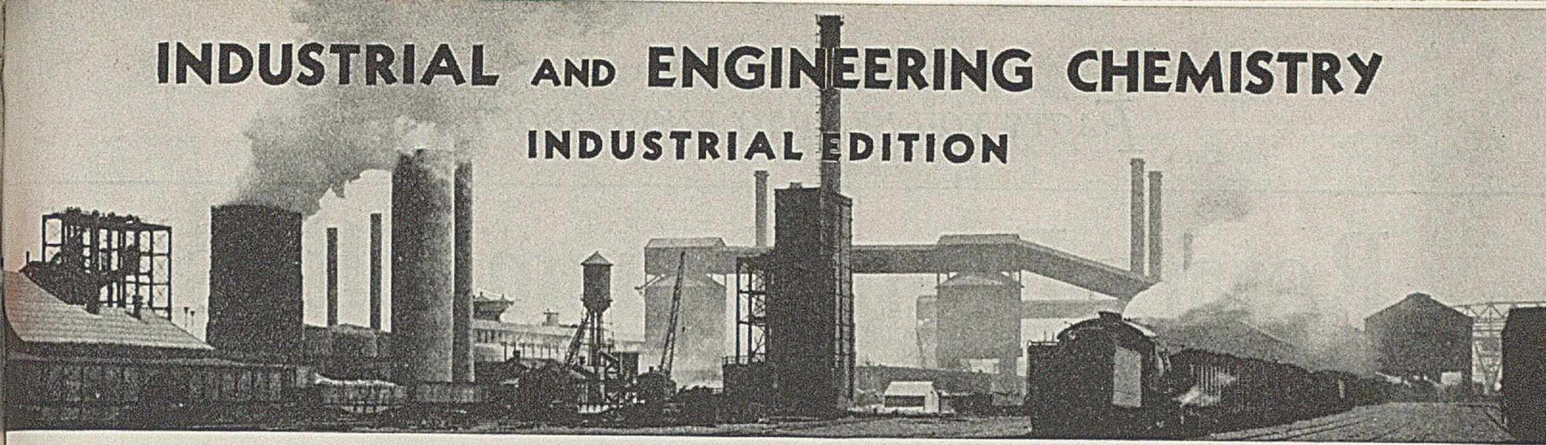
INDUSTRIAL AND ENGINEERING CHEMISTRY

INDUSTRIAL EDITION



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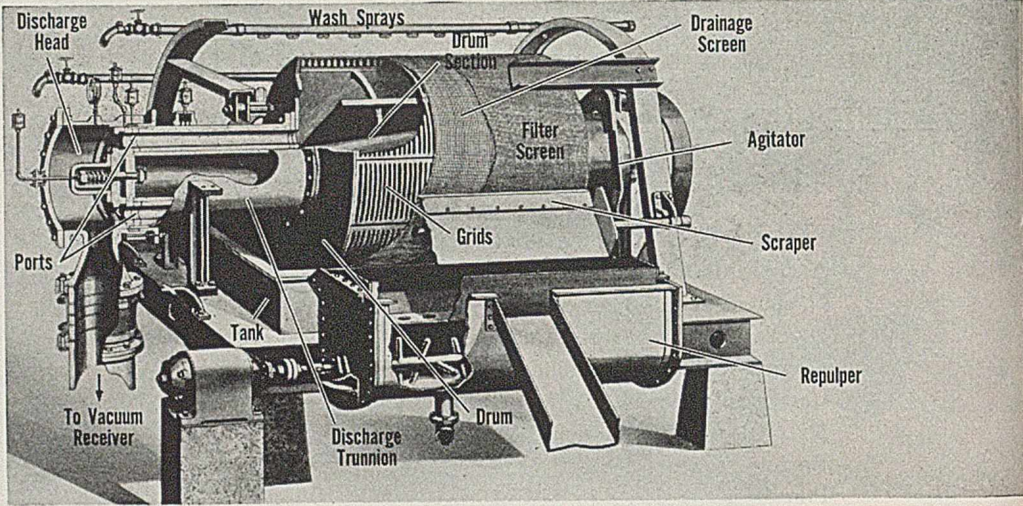
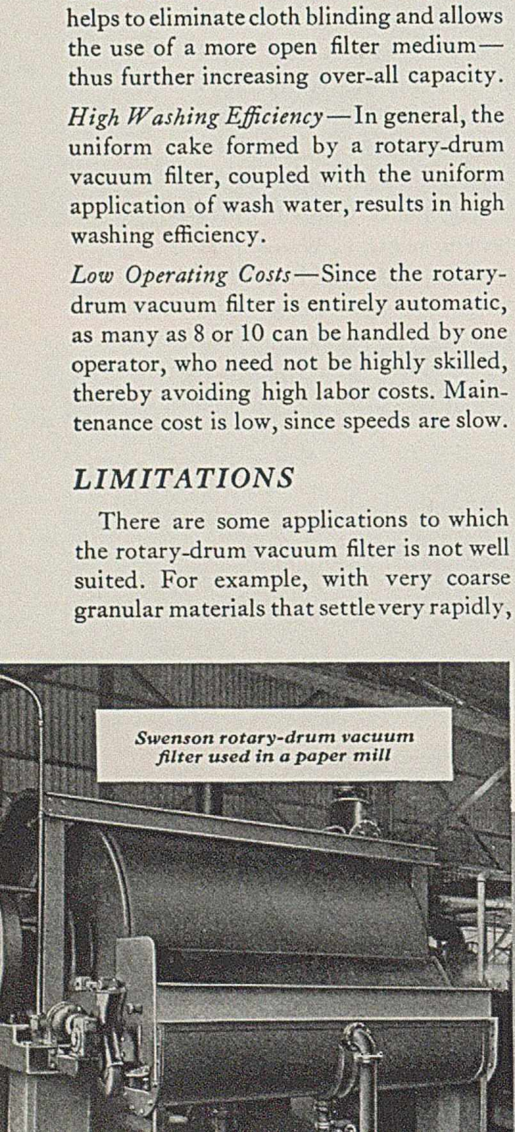
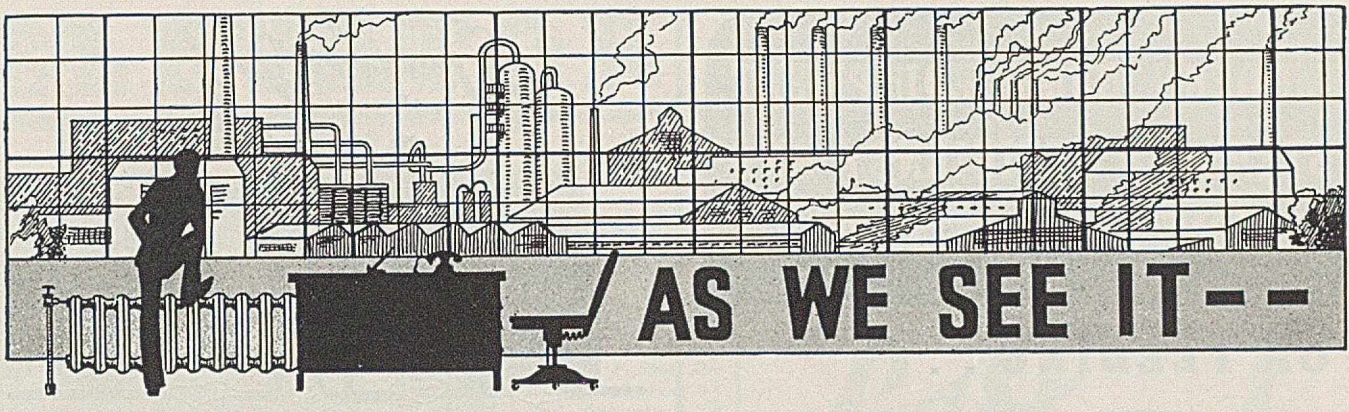

Discharge Head
Wash Sprays
Drum Section
Drainage Screen
Filter Screen
Agitator
Ports
Grids
Scraper
Tank
Repulper
To Vacuum Receiver
Drum
Discharge Trunnion





- **Textile** beginnings go back beyond written records, but in spite of the hoary age of these materials, new developments now follow one another in rapid succession. A symposium of eight papers describes the newest things in this field and suggests directions of future progress.

- **Resins** modify familiar fibers and impart new and valuable properties to them. Powers (page 1543) differentiates impregnations from coatings, and describes methods and results of the new technique.

