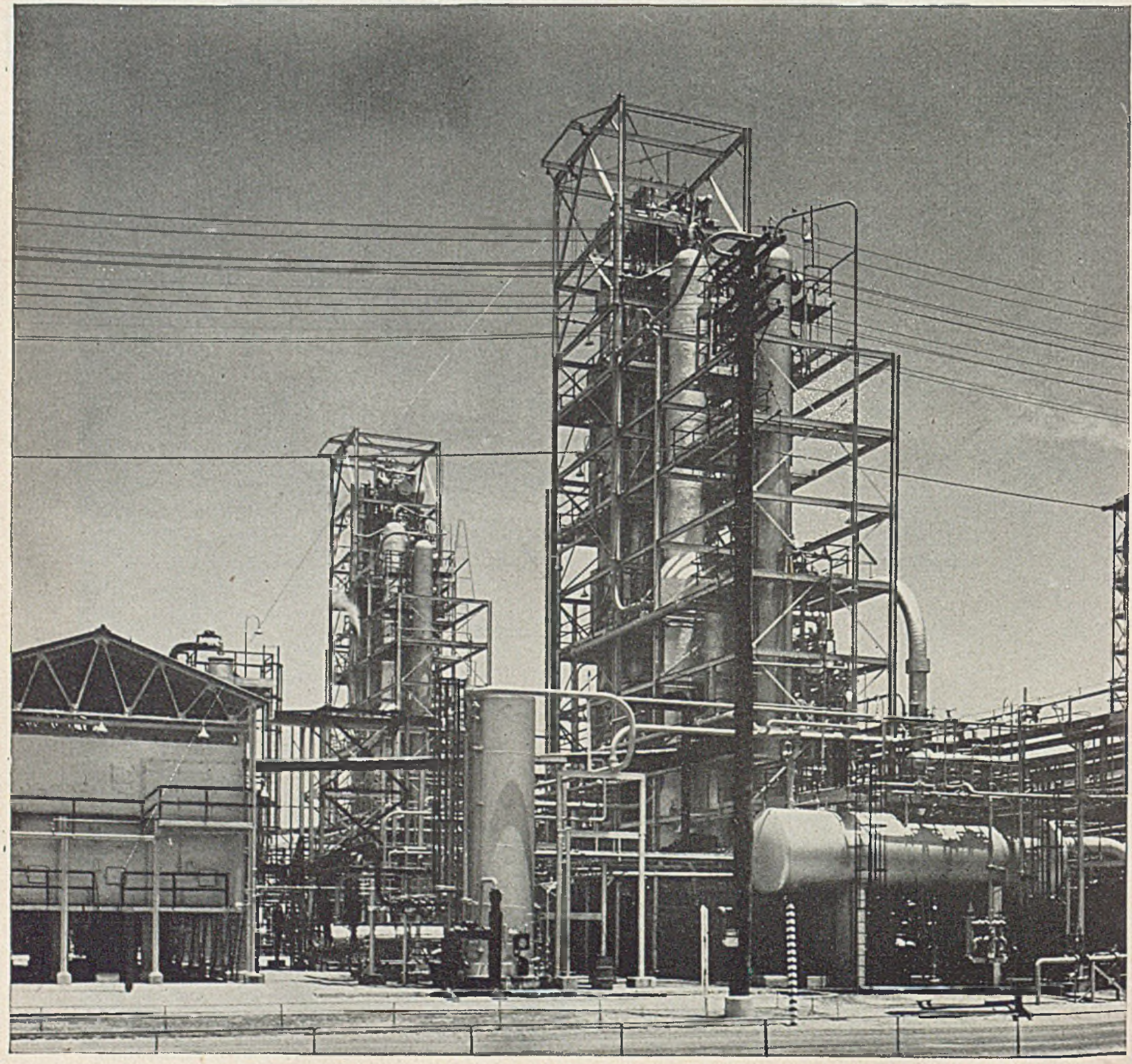

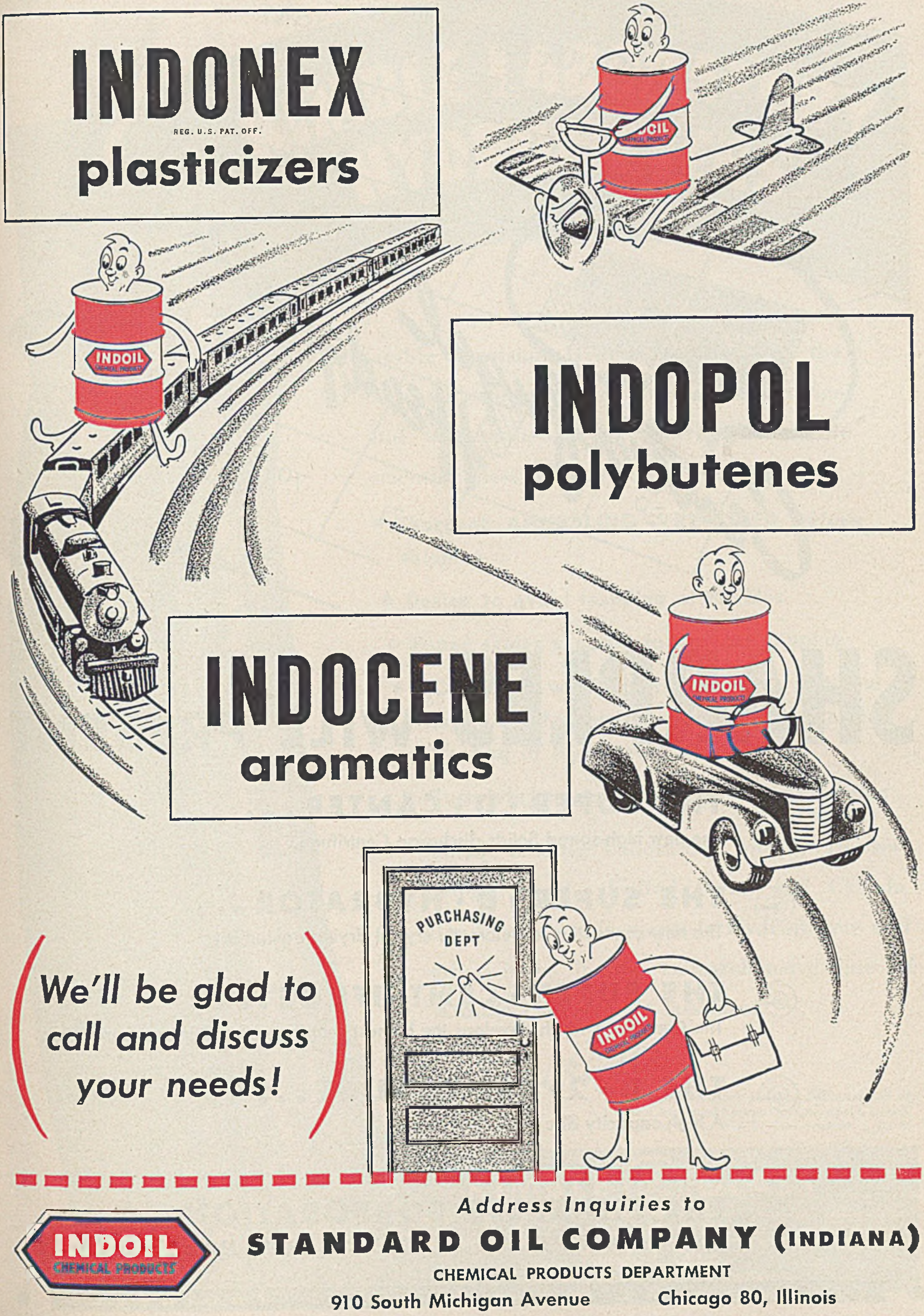
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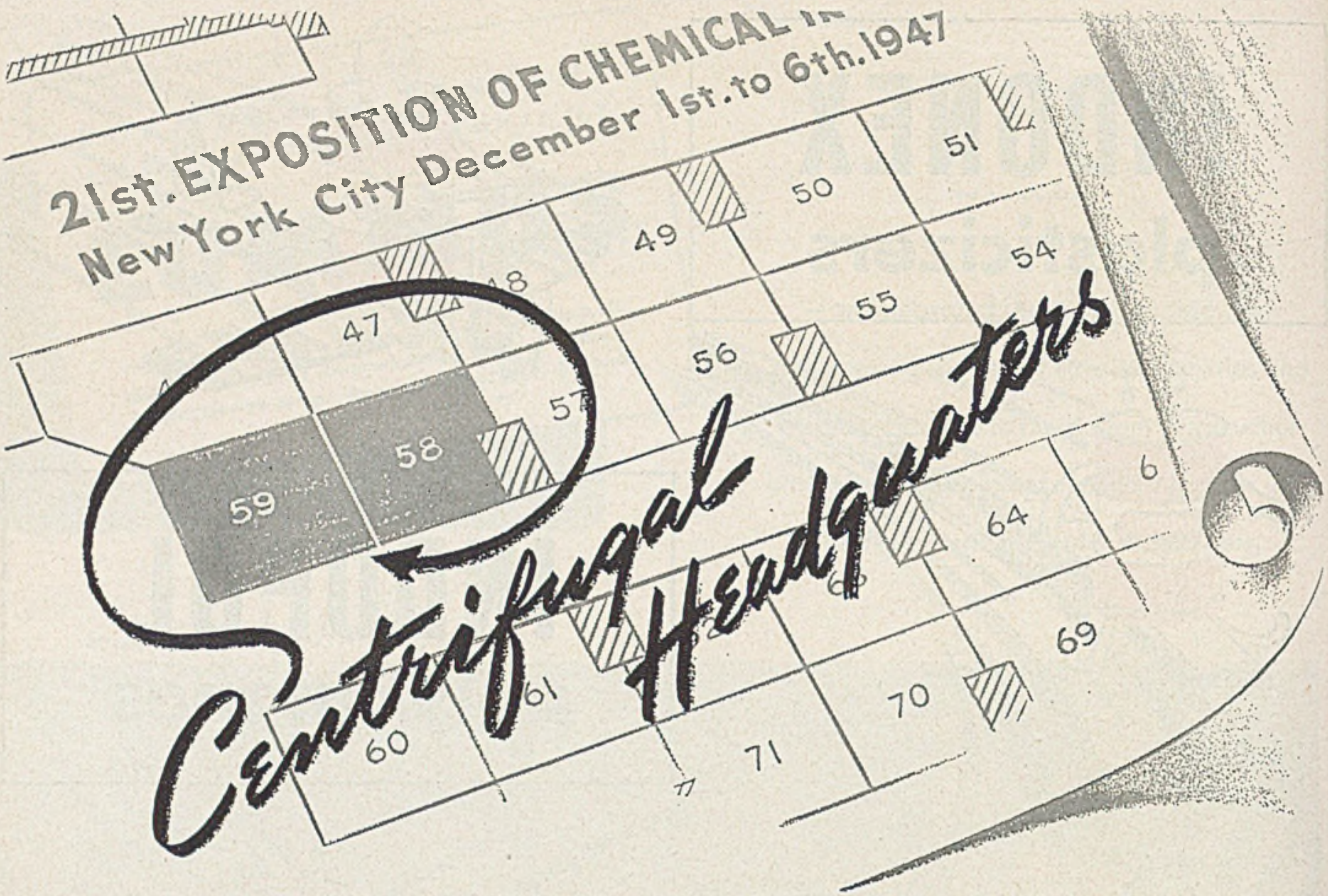
21st. EXPOSITION OF CHEMICAL IN
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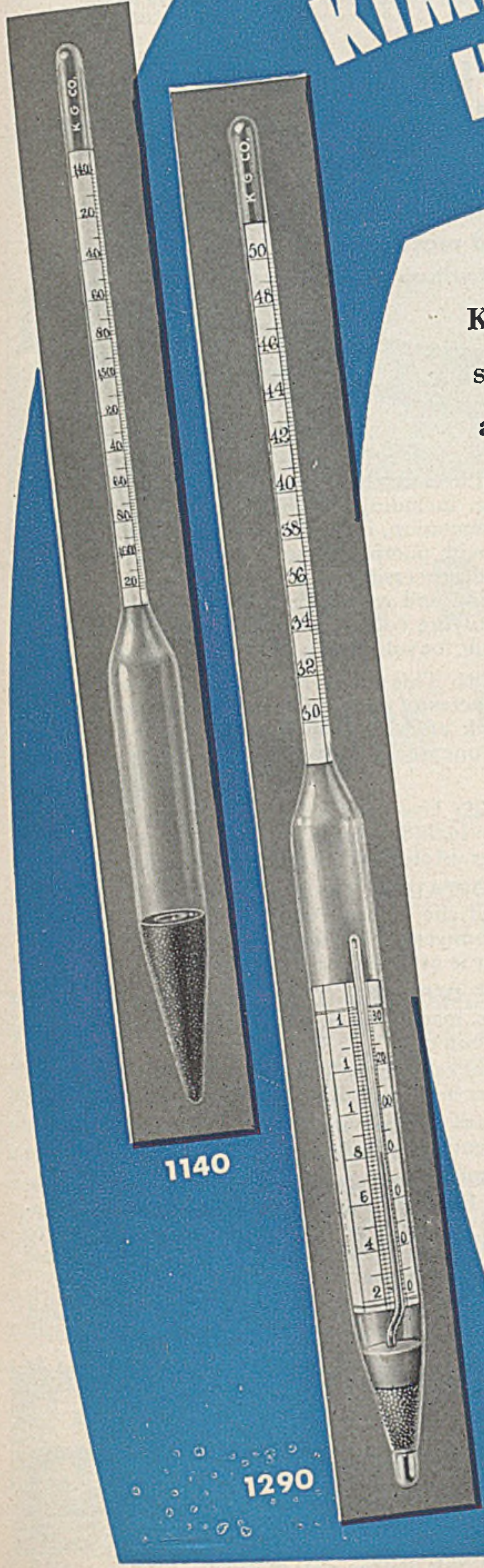

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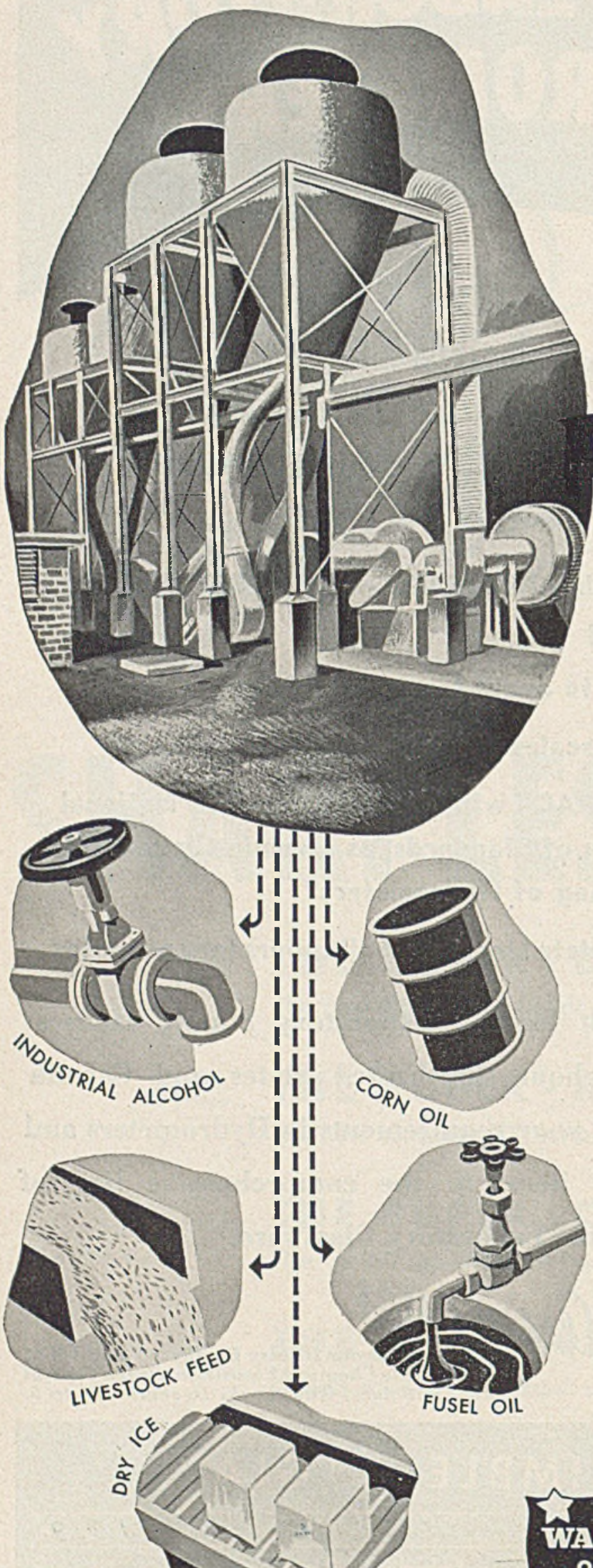