- **Electrical Fields** orient cut fibers to form pile fabrics of qualities superior to those made by older methods, according to Oglesby and Hoogstoel (page 1552), who describe the application of this force in a new field.

- **Cellulose Acetate Rayons** can be produced in many variations to meet the demands of fashion. Smith (page 1555) discusses this fiber, its properties, and uses.

- **Protein Fiber** is soon to be produced in this country from soybeans on a substantial pilot-plant scale, according to Boyer (page 1549). Properties of this fiber and its preparation, now of enhanced interest, are given in some detail.

- **Vinyon Fibers** are totally synthetic, since they are produced from raw materials of low molecular weight. Their preparation, properties, and principal uses are described by Bonnet (page 1564).

- **Nylon**, synthetic proteinlike polymer, forms extremely useful silklike fibers. Hoff (page 1560) goes into some detail regarding their unique properties and how these are produced in the manufacturing and processing operations.

- **Fiberglas**, the synthetic inorganic textile fiber, is finding important applications both as woven fabric and as loose fibers. Slayter (page 1568) suggests the limitations of the new fiber as well as its valuable uses.

- **"Prolon"** is suggested by Atwood (page 1547) as a preferred name for fibers spun from casein to differentiate them from other manufactured fibers. Their preparation and principal characteristics are given, as well as some idea of their importance abroad.

- **Corrosion** of iron and steel is inhibited by threshold treatment of water with hexametaphosphate, according to Hatch and Rice (page 1572). This effect, which is demonstrated by experiments, is in addition to the action of the same compound in preventing precipitation of scale in hard waters.

- **Filter Efficiencies** depend upon the media used, and choice of these is frequently limited by conditions inherent in the problem. New and improved media to meet increasingly diverse requirements are described by Van Antwerpen (page 1580).

- **Foaming** is important in many industrial operations, as either desired or objectionable. Clark and Ross (page 1594) present a method of measuring and evaluating this characteristic of liquids.

- **Coals** of various types possess different wetting characteristics inherent in their surfaces, and these are important in many operations. Brady and Gauger (page 1599) show how to express this characteristic numerically.

- **Coals**, both natural and artificially produced, have been subjected to solvent extraction by Berl and Koerber (page 1605) as a method of learning more of their constitutions.

- **Neutral Oils** produced by hydrogenation of coal can be characterized by their behavior with sulfuric acid, according to Eisner, Fein, and Fisher (page 1614), who suggest a rapid method of examination using this reagent.

- **Aerogels** are often, but not always, more efficient as catalysts than other forms of the same compounds, Kearby and Swann (page 1607) have found. Reported results deal with dehydrations and decarboxylations.

- **Furfural** was examined by Dunlop and Peters (page 1639) to determine its stability in a refined state at different temperatures. They conclude that it is stable to heat within the range of its industrial applications.

- **Alfalfa Silages** prepared by the phosphoric acid and the molasses methods have been compared over a period of time by Johnson and his co-workers (page 1622). They find that both methods give good results in the dairy industry.

- **Glucose** can be fermented to yield 5- and 2-ketogluconic acids depending on the organism used, according to Stubbs and his co-workers (page 1626). The conditions of fermentation and the products are discussed.

- **Carbons** of high adsorptive capacity have been made by Musser and Engel (page 1636) from cottonseed hull bran. Preparation of the char from carbonized bran by treatment with superheated steam and the properties of the product are described.

- **Superphosphates** made by treating phosphate rock with sulfuric acid contain calcium sulfate. The degree of hydration of this compound, according to Marshall, Hendricks, and Hill (page 1631), determines its effect on the product.

- **Cellulose Derivatives** form, and will continue to form, a large proportion of our plastics in spite of the growing number and volume of synthetic resins available, Ott (page 1641) believes. Characteristics of various cellulose derivatives and their economic positions are reviewed.

- **Soybean Protein Plastic** has been found by Brother, McKinney, and Suttle (page 1648) to form a strong laminated product which is improved by outer protecting layers of other plastics having higher moisture resistance.

- **Writing Inks** contain Prussian blue less often than is commonly supposed, according to Casey (page 1584), who goes at some length into the subject and its bearing on the examination of questioned documents.

D H Killeffer

WHEN our next issue reaches us, the calendar for a new year will be on our desks. That is a fitting time to look forward by a glance over our shoulders at just what has happened in our world in 1940. At least we shall review data and events of recent months to establish points of departure into a new and untried year; and like any new experiment, that should be interesting and possibly exciting.