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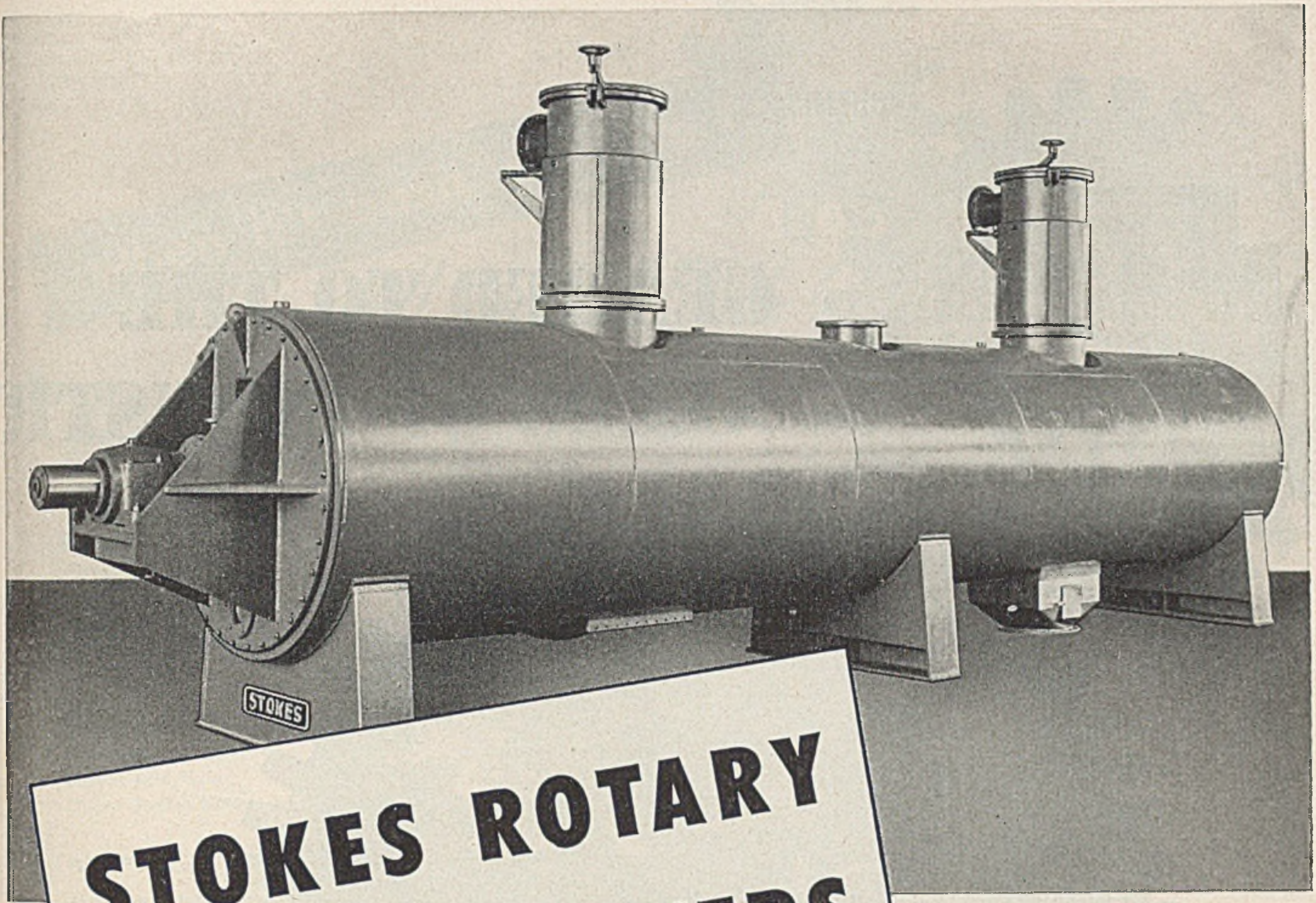

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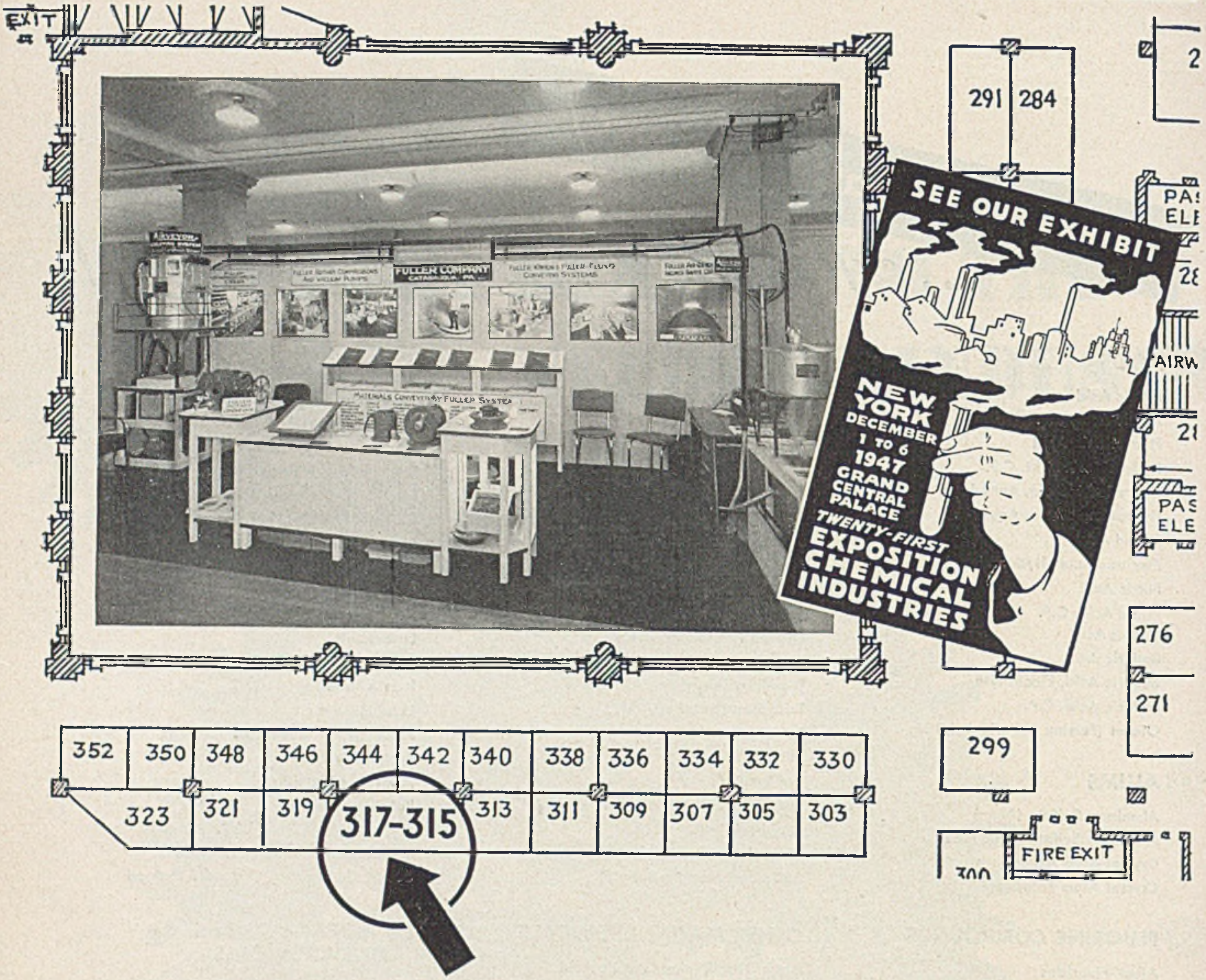

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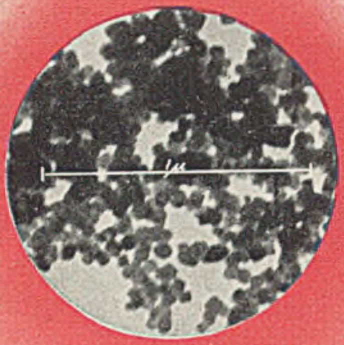

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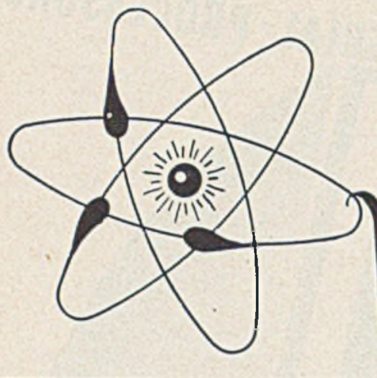

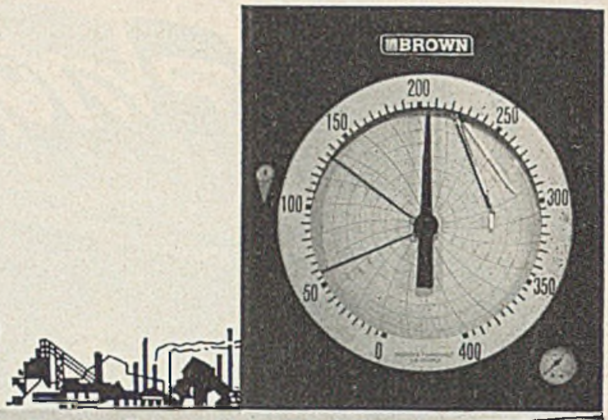

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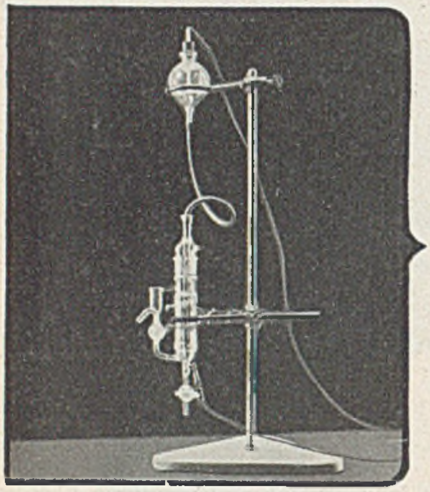
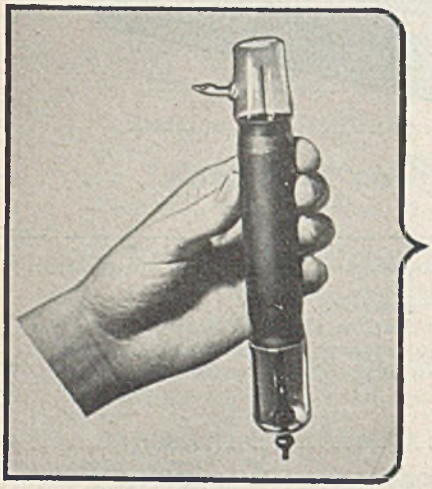


Photograph courtesy of E. H. Sargent and Co.



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WE PREDICT that these five measuring elements presage a phenomenal change in process control techniques during the next decade. The direct, continuous measurement and control of chemical composition will replace many of the inferential methods now in use. Analysis and measurement which formerly took days or hours of extremely skilled work has been reduced to minutes of routine procedure.

The Brown *ElektroniK* Potentiometer has been responsible for moving laboratory techniques into the plant. Greater accuracy, sensitivity and speed of response has made it a leader in the fields of chemical analysis and composition control.

THE POLAROGRAPH

The Polarograph is an analytical instrument, both qualitative and quantitative, for determining the chemical constituents of either aqueous or nonaqueous solutions. Both in micro and macro analytical work, the Polarograph replaces tedious and slow wet chemical methods. The high speed of the Brown *ElectroniK* recorder facilitates obtaining a well defined analysis curve.

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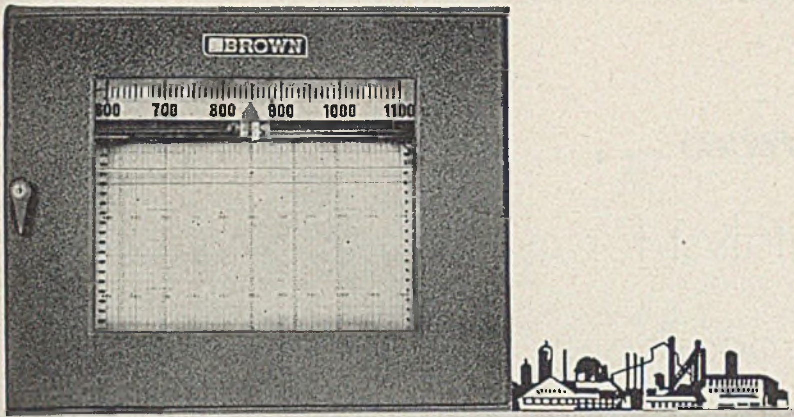
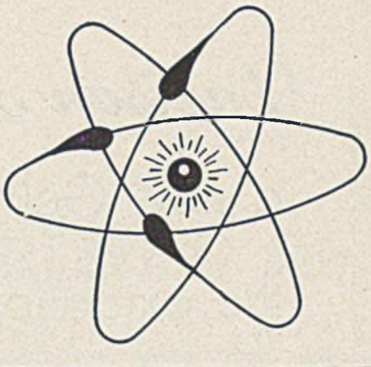
BROWN *ElectroniK*





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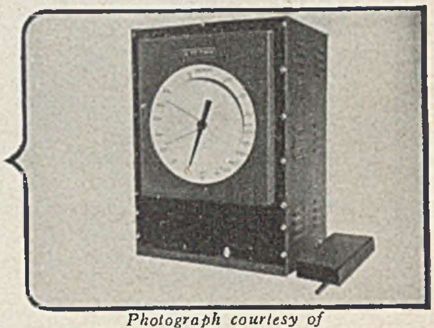

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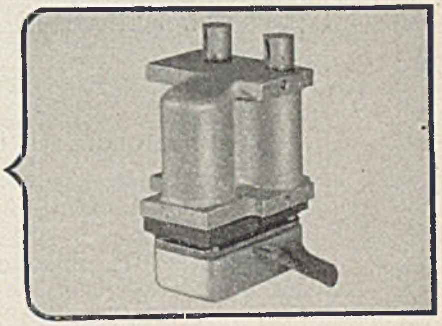
THE PIRANI THERMAL ULTRA VACUUM GAUGE

Many new processes require fast, accurate indicating, recording and controlling of ultra high vacuums. This is now practical using the combination of a thermal measuring gauge and the Brown *ElectroniK* Potentiometer.

Pirani gauges are available in ranges of 0 to 500 and 0 to 1,000 microns of mercury pressure absolute.

The fast Brown *ElectroniK* Potentiometer transforms these gauges into production tools.



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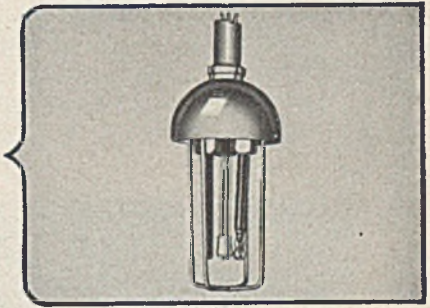
Davis Emergency Equipment Co., Inc.

THE GAS ANALYZER

The electronic measurement of combustible gases, vapors, oxygen and toxic gases is finding wide usage today.

The cell illustrated analyzes combustibles present in a gas sample which is burned upon contacting a hot platinum filament in the analyzing unit, changing its electrical resistance. These changes are instantly detected, indicated and recorded by a Brown High Speed *ElectroniK* Potentiometer. Alarms may be sounded or control contacts may be utilized to close doors, start fans or initiate other corrective or preventative action.



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THE pH ELECTRODES UNIT

The use of pH measurement and control is expanding sensationally into new processes and new industries. Standard Brown *ElectroniK* Potentiometers are available with pH ranges of 0-7, 3-10, 6-13, or 2-12 pH. The Brown *ElectroniK* Air-O-Line Controller has put pH control on a practical everyday basis. For further information, write to

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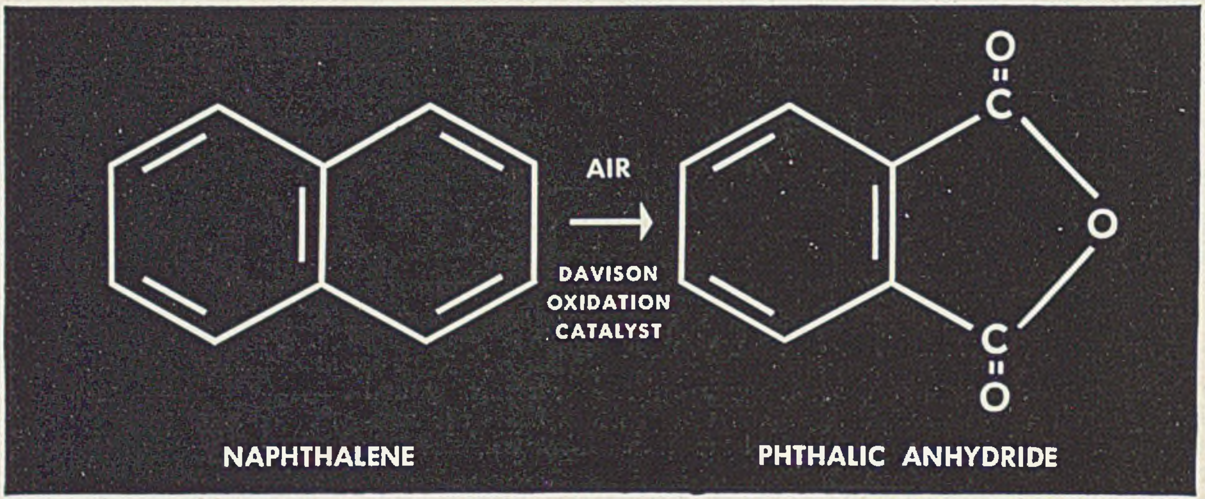
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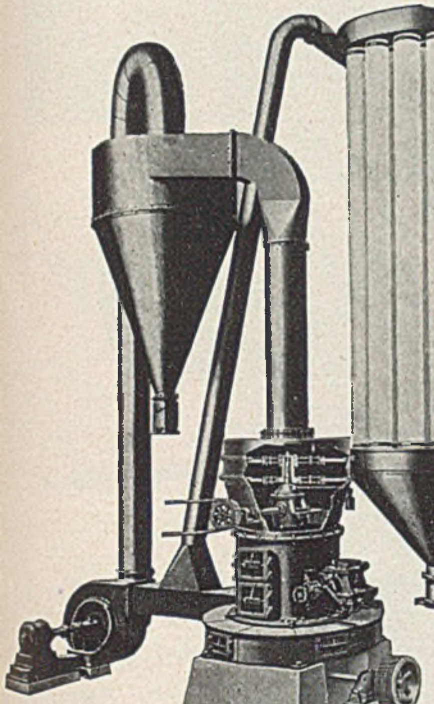