Risking a jinx, which might make the near year all wet, our review will be followed by a survey of surface-active (or wetting) agents brought up to date by the addition of products new since our previous survey of the field in 1939.

Furnace atmospheres, potent factors in metallurgical operations, get our next attention with a symposium on this important subject. Then we shall go in two quite different directions. The acid corrosion of steel is always an interesting topic, and on that we shall have more light. Activity coefficients of gases is a subject concerned only incidentally with the problems of metallurgy but nevertheless one on which interesting and useful information will be forthcoming.

Protective coatings require attention now as always. On this we shall learn more about drying oils and how changes in them are revealed by molecular distillation. The continuity of films is a highly practical problem, particularly as it relates to synthetic resin coatings now of growing importance in the industrial field.

Cellulose rather naturally continues that general subject. This time we shall learn about pectic acid in cotton fibers and about cellulose from hardwoods, which are far more practical matters than we might suspect before looking into them.

Lest we be accused of leaving out chemistry in the discussions of its applications, let us look next into the esters of the nitroalcohols, a new series of compounds of absorbing interest both chemically and industrially. From them, we may properly go to the system nitromethane-propanol-water, where physical chemistry joins organic. Then, too, there will be discussions of homologous series of alkanes of both straight and branched chains, and of reactions of allylic chlorides, now pressing for industrial attention.

Inorganic chemistry will also have attention with some interesting new bits of knowledge for our use. Caking of fertilizers, which makes them difficult to handle in the field, will be traced back to some of its causes, and suggestions will be unearthed for correcting this fault. A new form of zinc oxide from the calcination of zinc sulfite suggests itself as a heat-insulating agent. Color characteristics of cements will be examined, and the system sodium chloride–sodium nitrite–sodium nitrate, used in curing meat, will be investigated.

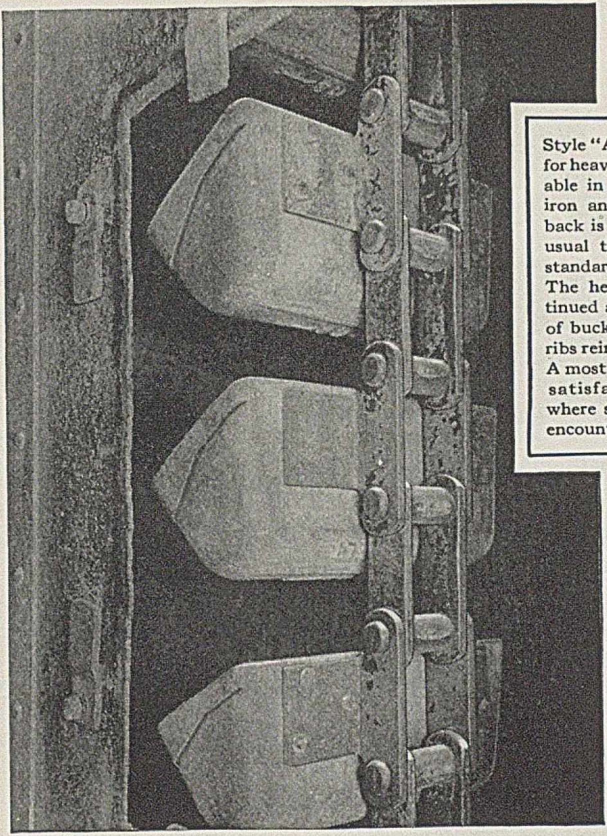
On a broad basis of interest is a discussion of the relative effectiveness of various chemicals in water solution as fire extinguishers. As an engineering problem, the design of efficient industrial exhaust systems will be presented.

And much more, especially the best greetings of the season from

Your humble spy

ELEVATOR BUCKETS

that Last Longer!



Style "AA-RB" bucket for heavy service. Available in both malleable iron and Promal. The back is made twice the usual thickness of the standard "AA" bucket. The heavy lip is continued around the ends of bucket and vertical ribs reinforce the front. A most substantial and satisfactory bucket where severe service is encountered.

● Use the correct bucket for the job. The Link-Belt line includes steel, malleable iron and Promal buckets of suitable size and type to meet any requirement. They are recognized as the standard for toughness—smooth, uniform construction and correct design . . . features that assure proper filling, free and clean discharge and long life.

Link-Belt malleable iron buckets are made of the same metal from which our high-grade malleable iron chains are cast. Promal buckets are stronger than buckets of malleable iron and offer a greater resistance to abrasive wear. Longer life in hard use and under severe abrasive conditions, quickly justifies their slightly higher price.

Fabricated buckets include seamless, welded and riveted construction, using metals and metal treatments which best fit these buckets for the work they are expected to perform.

Large stocks are carried at all Link-Belt plants and warehouses and by many distributors. Specially made buckets can also be supplied . . . galvanized, bronze, aluminum, and baked-enamel finish. General Catalog No. 800 contains complete engineering and descriptive data about operation and design of bucket elevators. If you don't have a copy, write for one today.

LINK-BELT COMPANY

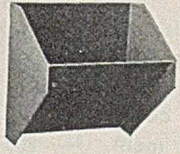
Indianapolis, Chicago, Philadelphia, Atlanta, Dallas, San Francisco, Toronto, Detroit, Boston, Los Angeles, Seattle, Portland, Ore. Offices, warehouses and distributors in principal cities.

8336A

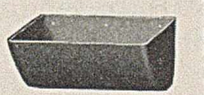
Style "A". Cast in malleable iron and Promal. This is the standard form and the most generally used for handling cement, coal, phosphate, pulp, etc. Style "AA" is similar in shape but has heavy reinforced front edges and corners which give increased life in handling material of an abrasive nature.

Style "B" malleable iron bucket is favored for use in inclined elevators and for handling coarsely broken materials.

Style "C" malleable iron bucket is designed for handling clay, sugar, finely pulverized ores and such other materials as tend to stick or pack.



"Continuous" type buckets are available in malleable iron and steel in a number of styles, with different shapes depending upon material to be handled and angle at which the elevator stands.

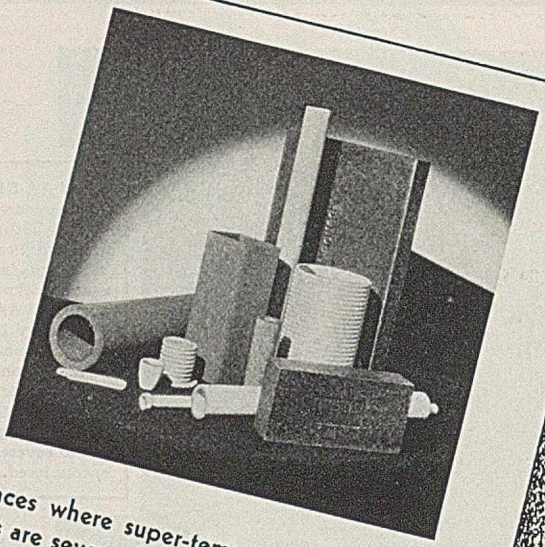


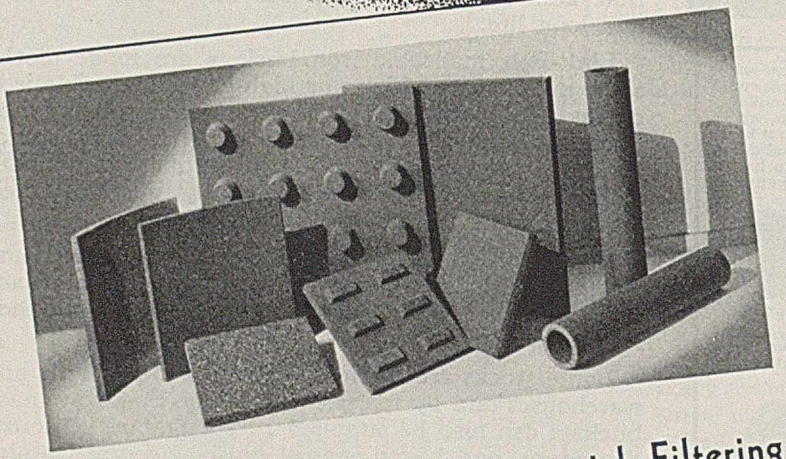
Corrugated seamless steel bucket. Made of one-piece pressed steel, with round corners and bottom; no laps, no rivets or seams. This bucket will stand more hard usage and is the strongest of any seamless bucket of the same gauge and size.