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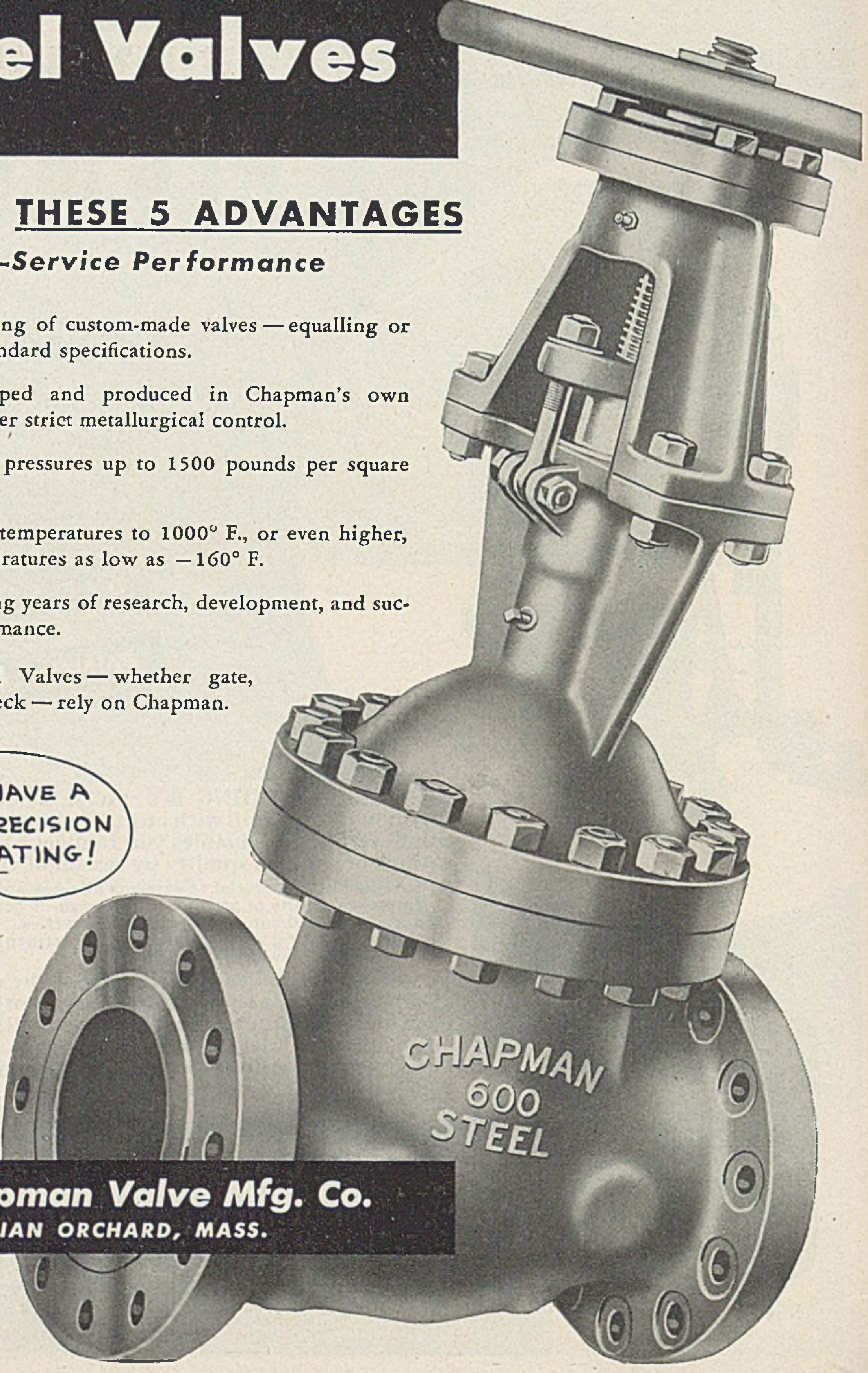

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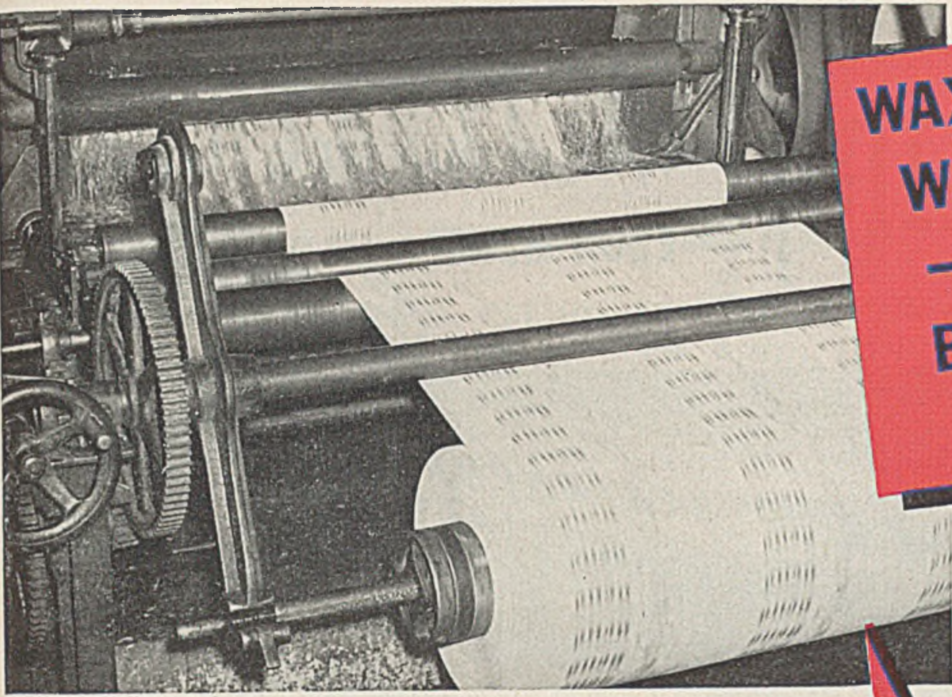

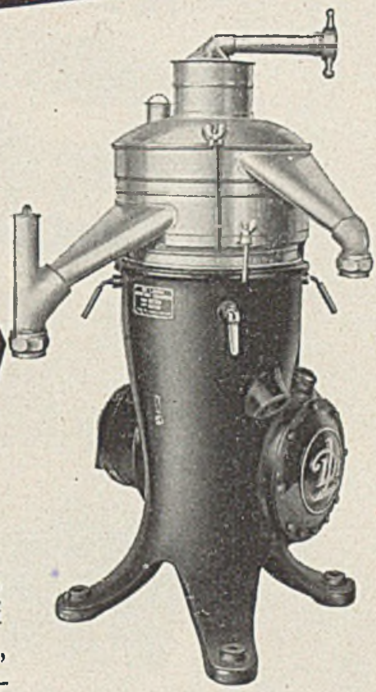

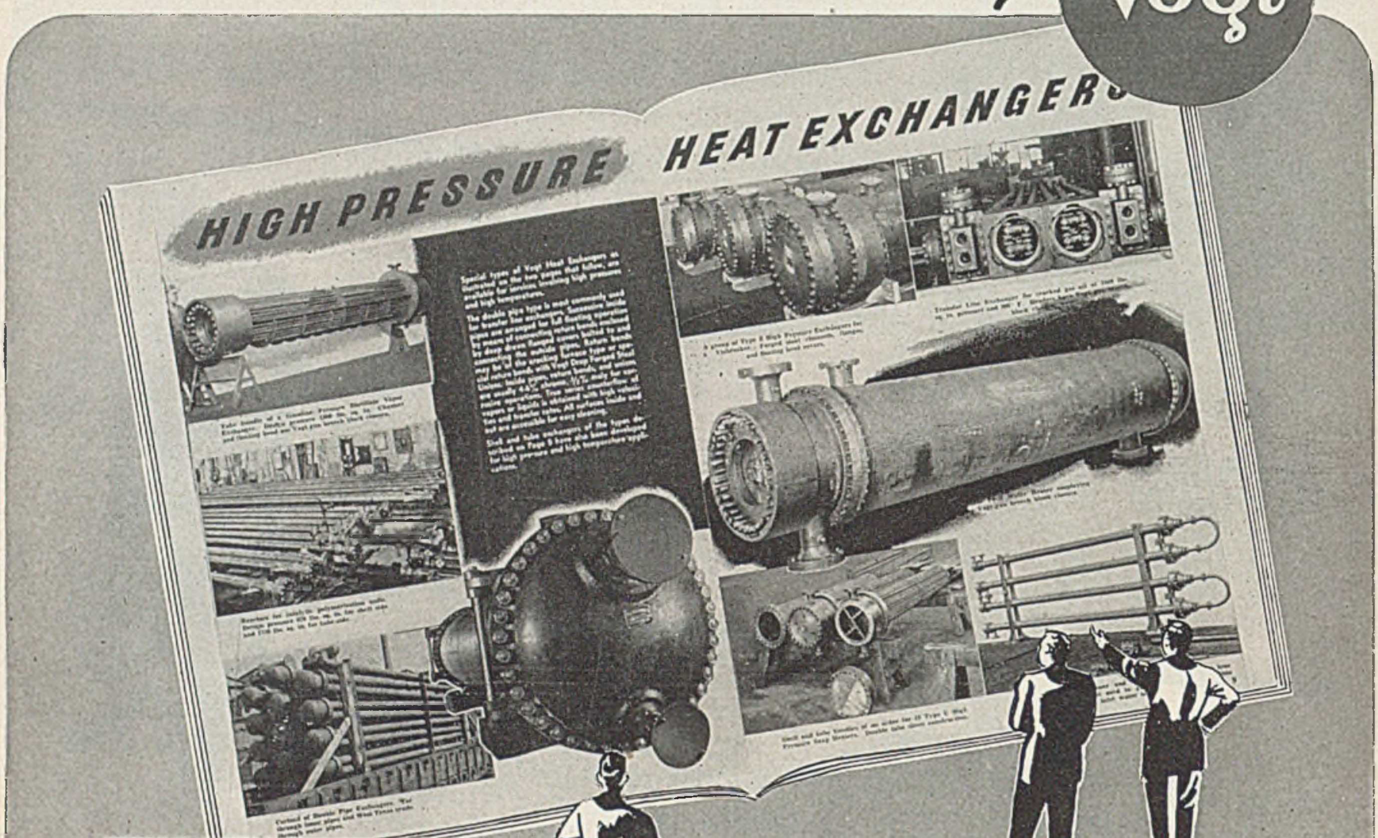
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CHEMICALS & MATERIALS

SYNTHETIC RESINS. Booklet, "The Uformites for Paper," discusses synthetic resins in modern paper-making procedure. Gives history of wet strength in paper and value in such applications as waterproof maps, paper towels, bags for chopped ice, moist fruit or vegetables, frozen foods, etc. Treats specific data on preparation, operating conditions, dilution of resin and broke recovery with resins. Resinous Products & Chemical Co. 1

TEMPER DESIGNATIONS. Booklet, "Alcoa Temper Designations for Cast and Wrought Products," effective on and after Jan. 1, 1948. Contains tables on designations for strain hardened tempers of nonheat-treatable alloys; and designations for heat-treated products including: wrought alloys; sheet and plate; extrusions; wire, rod, and bar; tubing, forgings, and rivets. Aluminum Co. of America. 2

LININGS. Bulletins illustrating chemical- and abrasion-resistant linings in thicknesses of $^1/_8$ to $^1/_4$ in. or more, and describing lined drums. Rubber, damaged by sharp objects, may be repaired by purchaser on site. Heil Process Equipment Corp. (*Bulletins 46 and 525*) 3

ION EXCHANGE RESINS. Booklet, "The Role of the Amberlites," describing role in water treatment and chemical processing. Lists contributions in transportation, chemical, canning, paper, textile, dye, and pigment industries. Discusses processes including deionization of locomotive water, isolation of rare earth metal salts, control of alkalinity, concentration of chemical elements, recovery of acids, prevention of scale in heat transfer processes, liberation of weak bases, and adjustment of salt content. Resinous Products & Chemical Co. 4

ORGANIC INSECTICIDE. Report by Connecticut Agricultural Experiment Station on "Direct Control of Ants" by chlordan. May be applied with hose and garden nozzle by spot treatment to nests or thorough watering with solution. Application and dosages mentioned. Julius Hyman & Co. (*Technical Supplement 202*) 5

WATER TREATMENT. Bulletin, "Alkalies and Chlorine in the Treatment of Municipal and Industrial Water," discusses softening, purification, taste and odor removal, corrosion control, boiler feed water treatment, use of alkalies, chlorine, and other chemicals and equipment, as well as lists of standard reference works on many of subjects covered. Solvay Process Co. (*Bulletin 8*) 6

ENTHALPIES. Bulletin, "Tentative Partial Enthalpies of the Lighter Hydrocarbons," authored by B. H. Sage, R. H. Olds, and W. N. Lacey. Tables consist of: partial enthalpies of methane, ethane, propane, *n*-butane, and *n*-pentane in the gas and liquid phases. Clark Bros. Co., Inc. 7

FLUIDS AND LUBRICANTS. Bulletin, "Ucon Fluids and Lubricants," describing use of new polyalkylene glycols and their derivatives for: general industrial lubrication, textile lubricants and conditioners, rubber lubrication, hydraulic applications, plasticizers and softeners, and heat-transfer media. Carbide & Carbon Chemicals Corp. 8

CARBON TETRACHLORIDE. Booklet containing technical and general data on carbon tetrachloride intended to serve as reference book. Discusses specifications, physical and chemical properties, azeotropic mixtures, vapor pressure-temperature relationship of the liquid and other chlorinated hydrocarbons, solubility of water in carbon tetrachloride, stability, action on metals, nonflammability, solvent power, binary mixtures, etc. Describes uses and applications and gives approved instructions for safe handling. Stauffer Chemical Co. 9

EQUIPMENT & SUPPLIES

MAGNETS. Catalog describing rectangular double-gap electro-magnetic, suspended, spout, and plate magnets, and wet type magnets for submerged installations. Applied for removal of tramp iron to protect equipment, purification of nonmagnetic products, pre-

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(NOVEMBER 1947)

vention of fires and explosions from sparks, and recovery of tools and magnetic scrap. Describes applications of magnets in mining, food, process, metalworking, rubber, textile, grain, and other industries. Includes drawings, illustrations of installations, specification data, etc. Dings Magnetic Separator Co. (*Catalog 301-A*) 10

PROTECTIVE APPAREL. Bulletin describing and illustrating aprons and sleeves of clear and frosted plastic for protection against various acids, caustics, oils, and solvents. Seams electronically sealed. 3 weights. Also discusses synthetic, neoprene coated, and work gloves for similar service. Industrial Products Co. 11

TURBO-SUPERCHARGER RINGS. Reprint describing roll bending and flash welding stainless steel turbo-supercharger rings, by P. B. Scharf. Dresser Mfg. Division. 12

PROPANE-BUTANE HOSE. Folder describing suitability of hose for handling highly volatile petroleum gases in liquefied form from bulk storage to tank car, and from tank car to home storage tanks. Made of multiple plies of high-tensile, closely woven cotton duck bonded by layers of oil-resisting rubber. Withstands high pressures encountered in propane-butane service. Contains spiral of static dissipating steel wire embedded in wall, and extending through length. Hewitt-Robins Inc. 13

FATIGUE TEST MACHINES. Six bulletins describing and illustrating 8 fatigue test machines, containing detailed specifications. Baldwin Locomotive Works. (*Bulletins 256 to 260*) 14

COATED UPHOLSTERY FABRICS. Folder illustrating and describing types of pyroxylin, vinyl plastic, and synthetic rubber coated fabrics. E. I. du Pont de Nemours & Co., Inc. 15

AUDIO-VISUAL REFERENCE LISTS. Three publications, "Selected Indexes and Sources of Photographic Visual Aids," "Selected References on Audio-Visual Education and Training," and "Some Sources of Educational 2 × 2-in. Slides." Booklets respectively list major sources of motion pictures, slide films, and slides available for educational, industrial training, medical, and other purposes; most of significant articles and books concerned with production and utilization of photographic audio-visual aids since 1940, plus some of earlier origin; and partial list of largest producers and suppliers of 2 × 2-in. slides on various subjects. Eastman Kodak Co. 16

DEWATERING ROTOSCOOP. Booklet describing and illustrating sand dewatering device capable of recovering available sand grains and similar materials and discharging product dry enough for truck transportation, or mechanical conveying to and from storage. Saves grain sizes lost in overflow water. 4 sizes: 6, 9, 12, and 15-ft. diameters; capacities from 20 to 150 tons/hr. Includes dimensions, hp., and weights. Link-Belt Co. (*Folder 2263*) 17

ELEVATOR BELTING. Folder describing belting constructed of rubber compounds bonded to high-tensile cotton carcass. Supplied in standard and shock-pad construction in all widths and plies; special construction for hot materials handling. Hewitt-Robins Inc. 18

CONVEYOR BELTING. Booklet describing following features: rubber compounds supply resistance to abrasion, aging, weathering, heat, and sun-checking; cotton reinforcements provide added strength, reduce stretch; scientific treatment against mildew; flexibility; resilient rubber frictioning between plies for adhesion; layers of skim rubber provide added cushioning to withstand shock loads. Available in straight-ply, stepped-ply, and shock-pad construction in all widths and plies; special construction for handling hot materials. Hewitt-Robins Inc. 19

CENTRIFUGAL PUMPS. Bulletin illustrating corrosion-resistant aluminum bronze pump. Replaceable wearing ring centrifugally cast, and heat treated to provide toughness and hardness. Complete series available in close coupled and pedestal types. Discusses design, construction, and drives. Ampco Metal Inc. (*Bulletin 85*) 20

VOLTAGE CONTROL. Data on variable transformers, voltage regulators, instantaneous electronic models, and electromechanical models, illustrating types. Lists adaptations, connections, and ratings including all standard types for single- or 3-phase operation. Available with or without motor drive. Superior Electric Co. (*Bulletin 547 and Price List*) 21

ENGINEERING DATA. Guide for engineer and draftsman in design of pipe coils and fin coils. Treats heat transfer "K" factors for all ranges of heating and cooling from −60 to +350° F., gives recommended air velocities and fin spacing for fin coils, and shows in detail how to calculate and design pipe and fin coils for all generally encountered heating and cooling loads. Discusses inspecting, testing and finishing coils, calculation of heating and cooling coils, methods of computing fin coil surfaces, application of coils to particular types of heating and cooling units, and gives properties of saturated steam. Rempe Co. (*Form 547-3M. Price, $1.50*) 22

EXTRUSION TAKEUP EQUIPMENT. Brochure, Part IV of series "Blueprint for Industry," containing technical engineering drawings and specification tables and analytical descriptions of modern methods in continuous extrusion takeup operations; treats wire, cable, plastic monofilaments, and tubings systems. High production extrusion system speed range up to 2000 ft./min. or higher. Industrial Ovens Inc. 23

COMMODITY SPECIFICATIONS SUPPLEMENT. Supplement to 1945 edition of National Directory of Commodity Specifications prepared by P. A. Cooley. With 1945 edition, provides complete listing, by name, designating number and issuing or sponsoring organization, of all standards, specifications, and methods of test in general use for commodities produced in or purchased by U. S. Government. National Bureau of Standards. (*Miscellaneous Publication M178 and Supplement. Prices, $4.00 and $2.25, respectively*) 24

STAINLESS AND ALLOY STEEL VALVES. Booklet describing use of valves for chemical, industrial, processing, and refinery services. Lists dimensions of numerous corrosion-resistant models for high temperature and high pressure requirements. Kerotest Mfg. Co. (*Catalog 47-AS*) 25

SCIENTIFIC EQUIPMENT. Booklet, "Announcer of Scientific Equipment," illustrating and describing recent developments of apparatus and supplies for laboratory work, including laboratory glassware, vacuum pump, variable transformers, rotary vane pump, gas drying unit, multiple pipette shaker, thermoswitch, and aluminized steel hot air sterilizers. Eberbach & Son Co. (*House Magazine 47-10-28*) 26

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INDUSTRIAL DATA DEPARTMENT
Industrial and Engineering Chemistry
332 WEST 42nd ST.