Super-Salem steel elevator bucket costs no more than the standard Salem. It is reinforced at digging lip, front corners and along back. Very strong and offers super-resistance to abrasive wear. The extra strength is obtained without increase in bucket weight. Numerous other Link-Belt steel buckets of suitable designs for handling grain, are available.

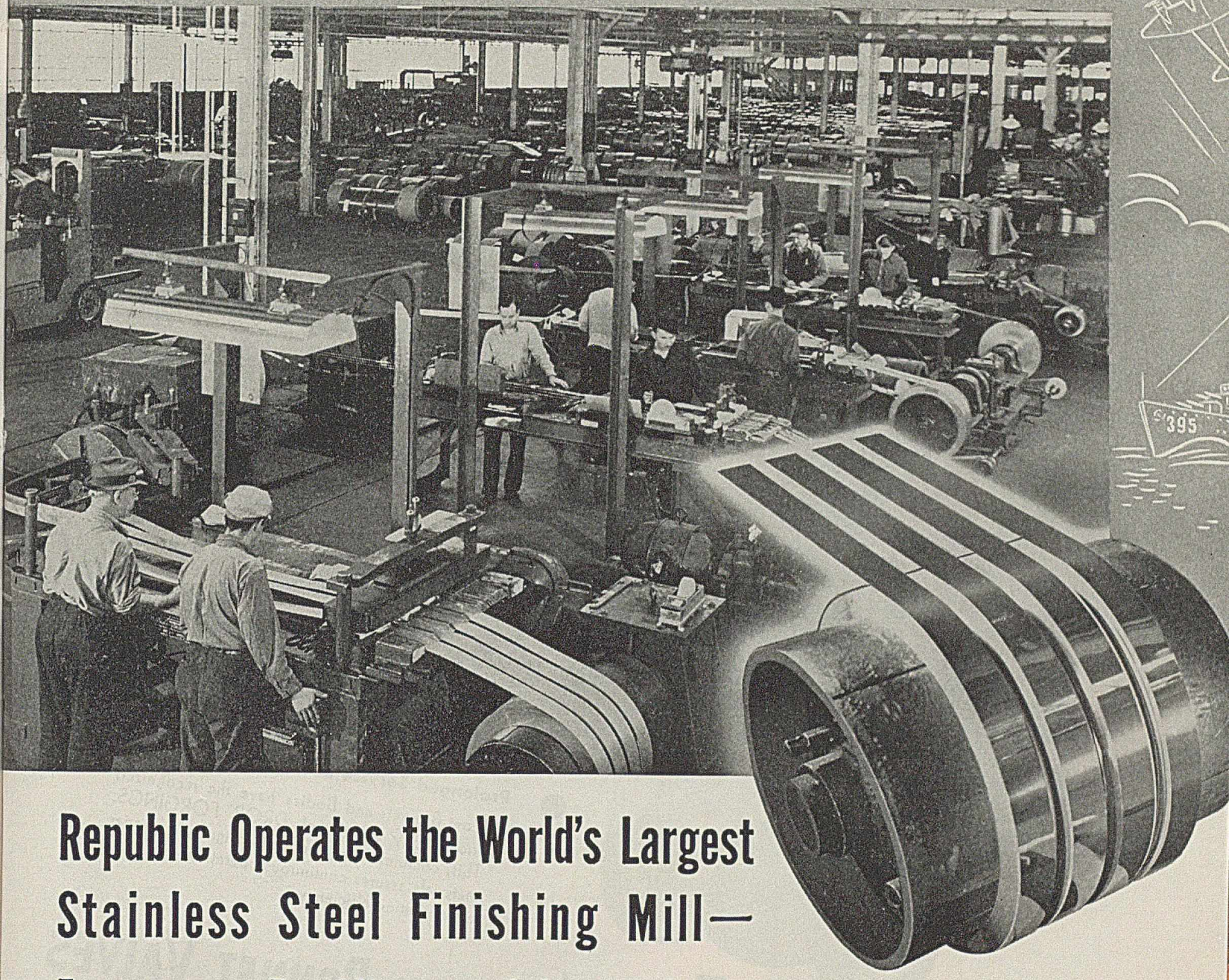
LINK-BELT
ELEVATOR BUCKETS

> > > > A TYPE AND SIZE FOR EVERY SERVICE AND CAPACITY





Steel- FIRST LINE OF NATIONAL DEFENSE



Republic Operates the World's Largest Stainless Steel Finishing Mill—

Ten years ago, Republic operated the world's largest stainless steel finishing plant. Each year it seemed to become smaller as ENDURO Stainless Steel found its way into new products—automobiles, trains, airplanes; chemical, textile and food processing equipment; home appliances and even fine jewelry.