CONTINUOUS BLOWOFF SYSTEMS. Publication illustrating 5 flash-tank and heat-exchanger systems for recovering wasted heat in boiler blowoff water. Flash principle permits regeneration of low pressure steam for feedwater or plant heating. Remaining heat in concentrated blowoff water transferred to incoming feedwater through heat exchanger. Chart shows simplified savings estimate. Cochrane Corp. (*Publication 4410*) 27

RUBBER MATS AND MATTING. Catalog section dealing with rubber mats and matting, and describing in detail function, construction, and specifications of each type. Includes: platform and standard perforated mats, runner, multi-link mattings, molded and perforated door mats, shower stall, bath, stove, drainboard, and office chair floor mats. B. F. Goodrich Co. (*Catalog Section 6100*) 28

INSTRUMENTS

ELECTRONIC SCRIBER. Booklet describing and explaining scriber functions for measurement, indication control, and permanent record of variables in process industries. Design, operating, and specification data contained. Deviation of 0.004 in. to 0.006 in. of detector of measuring system sufficient to cause pen response. Tamperproof housing, automatic chart reroll and tear-off, back-lashb reaker, voltage selector plug, multi-tube safety factor, and direct reading are features. Wheelco Instruments Co. (*Bulletin C2*) 29

STIFFNESS TESTER. Bulletin describing motor-operated tester illustrates applications in paper, textiles, leather, plastics, metal foil and finishings; range and capacity given for standard sizes. Not recommended for heavy, limp materials. Height, 17 in., base, 7 in. × 10.5 in. Weight, 14 lb. Motors supplied for use on 115 v., 60 cycles a.c., 25 or 50 cycles. W. & L. E. Gurley. (*Bulletin 1430*) 30

MICRO-GAS ANALYZER. Folder illustrating analyzer for determination and analysis of gases and vapors within toxic range. Principle: electrical conductivity of solutions. Includes toxicity table for 73 gases, specifying maximum allowable concentration for each. Specifications: 110 a.c., 60 cycles; dimensions, 8.5 × 20 × 12.25 in., weight, 33 lb. Davis Emergency Equipment Co., Inc. (*Technical Bulletin 1143*) 31

FLOW RATE MEASUREMENT. Bulletin, "A New Era in Liquid & Gas Flow Measurement," describing and illustrating flowrator meter. Discusses basic principles, flexibility, accuracy, calibration linearity and range, immunity to variations in fluid viscosity, etc. Meter consists of: tapered borosilicate glass tube set vertically in fluid piping system with large end at top, and metering float free to move vertically in tapered glass tube. Fischer & Porter Co. (*Catalog Section 10-D*) 32

NEW PRODUCTS

CHEMICALS & MATERIALS

SHINGLE COATING. Coating of linseed oil material or rubber base paint. 2-coat application bonds chemically and physically to asbestos siding. Ready-mixed. 1 gal. covers 300 sq. ft. A. C. Horn Co., Inc. (*Horn-O-Kote*) 33

SYNTHETIC ADHESIVE. Resin-latex emulsion cement permanently adheres ungummed paper labels to electrolytic tin plate, terne plate, varnished, lacquered, painted, and enameled surfaces, etc. Suitable for bonding operations involving similar and dissimilar materials. Labels retain adherence to surface after aging at 225° F. for 7 days and exposure 100 hr. at 100% relative humidity at 100° F. No objectionable odor when panel sealed in airtight container at 100° F. for 24 hr. Available in 1 to 55 gal. drums. Paisley Products Inc. (*No. 1707*) 34

FIRE-RESISTANT PAINT. Ready-mixed, self-sealing, covers wallpaper, plaster, brick, steel, composition, or wood in 1 coat. Washable. Plicote Inc. (*Fire Stop*) 35

BLOOM INHIBITOR. Data on bloom inhibitor for natural rubber and mixtures of natural rubber and GR-S compounds. Modified resin acid which is neutral with thiazole acceleration in natural rubber. Softening point 145° to 155° F. Shatters at room temperature; may be added to batch without melting. Specific gravity, 1.082. Recommended dosage 2 to 4 parts/100 rubber hydrocarbon. Applicable to tire coat and friction stocks, tire repair materials, laminated mechanical parts, footwear frictions and gum parts, etc. J. M. Huber Corp. (*Bulletin NATAC*) 36

NEOPRENE PAINT. Paint coating protects surfaces exposed to fats, oils, greases or corrosive chemical liquids, solids or fumes. Adheres to wood, metal, etc.; is odorless; resists abrasion. Rubberlike, aromatic solution with addition of materials forms chemically resistant paint. Translucent amber. May be sprayed or painted. Union Bay State Chemical Co. 37

EQUIPMENT & SUPPLIES

INDUSTRIAL APRON. Heavy-duty apron of Koroseal film. Resists acids, greases, caustics, gasoline, animal fats and blood, vegetable fats, solvents, and soaps. Available in sizes 29 × 35 in., weight, 14 oz.; and 35 × 45 in., weight, 1.5 lb. Tape, hem, and grommet construction. Reinforced points. B. F. Goodrich Co. 38

MAGNETIC HOLDING ASSEMBLIES. Alnico magnet assemblies. 5 types in 17 sizes from pull of $1^{1}/_{2}$ to 500 lb. Vacuum impregnated to prevent moisture penetration, cadmium plated to prevent external corrosion. Smallest size $^{5}/_{16}$ in. in diameter. General Electric Co. 39

ALL-ALUMINUM PREFAB. Quonset hut design building, suitable for extreme weather conditions. Size, 36 × 60 ft. Standardized 6-ft. sections enable lengthening. Arches anchored to concrete foundation 1 ft. above ground. Reflects up to 95% of radiant heat. 5220 cu. ft. space, 2160 sq. ft. floor area. Sliding doors 11 ft. high, 16 ft. wide. Weight, 7000 lb. Cost, $1.56 per sq. ft. Reynolds Metals Co. (*Alumi-Drome*) 40

PULP FILTER AND WASHER. Filter with stainless-steel shells and screens, nickel-alloy cocks and fittings, and streamlined design. Usual handwheel replaced by hydraulic cover-lift to reduce over-all height and simplify operation. Automatic cell lock prevents misalignment of pulp layers. Washer removes danger of "balling" pulp. Features welded tank eliminating gaskets, 5 hp. requirements, fast circulation at slow speeds, small floor space requirement, and nonclogging discharge valve. Niagara Filter Corp. 41

PNEUMATIC MATERIALS HANDLING SYSTEM. System reduces usual product loss through collector exhaust by 10%, eliminates need for second filter collector. Can exhaust in same room with collector. No residue; injurious dusts cannot escape through piping connections, as system is under reduced pressure; suction keeps system free from bugs or weevils. Sprout, Waldron & Co. (*Pneu-Vac*) 42

FLAT BELTING. Flat transmission belting of straight-edge construction for heavy-duty drives. Flexible, built of hard silver duck. Plies insulated with gum rubber compound. Available in 500- to 550-ft. rolls. Hewitt-Robins Inc. (*Monarch Amber*) 43

SPRAY HOSE. Two types of agricultural spray hose for pressures up to 800 lb./sq. in. One of oil-resisting synthetic tube to withstand emulsion sprays, other nonoil resisting for nonoil predominating conditions. Both resistant to insecticides, solvent solution, abrasion, weathering, and sun-checking. Hewitt-Robins Inc. (*Monarch and Ajax*) 44

FIRE AND CHEMICAL HOSE. Lightweight duck hose with high burst resistance. Duck protected against mildew deterioration by chemical treatment, and against acid fumes by rubber cover. Rubber tube and cover compounded to withstand oiling without cracking. Hewitt-Robins Inc. 45

OIL STANDBY EQUIPMENT. Available for use with gas burner equipment. Utilizes No. 3 furnace oil or lighter; provides same B.t.u. input/hr. as provided with gas burner equipment. Surface Combustion Corp. 46

Axial Flow Fans. Available in 2 types: straight-through or convertible elbow. Furnished with 3-bladed aluminum alloy wheel or 8-bladed steel wheel. Applications include: air conditioning, dust and fume removal, machinery cooling, mechanical draft for combustion, and industrial drying and processing. Vertical or horizontal operation. Capacity to perform against resistance of wind and duct systems. Sizes, 18 to 72 in., displacement, 2000 to 115,000 cu. ft./min. at 3 to 0 in. static pressure. Westinghouse Electric Corp. 47

Thermostatic Valve. Expansion valve for refrigeration applications. Check valve incorporated in regular size body. Positive control without feeler bulb. Close maintenance of superheat control −5° F. superheat with ±5° F. for control; saves space, compensation for pressure drop in evaporator designed into valve; no time lag in control; no special installation required. Tenney Engineering Inc. 48

Pressure Regulator. Automatic regulator operating on physical principle of Cartesian Diver. Self-contained. Heavy-duty, all metal unit. Maintains pressure or vacuum to within 0.1%. Corrosion-resistant unit measures 7.5 × 3.25 in. Weight, 6.5 lb. Emil Greiner Co. (*Bulletin ICM-96*) 49

Jackhamer. Data on air-operated utility jackhamer. Rock drill, standard jackbits, automatic rotation. Oil reservoir in handle supplies lubrication. Weight, 14 lb.; length, $17^{1}/_{8}$ in.; shank, $^{7}/_{8} \times 3^{1}/_{4}$ in. Hose, $^{3}/_{8}$ to $^{1}/_{2}$ in. Ingersoll-Rand Co. (*Form 4065, J-10*) 50

Silver Soldering Outfit. Single-unit outfit for silver soldering together with silver solder brazing kit. For light bench work on metal up to 0.25 in. thickness. Unbreakable, noncorrosive burner with leakproof joints. American Products Corp. 51

Water Suction Hose. Smooth bore water suction hose of chernack loom type construction. Light weight. Can be reformed to shape if crushed or kinked. Hewitt-Robins Inc. 52

Gas Combustion Assemblies. Pre-engineered, packaged units adaptable to firing boilers, air heaters, dryers, ovens, kilns, etc. Combine air handling, gas supply, mixing, and burning elements. Single burner or twin-nozzle burners. Capacities: 400,000 B.t.u./hr. rated at 8 boiler hp., with $1^{1}/_{2}$ in. gas inlet and $^{1}/_{3}$ hp. blower, to 3,300,000 B.t.u./hr. and 66 boiler hp., 3 in. gas inlet and 3 hp. blower. Burn low pressure gases from 400 B.t.u. upward, at 3 in. to 11 in. water pressure. 4 variations of control with each size. Bryant Heater Co. (*Bryant Pow-R-Semblies*) 53

Gas Alarm System. Continuous remote head type system detects presence of combustible vapor and/or gas, gives audible signal before mixtures become dangerous. Operating principle based on combustion of flammable gas-air or vapor-air mixtures on heated filament in analyzer head. Control cabinet cover prevents tampering. Transparent words in cover become illuminated when respective relays close. Davis Emergency Equipment Co., Inc. 54

Electrode. All position, mild steel electrode. A.c. and d.c. reverse polarity current. Preheating not required. Recommended applications: welding high sulfur, free machining steels, welding hardenable steels where no preheat is used, etc. Wilson Welder & Metals Co., Inc. (*Wilson 512*) 55

Industrial Wheels. Aluminum alloy wheels range from 4 to 12 in. in diameter. Available with molded-on Grade A rubber or all aluminum treads. Roller or ball bearings or bronze bushings. Aerol Co. 56

Germicidal Unit. Destroys airborne bacteria in 8 sec. 2 types: to kill airborne bacteria through indirect radiation; to destroy molds, bacteria virus, and fungus through direct radiation on surfaces and in liquids. Lamps in units produced in 2 lengths—15 w. in 18 in., and 30 w. in 36 in. Lamp life 4000 hr. in 3-hr. cycles. Duro Test Corp. 57

Bottle Oiler. Flat side shallow body oiler for tight quarters. Over-all length, $3^{3}/_{8}$ in. Automatic operation, visible oil supply. Circular shows typical installations, application methods, dimensions, and prices. Lunkenheimer Co. (*Circular 560-RL*) 58

INSTRUMENTS

Air-Fuel Ratio Controller. Controller employing electric-motored valve drives and requiring no hydraulic piping. Rugged, balance-type, having ample flexibility for various operating conditions. Ratio adjustable manually. Maintains air-fuel ratio constant at desired point, as fuel flow changes, or can provide automatic variation of ratio. Leeds & Northrup Co. 59

Electronic Remote Control Unit. Control system for valves, dampers, and other mechanical mechanisms described in booklet containing complete performance and operational data. Consists of transmitter, control amplifier, and receiver. Dustproof cast metal cases. Askania Regulator Co. (*Technical Bulletin 138*) 60

Electronic Amplidyne. Consists of high-gain balanced d.c. electronic amplifier and motor amplidyne. High-capacity amplifier useful in motor controls where precise regulation of current, voltage, and speed are required. Output, 1.5 kw., 250 v. Regulated adjustable-voltage power supply for d.c. motors up to 1.5 hp. and regulated exciter for larger drives up to 200 hp. Useful on 220- or 440-v., 3-phase, 60-cycle power supply. Speed range 20:1 or greater. General Electric Co. (*Bulletin GEA-4889*) 61

Testing Machine. Precision tests physical properties of plastics, rubber, nonferrous metals, textiles, fibers, etc., with error not exceeding 0.5% of reading or 0.1% of range. Features: continuously-variable 400:1 positive speed range; horizontal rigidity; elimination of backlash; and accuracy in low ranges. Maximum capacity 5000 lb. Uses mechanical screw system. Loading speed steplessly variable from 0.05 in. to 20 in./min.; constant within ±2%. Ranges: 5000 lb. in 5-lb. units, 0–1000 lb. in 1-lb. units, 0–200 lb. in units of 0.2 lb., and 0–50 lb. in units of 0.05 lb. Baldwin Locomotive Works. 62

Geiger Tube. Alpha or soft beta counter recording 25% of total disintegrations for alpha particles from uranium; and 36% disintegrations for soft beta such as from C^{14}, Fe^{59}, and S^{35}. Windows from 0.7 mg. to 2.3 mg./sq. cm. in thickness; life, 10^{9} counts. Mica window, 2.5 in. in diameter. Over-all dimensions, 3.5 and 5 in. in diameter and length, respectively. Cyclotron Specialties Co. (*Tube 410-A*) 63

Oscillograph Camera. Continuous-recording camera for cathode-ray oscillograph images. Applicable to many standard 5-in. cathode-ray oscillographs. Single-frame exposures of stationary patterns or continuous recording of changing phenomena. Film speed variable from 1 in./min. to 5 ft./sec. Permits simultaneous viewing and recording on 35-mm. film or perforated sensitized paper. Magazines for 100- to 1000-ft. film available. A. B. Du Mont Labs. Inc. (*Du Mont 314*) 64

Automatic Scaling Unit. Scaling device for use with Geiger-Müller counters in radioactivity research. Operates on impulses from Geiger-Müller tube and actuates register once for each group of impulses received. Scaling factors of 2, 16, 32, or 64. Switch allows selection of 10, 100, or 1000 times selected scaling factor for predetermined count. Automatically shuts off after number of counts is recorded. Indicates time required for counts if connected to electric timer. Self-contained high-voltage supply, 700 to 2500 v., with electronic regulation of 0.01% change in line voltage. Instrument Development Labs. 65

Wrinkle Recovery Tester. Measuring device permits determination of amount of wrinkle resistance in woven fabrics. Permits reading of recovery angles from 0° to 180°. Monsanto Chemical Co. 66

Electrode pH Meter. Portable glass meter can be plugged into standard 110 v., 50/60 cycle a.c. line. Covers full scale of 0 to 14 pH, makes mv. readings within range 0 to ±410 mv. pH measurements accurate to 0.03 pH, mv. readings to 2 mv. Built-in temperature compensator dial calibrated 0° to 100° C. Measures 12 × 9.5 × 8.5 in. over-all, net weight, 14 lb., power consumption, 35 w. National Technical Labs. (*Model H pH Meter*) 67

There are 31 advertisements for Fluor Pulsation Dampeners on this page

Introduced two short years ago, the Fluor Pulsation Dampener has already won major recognition in the oil, gas and allied industries. Proof? A total of 308 installations-to-date by the 31 companies listed below:

Absorption Plant, Inc.
Cities Service Gas Company
Continental Oil Company
El Paso Natural Gas Company
Equitable Gas Company
General Petroleum Corporation
Gulf Oil Corporation
Hope Natural Gas Company
Manufacturers Light & Heat Co.
New York State Natural Gas Corp.
Northern Natural Gas Company
Ohio Oil Company
Oklahoma Natural Gas Company
Owens-Illinois Glass Company
Pure Carbonic, Inc.
Republic Light, Heat & Power Co.
Richfield Oil Corporation
Shell Oil Company, Inc.
Sinclair Refining Company
Southern California Gas Company
Standard Oil Company of Ohio
Stanolind Oil & Gas Company
Superior Oil Company
The Texas Company
Tide Water Associated Oil Company
Union Gas Company (Canada)
Union Oil Company
United Fuel Gas Company
Virginia Gasoline & Oil Company
Virginia Gas Transmission Corp.
Warren Petroleum Corporation

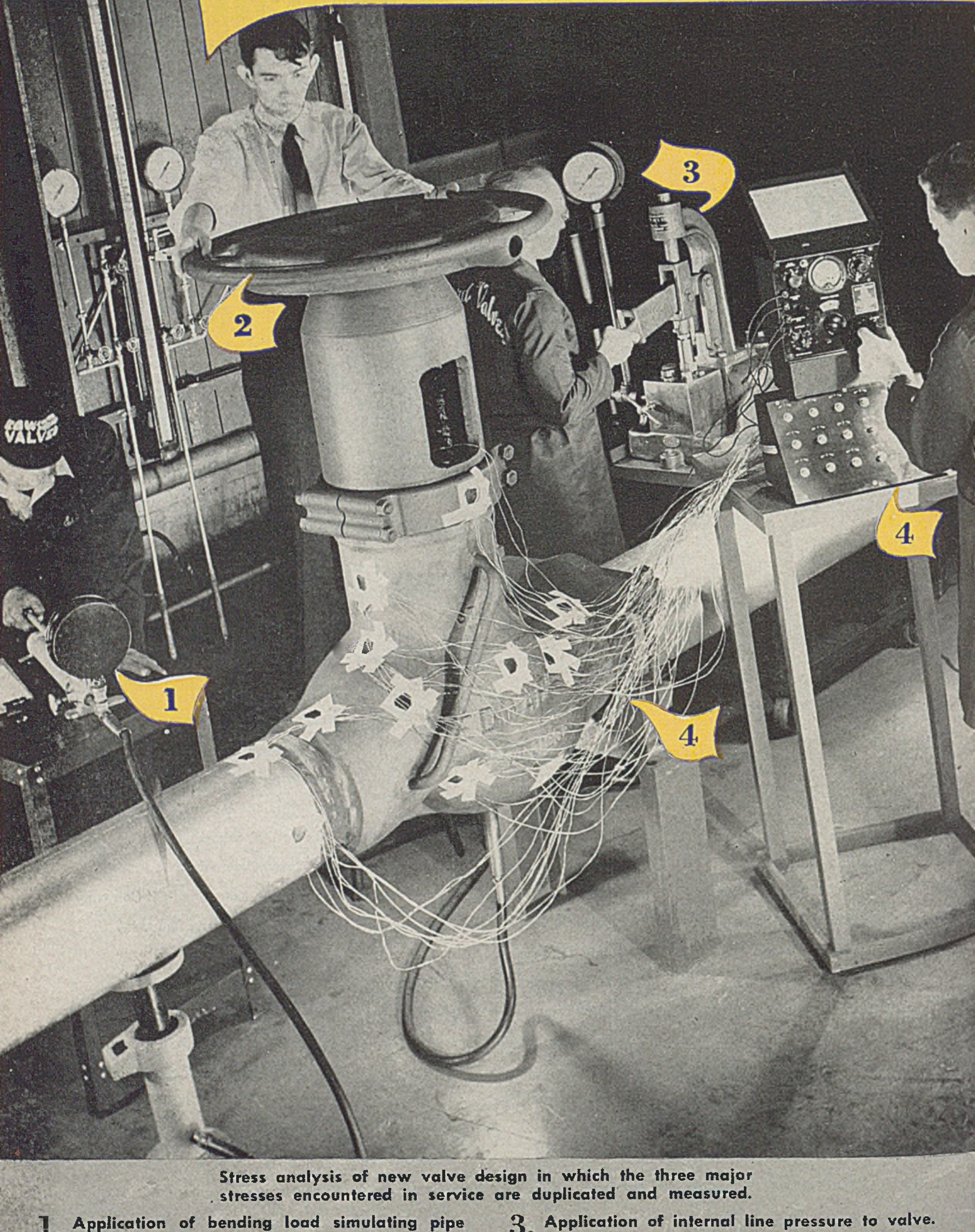
THE FLUOR CORPORATION, LTD., *Los Angeles 22* · NEW YORK · PITTSBURGH · KANSAS CITY · HOUSTON · TULSA · BOSTON

Be Sure with Fluor

fc SINCE 1890

PRODUCTS: *Cooling Equipment, Mufflers, Gas Cleaners, Pulsation Dampeners*
SERVICES: *Designers and Constructors of Refinery, Chemical and Natural Gas Processing Units*

Tests Prove It! It pays



Stress analysis of new valve design in which the three major stresses encountered in service are duplicated and measured.

1. Application of bending load simulating pipe line stresses.
2. Application of load resulting from seating valve
3. Application of internal line pressure to valve.
4. Measurement of resulting strains with SR-4 strain

to specify *Edward* STEEL VALVES

New Edward Designs Reduce Pressure Loss, Give Up to 30 Per Cent More Flow, Cut Wear-Producing Turbulence, Assure Maximum Strength

TRIAL AND ERROR is one way to develop valve designs—the old way—slow, inaccurate, uncertain.

THERE'S A BETTER WAY: The Edward pre-test procedure—an orderly, step-by-step, fact-to-fact progress that eliminates guesses and approximations.

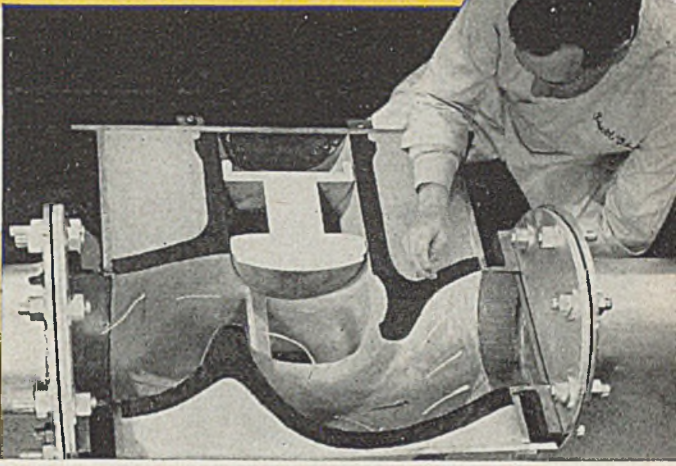
IT STARTS with building a valve cross-section using modeling plastics, testing it, changing it, testing again and again until internal contours as near perfect as possible for free flow are developed.

FROM THAT perfected model are made plaster casts of the flow passages, cross-section templates, patterns, and finally steel castings. Actual tests then prove the valve's flow rate and capacity, its freedom from excessive and erosive turbulence. A completely different set of tests prove the valve's structural soundness, its resistance to every strain, its shaping to compensate for distortions of high pressure, high temperature operation.

TO ESTABLISH this procedure Edward developed a whole new range of test equipment, much of it not duplicated anywhere. But it was worth it, for the results are definite and measurable. Typical are these

SPECIFIC ADVANTAGES

- Up to 30 per cent more flow (*more volume where you need it*).
- Less pressure loss (*smaller piping and valves often possible*).
- Less wear on vital parts (*sharp turns which cause wear-inducing turbulence are eliminated*).
- Safety (*engineered to proved safety factor*).
- Tighter (*built to compensate for distortions of operation*).
- Easier to operate (*because of Edward patented Impactor handwheel and EVal-thrust yoke bushing*).



Tiny streamers in test half-section model of new Edward globe valve show actual flow conditions. Test is one of many to guide Edward design engineers.

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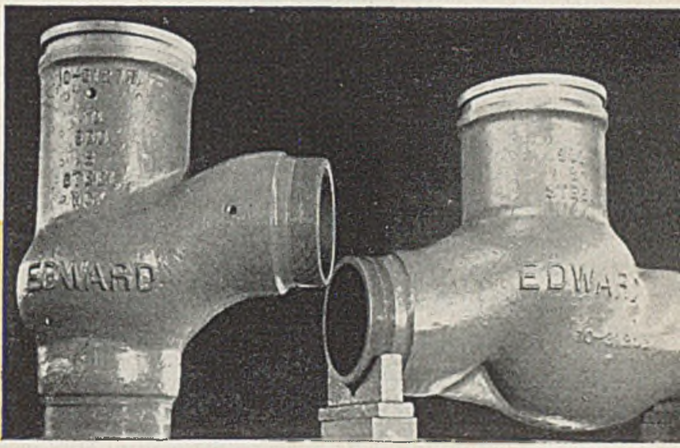

Body castings for new welding end Edward pressure-sealed valves. Wall shapes and internal contours are the results of years of original flow research. End threads are for shop testing.

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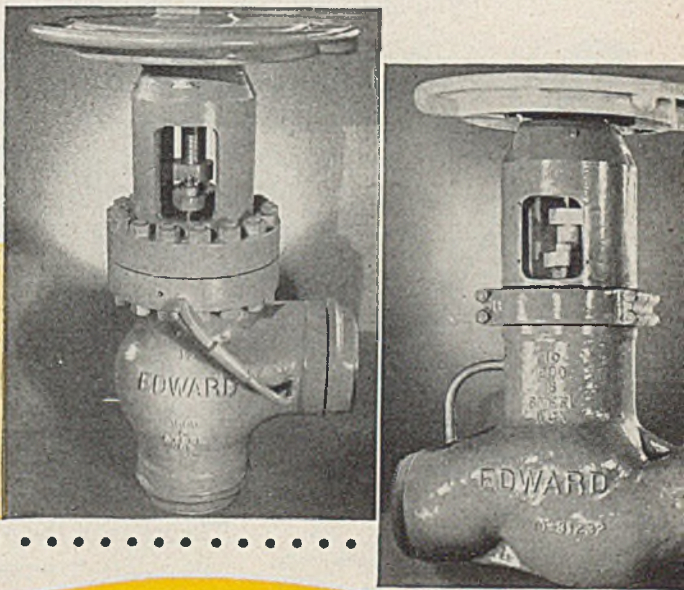


Two of the newer Edward valve designs. Left, 12 in. 1500 lb flanged bonnet angle; right, 10 in. 900 lb pressure sealed globe. Both have patented Impactor handwheel and Edward Equalizer.

• •

Edward Valves, Inc.

SUBSIDIARY OF ROCKWELL MANUFACTURING CO.
EAST CHICAGO, INDIANA

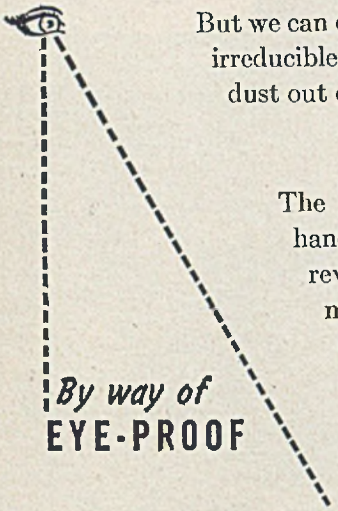
INDUSTRY PAYS an incalculable bill each year for its inability to garner all its dust. What is your individual share of that tab? How much money, in the form of real pay dust, are you blowing away? Does your present dust-collection system approach 100 per cent recovery? Even if it is as high as 99.5 per cent, what does the remaining 0.5 per cent mean in loss to you? Only 100 lb. a day means approximately 15 tons a year.

The MIKRO-COLLECTOR
will be on display at the
Exposition of Chemical Industries,
Grand Central Palace, New York City
Dec. 1-6
Booth 300-302 Mezzanine Floor

You alone can provide the answers.

But we can offer a suggestion as to how to reduce your losses to the irreducible minimum: The **MIKRO-COLLECTOR** will keep your dust out of the air and your

Profits in the Bag.



1—A freshly laundered white handkerchief, held over the exhaust during the filtration of finely ground colored pigment, shows no discoloration.

2—After days of such operation, the outer surface of the cylindrical, felt filter bag remains as clean as when first installed.

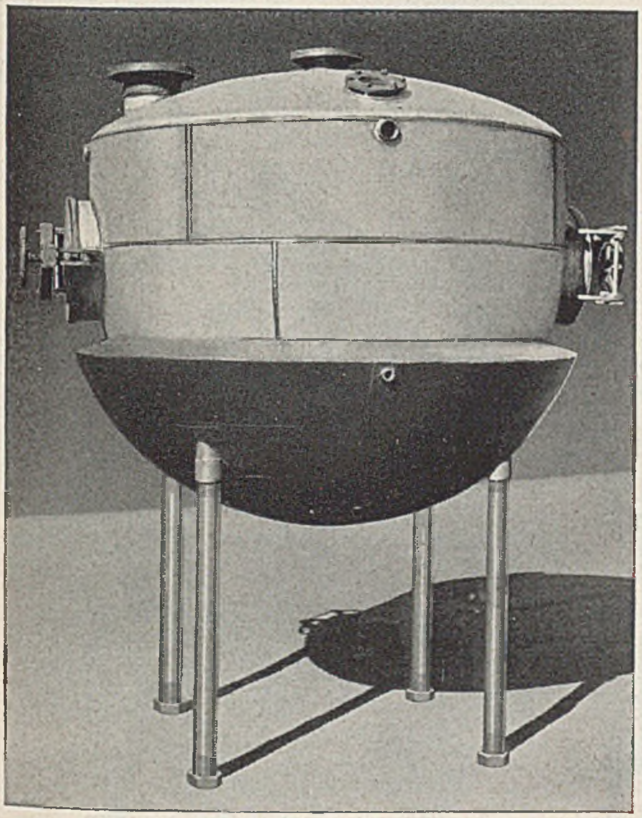
The **MIKRO-COLLECTOR** with its phenomenal ability to handle even those damp and hitherto baffling dust loads . . . its revolutionary principles, which assure a perpetually clean filter, marking the first radical change in the art of dust-collection in a quarter century . . . supplements our line of MIKRO-PULVERIZERS and MIKRO-ATOMIZERS in use throughout the world. But it performs with equal efficiency as an auxiliary to any type of grinding machinery, or in general air-clarification.

The value of the **MIKRO-COLLECTOR** in dollar-and-cents . . . its ability to amortize its cost quickly . . . lies in its 99.99 per cent minimum recovery of most solids even in the low micron ranges.

When you want COMPLETE recovery . . . whether of dry dust or dust containing a considerable percentage of water or oil. . . . it will pay you to investigate the performance of this equipment. Write for your copy of the **MIKRO-COLLECTOR** Bulletin.

PULVERIZING MACHINERY COMPANY
40 Chatham Rd., Summit, N. J.

Could YOU Use This Still?



Very likely not. But in your own business—in this day of extensive research and continuous, rapid development—the day is sure to come when you will need vessels or other processing units every bit as specialized or unconventional.

★ ★ ★

When your work in applied chemistry does result in new products, methods or processes calling for unusual equipment or materials, then you will be glad to know about Emerson-Scheuring. For, in our quarter-century of welding and fabricating corrosion-resistant metals, a large part of our job has been the production of special equipment for unusual processing purposes.

As a result, we have built up a highly skilled and resourceful organization of craftsmen who accept uncommon and intricate problems as routine. And to back up this expert staff, we have assembled manufacturing, welding, forming and machining equipment to permit all production operations to be completed under our direct control—within our own plant.

So, when you have need for special equipment to do a specialized job, keep Emerson-Scheuring in mind. We are equipped to work directly from your own specifications, or our engineering department is prepared to work with you in developing complete specifications, as it has with many leading companies in the pharmaceutical and allied processing fields.

EMERSON-SCHEURING TANK & MANUFACTURING CO., INC.
2077 Martindale Avenue • Indianapolis 7, Indiana

At Left: Stainless steel still, 72″ I.D., fabricated from Type 304 material. Two 16″ side-entering manholes. No. 4 finish inside. Hemispherical bottom, jacketed and insulated. Standard flanged and dished top head. Jacket pressure—35 lbs.; internal pressure—vacuum.

Emerson-Scheuring

FABRICATORS OF PROCESSING AND SPECIAL EQUIPMENT IN STAINLESS STEEL, HASTELLOY, PURE NICKEL, ALUMINUM, MONEL AND OTHER ALLOYS.

POWELL VALVES for the Chemical all your

For more than a century Powell has been meeting every new demand for industrial flow control equipment as it has arisen.

More than twenty years ago Powell foresaw the vast growth and diversification that was to come in the chemical and process industries. Acting on this foresight, Powell established its Special Design and Alloy Valve Division and started to build a complete line of valves to handle every known kind of corrosive media. And for many years thereafter, Powell was the *only* manufacturer of corrosion-resistant valves.

Now the Powell Line of Corrison-Resistant Valves, including many special designs, is available in the widest range of pure metals and alloys ever used in making valves. This line, together with Bronze, Iron, and Cast Steel Valves of every required type, design, size and pressure, makes Powell today *the ONLY manufacturer offering a COMPLETE line of valves for the Chemical and Process Industries.*

The Wm. Powell Co., Cincinnati 22, Ohio

DISTRIBUTORS AND STOCKS IN ALL PRINCIPAL CITIES

SEE OUR EXHIBIT
BOOTH 54
21st Exposition of Chemical Industries
Grand Central Palace, New York City
December 1 to 6, 1947

Fig. 2327 — Stainless Steel Angle Relief Valve with enclosed spring.

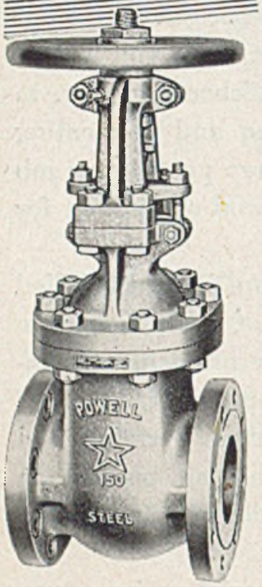


Fig. 1503—Class 150-pound Cast Steel O. S. & Y. Gate Valve with flanged ends.

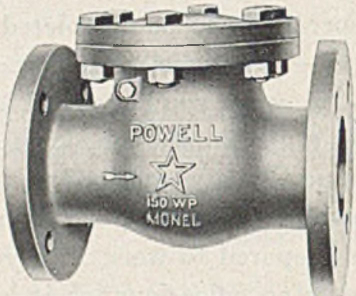


Fig. 2433—All Monel Metal* Swing Check Valve for 150 pounds W. P.

Fig. 2051 S. W.—Stainless Steel 150-pound O. S. & Y. "Y" Valve with Powell Patented Seat Wiper.

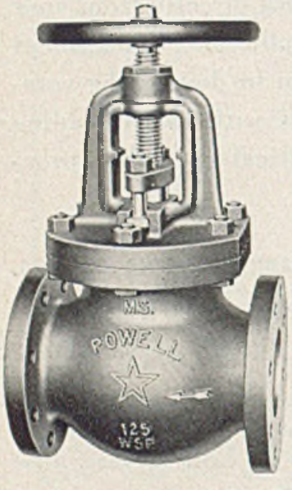


Fig. 241—125-pound Iron Body Bronze Mounted O. S. & Y. Globe Valve. Also available in All Iron.

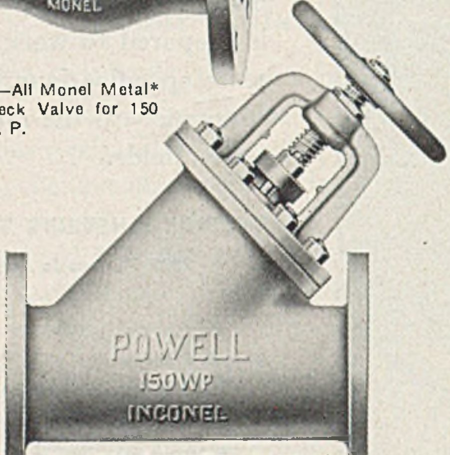


Fig. 1944—Large Size 150-pound Inconel* O. S. & Y. "Y" Valve. Made in sizes 2½" to 12", incl.

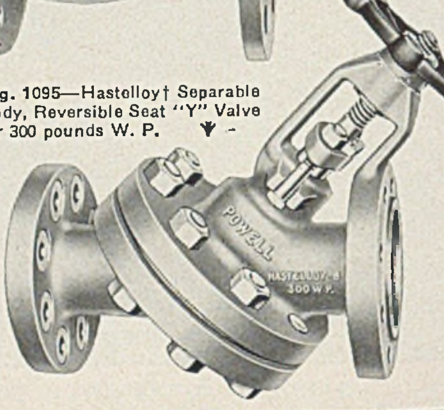


Fig. 1095—Hastelloy† Separable Body, Reversible Seat "Y" Valve for 300 pounds W. P.

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Fig. 2097—Stainless Steel Glass Sight Feed or Look Box. Pipe sizes, ½" to 6".

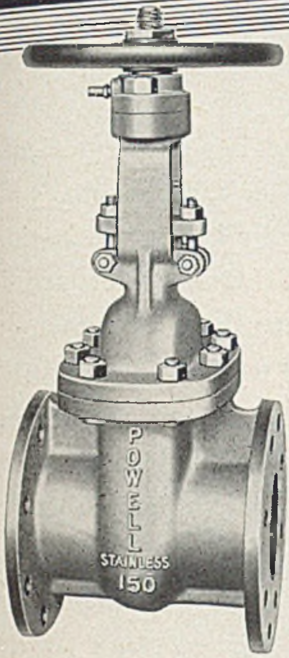


Fig. 2453-G—New, standard 150-pound Stainless Steel Gate Valve with outside screw rising stem, bolted flanged yoke-bonnet and taper wedge solid disc.

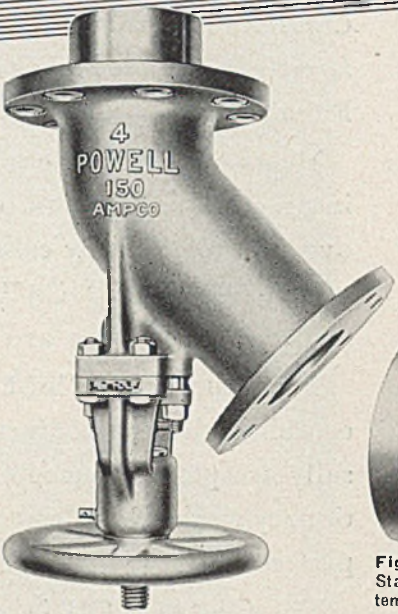


Fig. 2309 — 150-pound Ampco Flush Bottom Tank Valve for attaching to metal tanks and autoclaves.

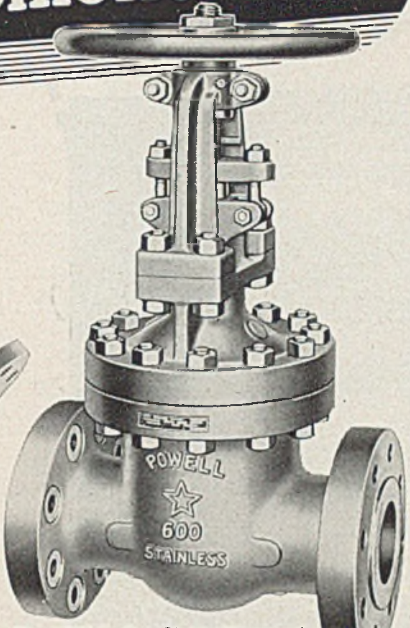


Fig. 6003 S. S.—Class 600-pound Stainless Steel, high-pressure—high temperature, O. S. & Y. Gate Valve.

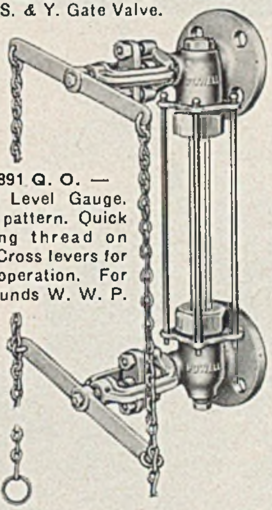


Fig. 1891 Q. O. — Liquid Level Gauge. Offset pattern. Quick opening thread on stem. Cross levers for chain operation. For 150 pounds W. W. P.

▲ **Fig. 375**—200-pound Bronze Gate Valve with union bonnet, inside screw rising stem and renewable, wear resisting "Powellium" nickel-bronze disc.

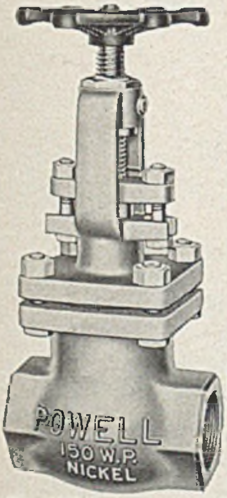


Fig. 1968 — 150-pound Nickel Gate Valve with screwed ends, outside screw rising stem, bolted flanged yoke-bonnet and taper wedge solid disc.

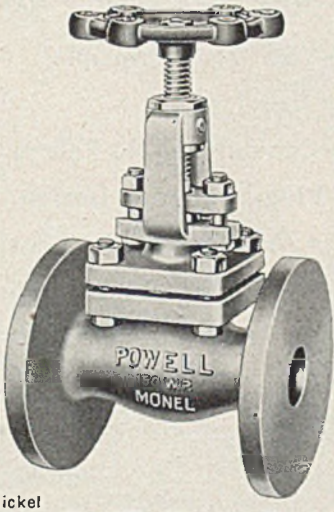
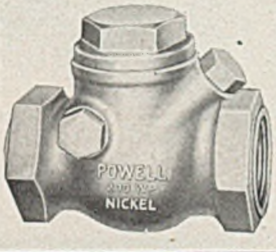


Fig. 1979—150-pound Monel Metal* Globe Valve. Flanged ends, bolted flanged yoke-bonnet and outside screw stem.

Fig. 1845—200-pound Nickel Swing Check Valve. Screwed-in cap and regrindable, renewable disc. ➔



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25% Cr. 12% Ni.

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Monel Metal*
Inconel*
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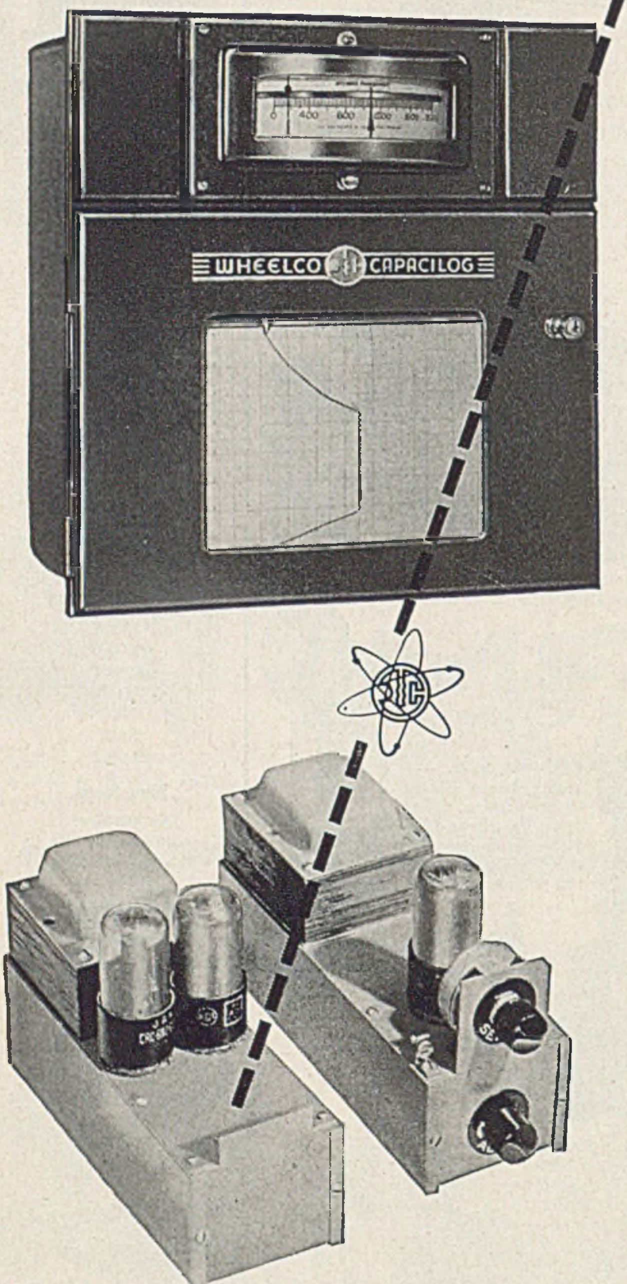
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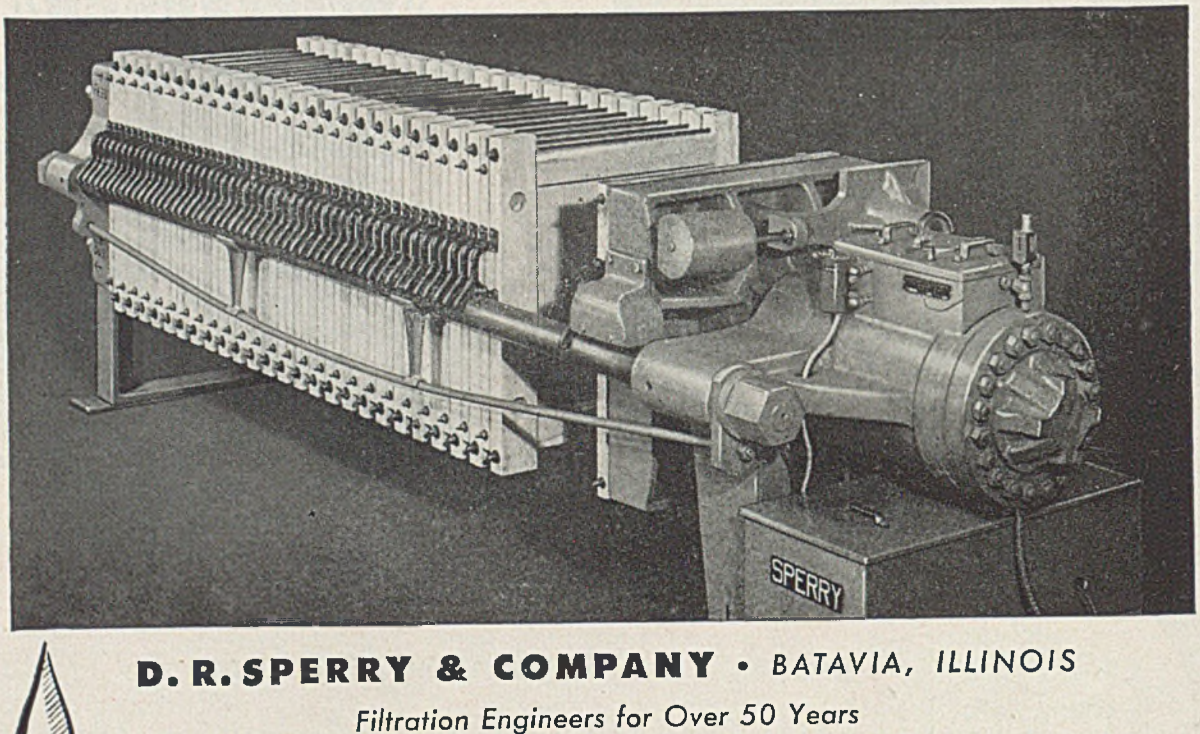
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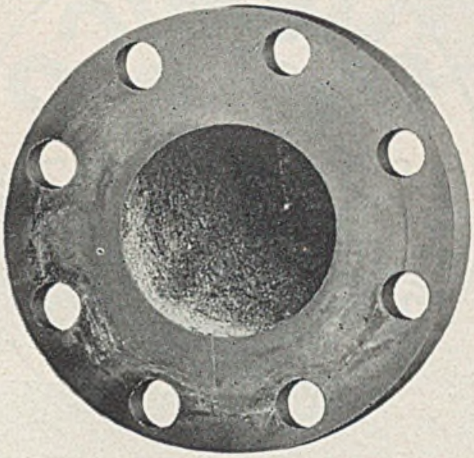

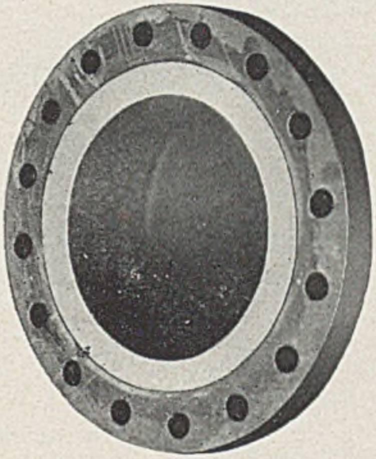

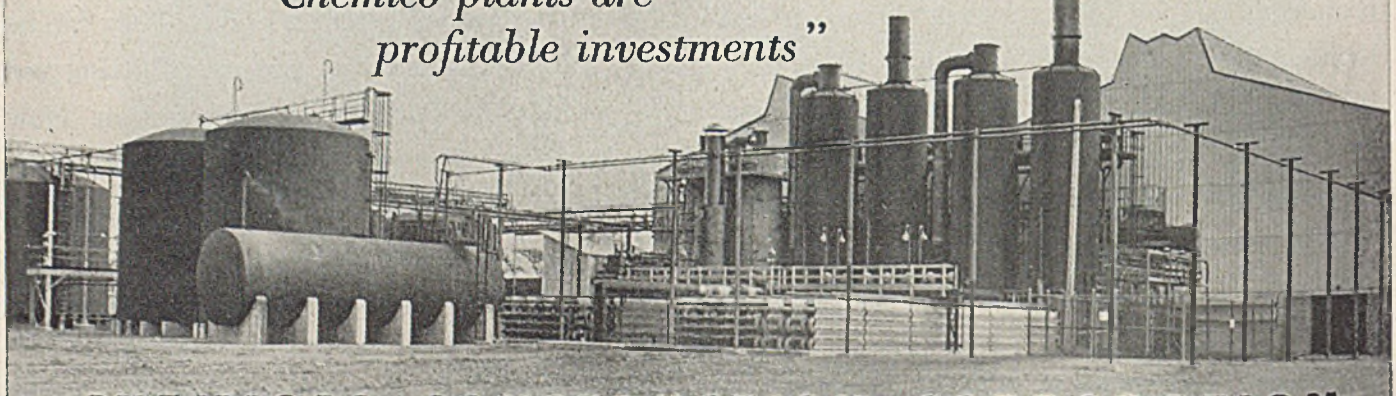

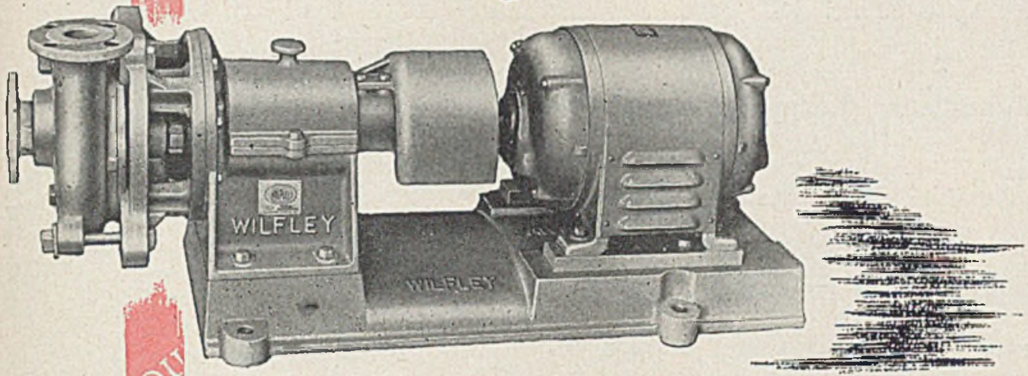
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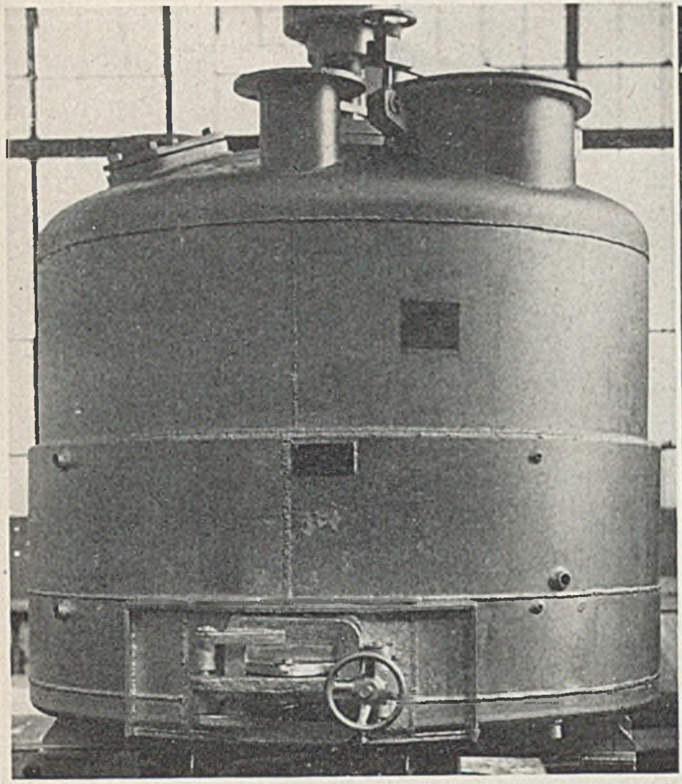

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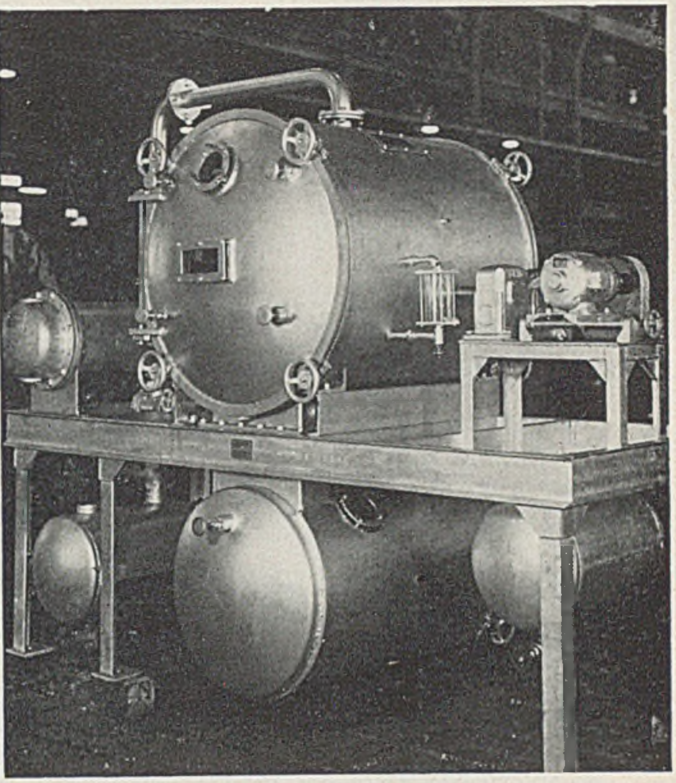

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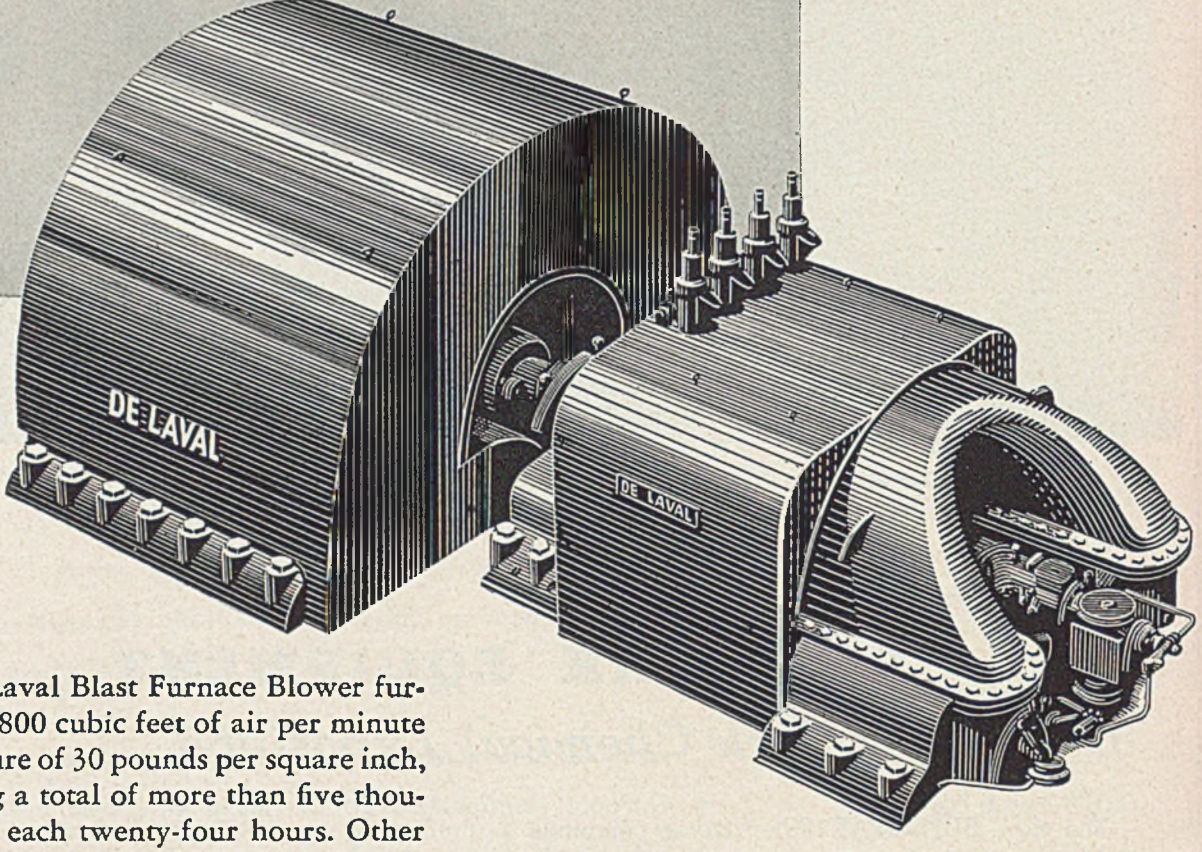
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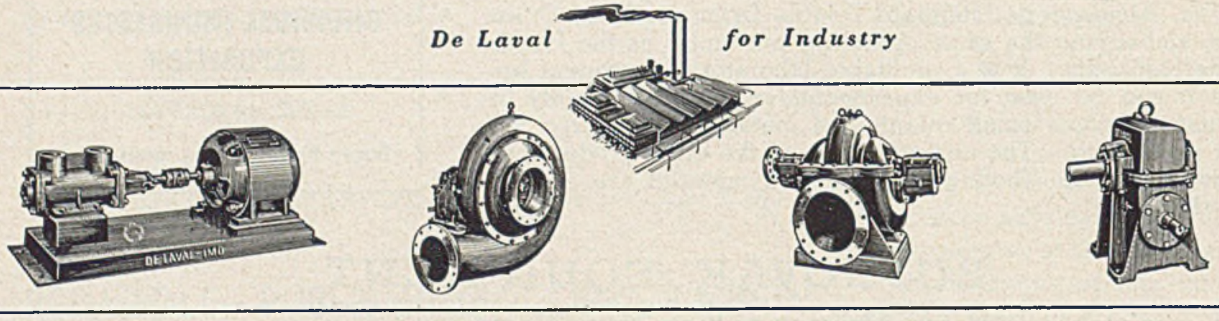
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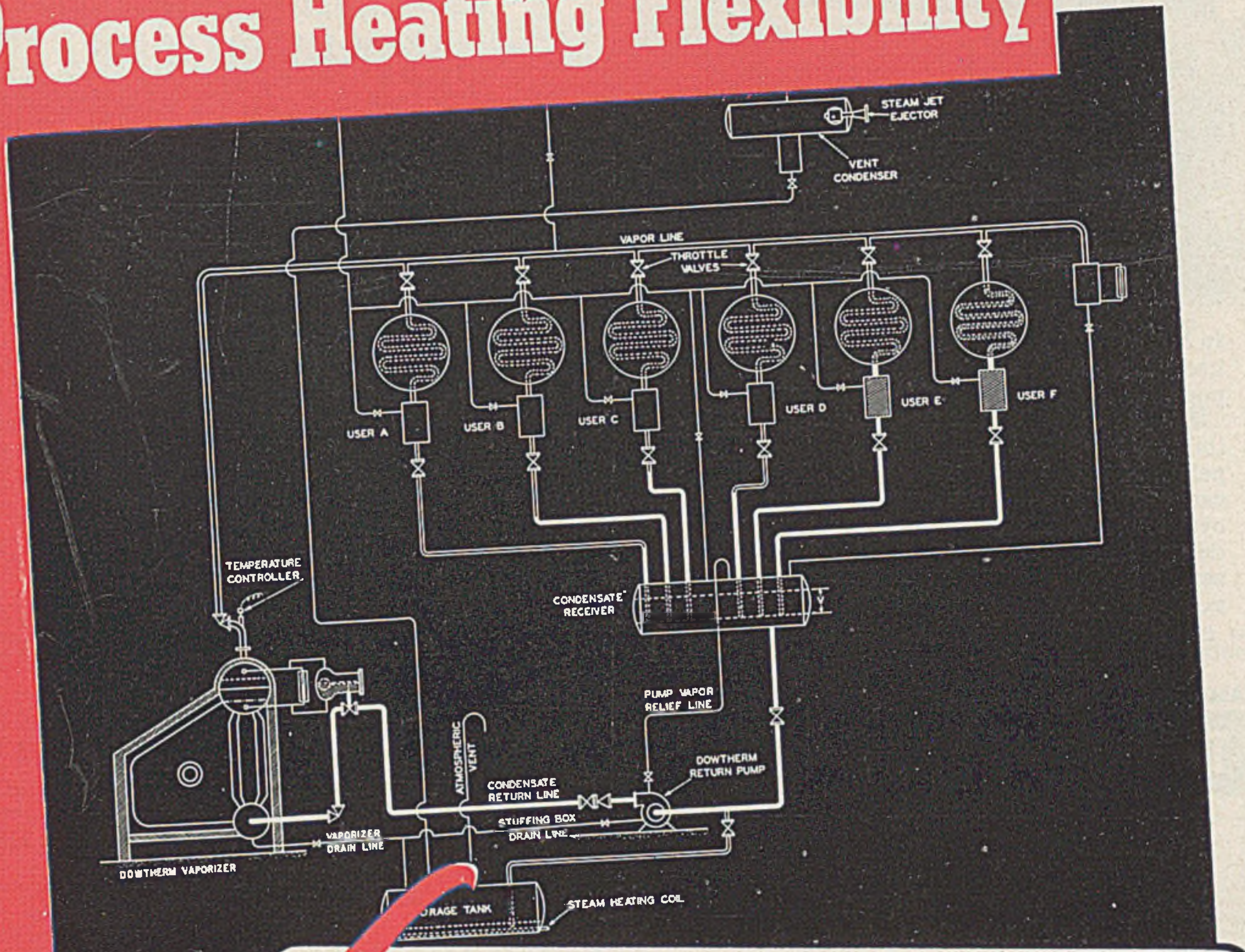
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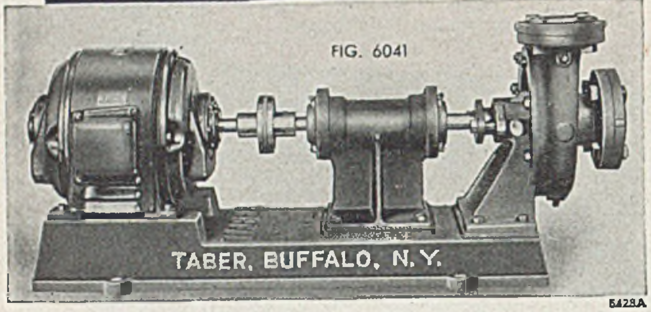
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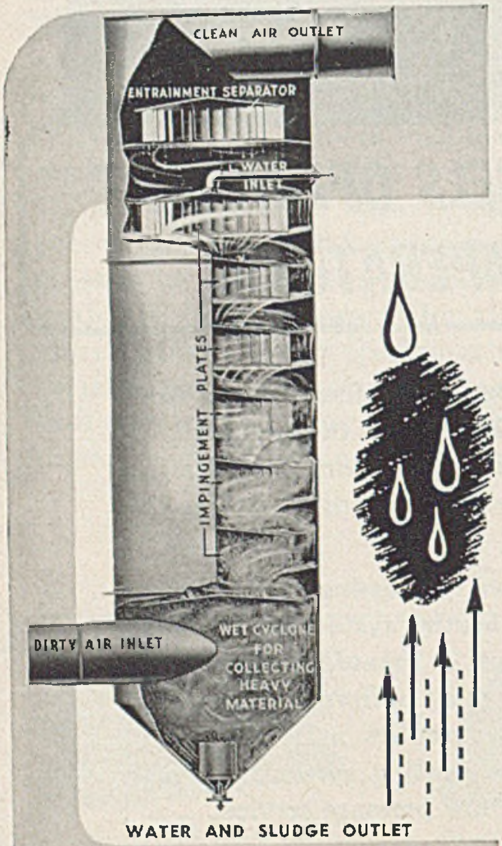
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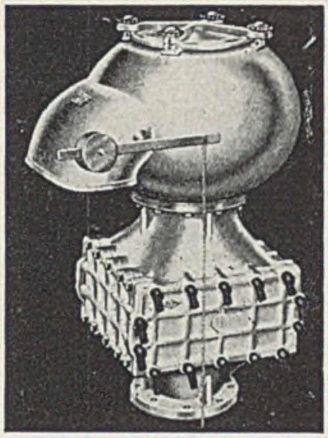

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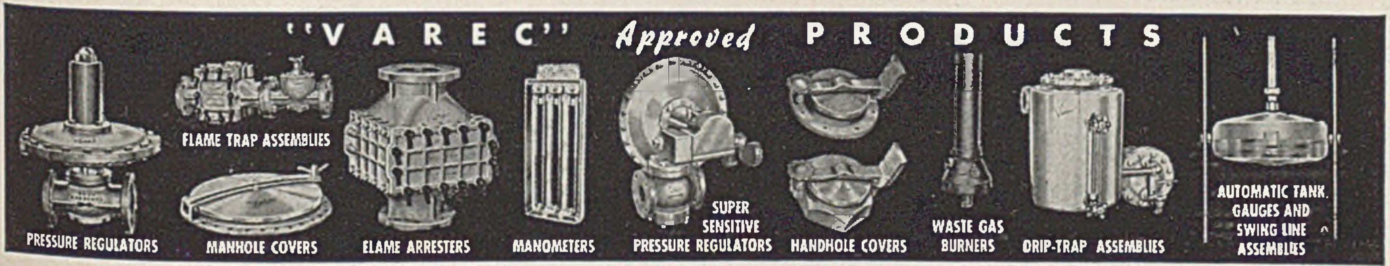

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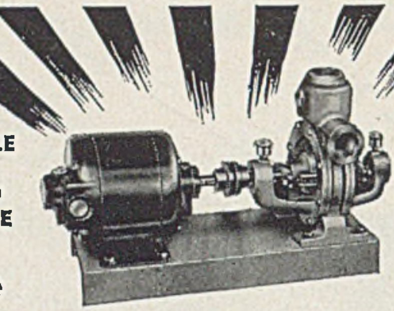

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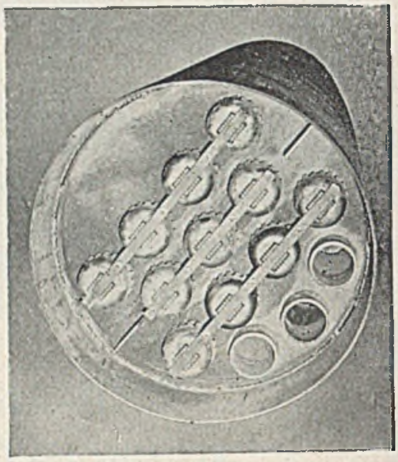

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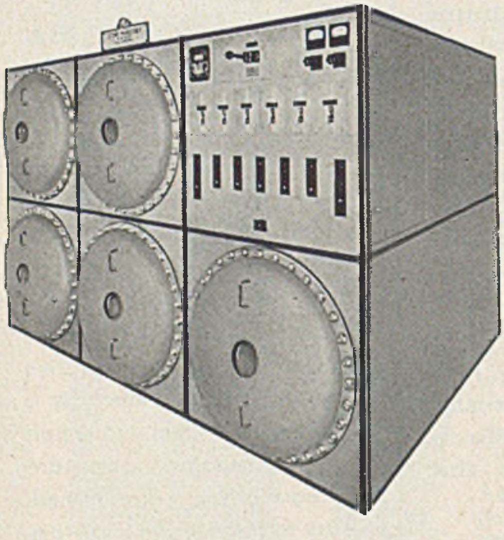

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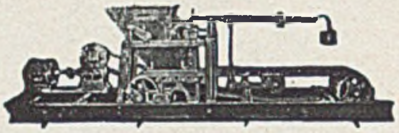

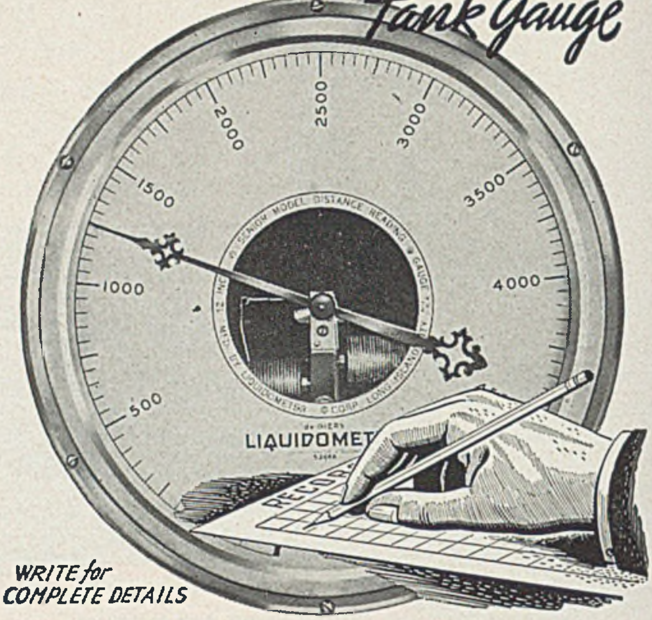
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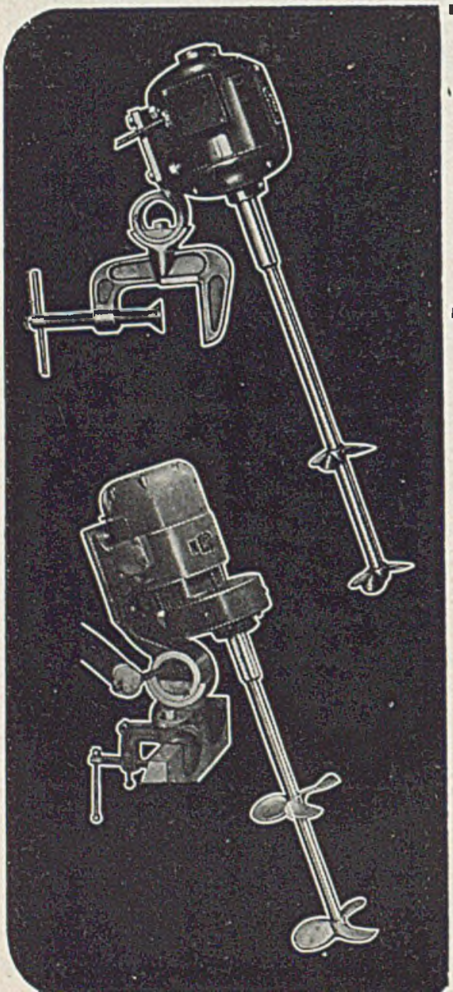

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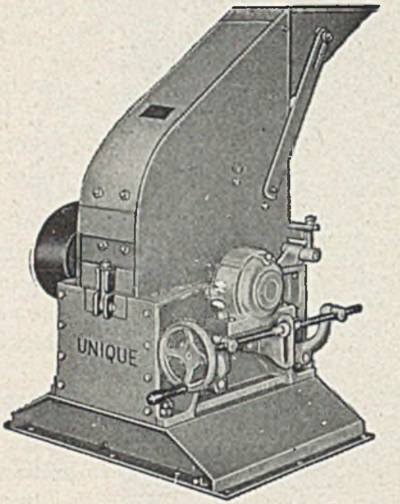
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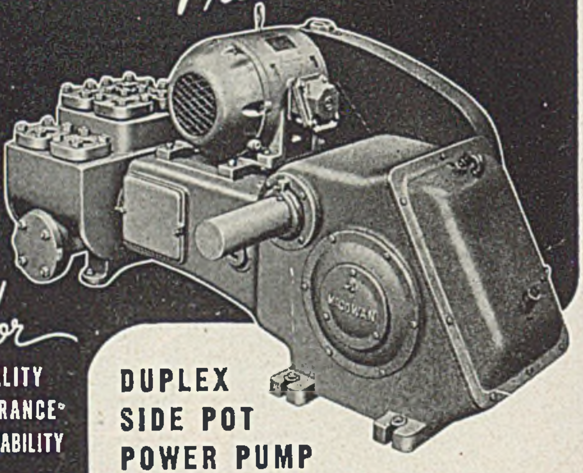
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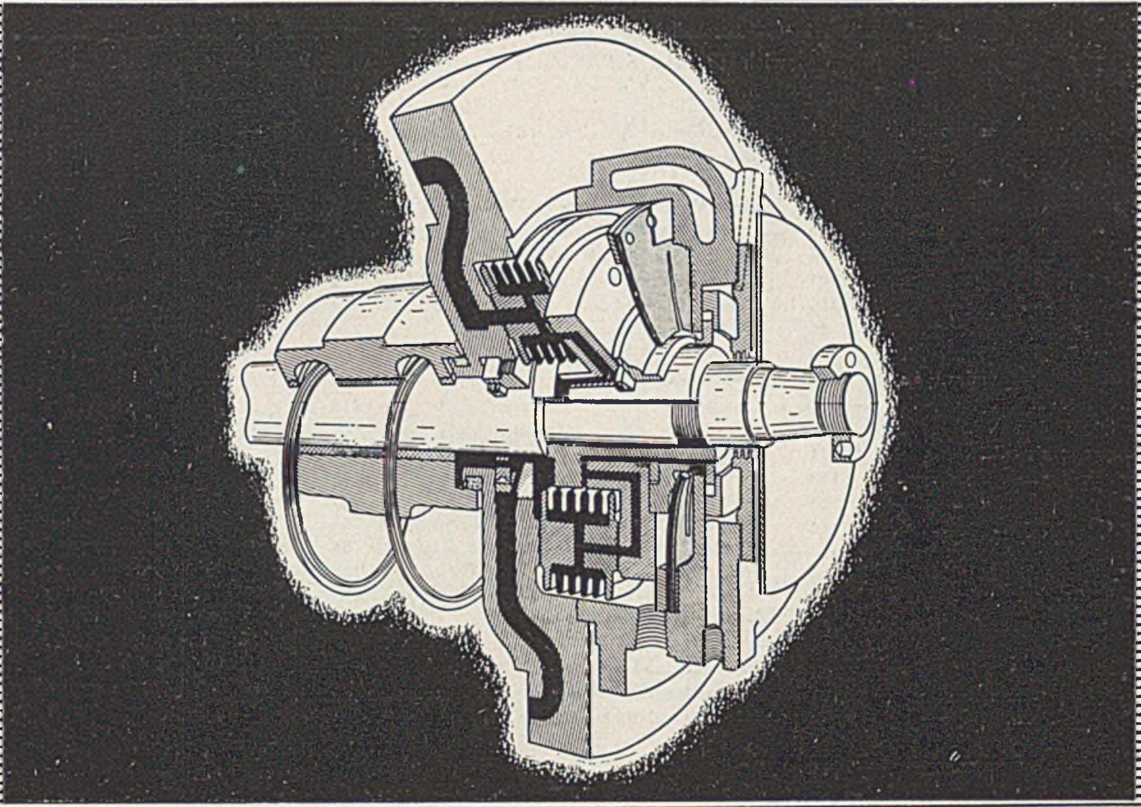

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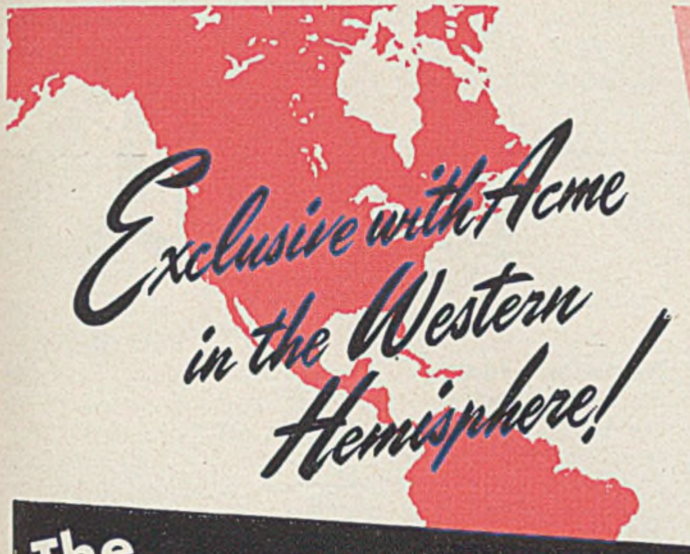

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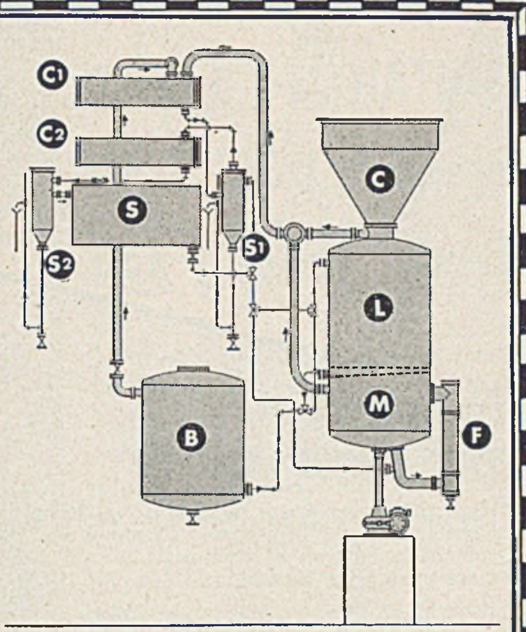
6. Merz plants permit the individual treatment of all kinds of oils, seeds and residues at a definite temperature and allow the use of all kinds of solvents, whether inflammable or non-inflammable, and either hot, cold, or in vapor form.

** Equally important advantages exist in other applications of the Merz process. Write for complete details regarding Merz plants and their advantages for your own material.*



LAYOUT OF A TYPICAL MERZ PLANT FOR THE RECOVERY OF VEGETABLE OILS
Illustrating just one application for Solvent Extraction

DESCRIPTION OF PROCESS: Crushed seed is charged into Extractor **L** from Hopper **C**; solvent from Tank **S**, and weak solution from the preceding charge stored in Miscella Tank **B** are fed into the Extractor **L** where it quickly dissolves the oil. This solution passes through a specially designed filter bottom to Chamber **M**, separated from Extractor **L** by an intermediate division bottom, and connected with Calandria Heater **F**. Circulating rapidly, the evaporation of the solvent commences at once. While the concentrated solution passes back to **M**, and is there mixed with fresh solution coming from **L**, the solvent vapors rise to the Condensers **C-1**, and **C-2**. There the solvent is recovered according to requirement, either hot (Water Separator **S-1**), or cold (Water Separator **S-2**), and returned to Extractor **L** until a test indicates that practically no oil remains in the seed. The weak solution in **L** is then usually collected in **B** and used again in the following charge. Any solvent remaining in the seed residues, as well as in the oil, is driven off by live steam, accelerated by the use of suitably designed mechanical stirring gear, which also aids in discharging the residue.

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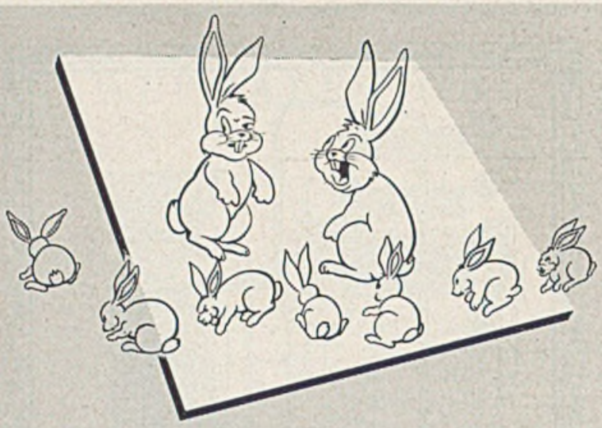


Sidelights and TRENDS

November 1947. Tin production in Malaya and the Netherlands East Indies is increasing. In the second quarter of this year Malaya turned out 8217 tons, 3603 tons or almost 44% more than in the first quarter. In June 370 mines were operating, compared to 295 in April. Production in the East Indies this year is expected to total 21,000 tons, compared to 8747 in 1946. (*World Report*, p. 1, Oct. 14, 1947)

■ The wool-combing industry in Bradford, Yorkshire, England, causes a sewage problem of considerable magnitude; the sewage contains an average of 640 parts per million of highly emulsified grease, despite the fact that some wool combers themselves recover part of the wool grease from their effluents. Successful treatment now utilizes sulfuric acid to precipitate the bulk of the fatty and waxy matter prior to biological filtration. (*Chemical Trade Journal*, p. 321, Sept. 26, 1947)

■ French blast furnaces now are smelting 385,000 tons of iron a month, 77% of the 1938 rate. In operation are 66 blast furnaces, compared to 86 before the war and 9 at the time the Germans were driven out. (*World Report*, p. 1, Sept. 30, 1947)

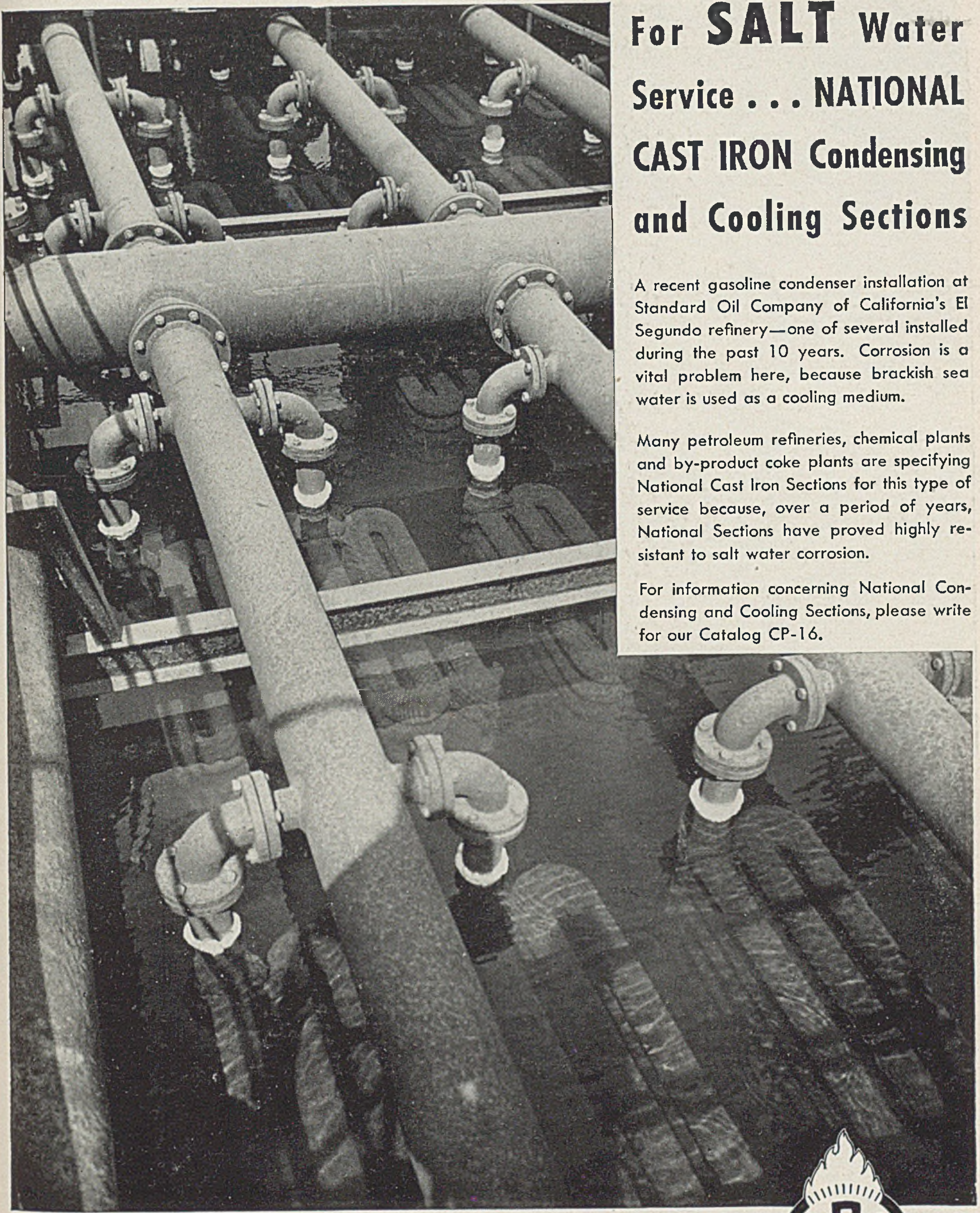
■ GR-S produced by coagulation of highly diluted latex with dilute alum solution has been found to be approximately equivalent to deproteinized natural rubber in moisture absorption. By using fresh coagulum constantly, without recirculation of serum, the amount of water-soluble ingredients occluded in the polymer can be kept at a minimum. (*India Rubber World*, p. 781, Sept. 1947)

■ A predigested form of vitamin A has been developed. Children suffering from cystic fibrosis of the pancreas, who cannot digest the common ester form of vitamin A, often contract pneumonia as a result of the lung injury caused by the vitamin deficiency. The predigested alcohol form is easily absorbed into the blood. (*Drug and Allied Industries*, p. 14, Sept. 1947)

■ Approximately 73% of the mineral output of Tunisia is exported. Total mineral exports in 1946 were three times as large as in 1945. Shipments of phosphates, slightly higher than in 1938, amounted to 1,645,000 metric tons. (*Foreign Commerce Weekly*, p. 13, Sept. 20, 1947)

■ United States and Canadian Governments have reached an agreement to exchange electric power by means of a high voltage connection between lines of the Bonneville Power Administration and the British Columbia Electric Railway Company. The new connection will send unused off-peak Canadian surpluses to the Pacific Northwest when a power shortage is forecast for Oregon and Washington, and hitherto unused power generated during night hours and week ends at Grand Coolee and Bonneville will be utilized in the Canadian company's system. (*Business Week*, p. 36, Sept. 13, 1947)

Don't overlook the Industrial Data department, a new monthly feature. It appears on page 121 A of this issue.



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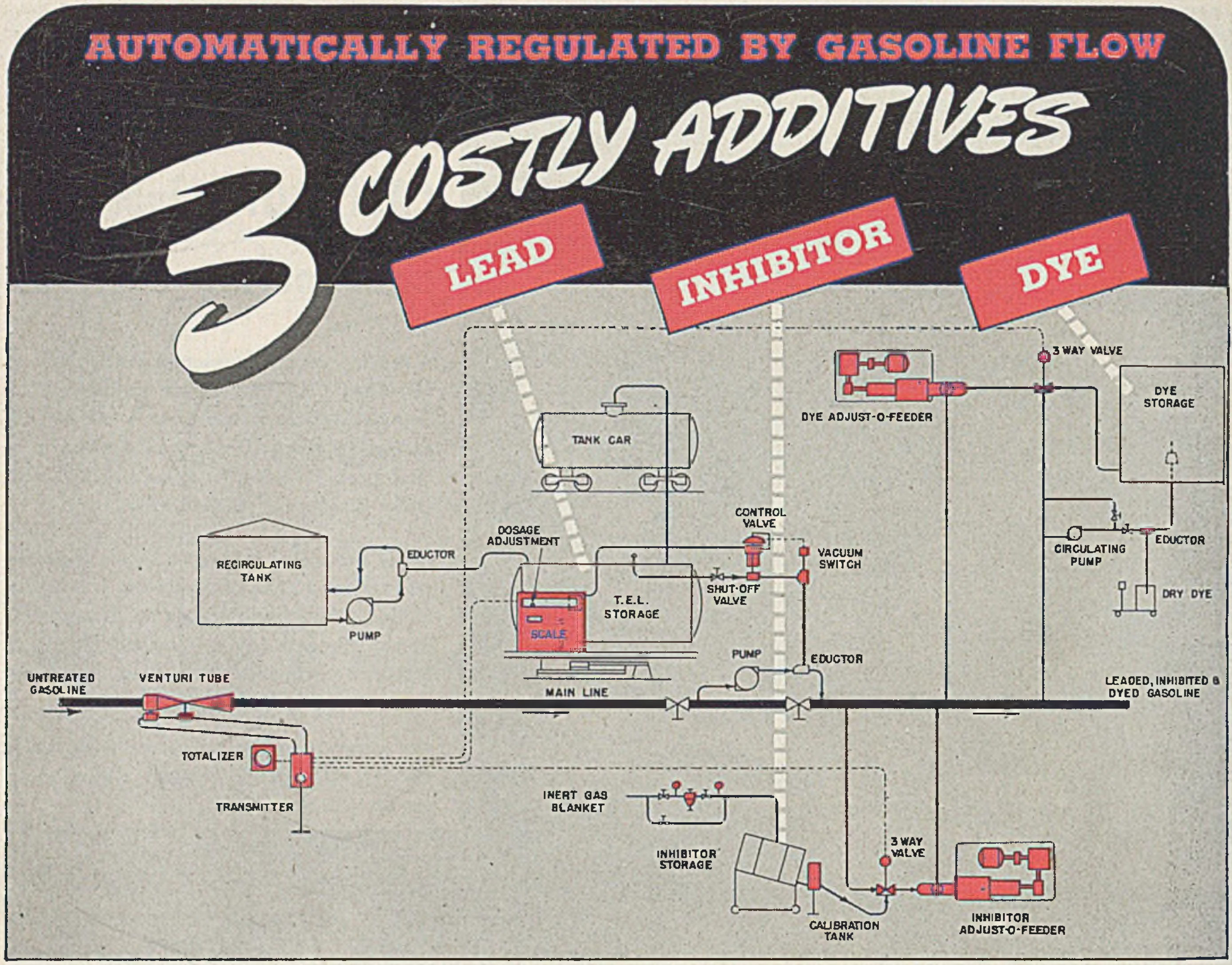

This schematic flowgram illustrates %Proportioneers% Treet-O-Control method of regulating lead, inhibitor and dye injection to a flowing stream of gasoline from a low loss Venturi differential producer.

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