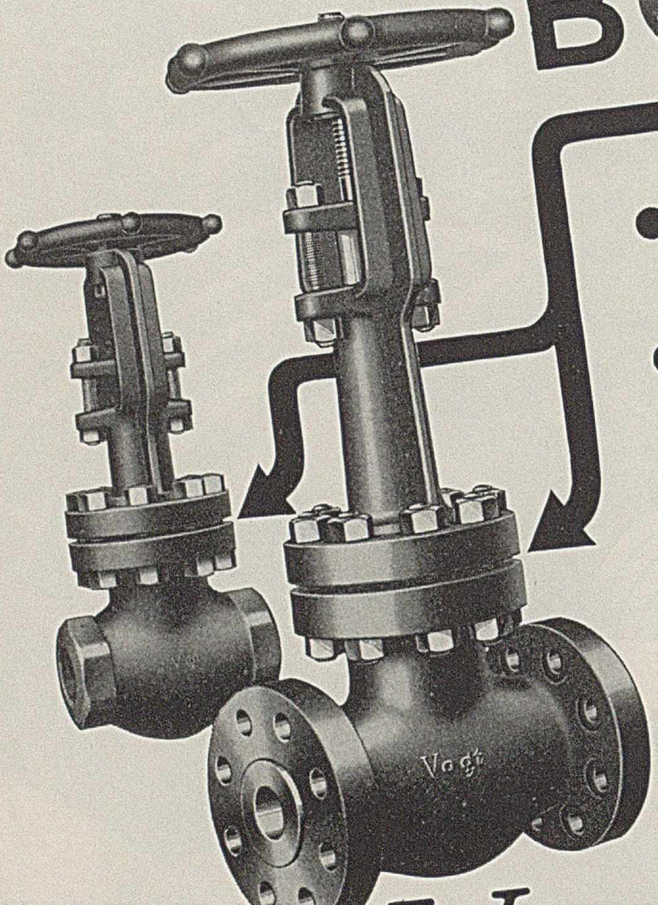
Actually, the plant has been enlarged—now covers five acres of floor space—and much new finishing equipment has been added so that, today, Republic still operates the largest stainless steel finishing plant in the world.

Now, to the huge peace-time need for ENDURO for a wide variety of every-day uses is added the demand of industry working feverishly in the defense of America—for bomb chutes in planes, galleys in naval craft, floats for flying boats and a host of other uses where high strength and heat- and corrosion-resistance are imperative.

Republic has looked ahead — has expanded all its facilities — and, fortunately for every man and woman interested in preserving our freedom, is able and anxious to help in the crisis that now squarely faces America — with more and better ***steel — first line of national defense.***

The line of steels and steel products manufactured by Republic is so diversified that we have prepared a complete listing in Booklet No. 199. A copy will be sent you upon request.

REPUBLIC STEEL CORPORATION • CLEVELAND, OHIO


Vogt


Vogt
DROP FORGED STEEL
GATE VALVES
HENRY VOGT MACHINE CO., INC. LOUISVILLE, KENTUCKY


Vogt
FOR BETTER VALVES

950° "Stop kidding me! There's no lubricant that will operate in a red-hot valve at 950°," declared the visiting engineer. *But there it is!* In service for many months on a cracking line, in a refinery, this Nordstrom Hypreseal Valve has been making history. In many other refineries, operating topping units, this same type of valve is likewise rendering perfect service at temperatures of 675° F., without a leak; always easy to turn, even if carbon slugs settle in the line. There's no place in which any deposit can lodge. This amazing valve is made of special alloy; the body and plug are Merchromed; (patent pending). The plug is hot lapped at approximately the service temperature. The lubricant is a special compound developed by Nordstrom for this drastic temperature. Just more proof that Nordstrom Valves are truly engineered for the "toughest jobs." Keep upkeep down with Nordstroms.

—naturally it's a **NORDSTROM VALVE**

Introducing MERCHROMED Valves

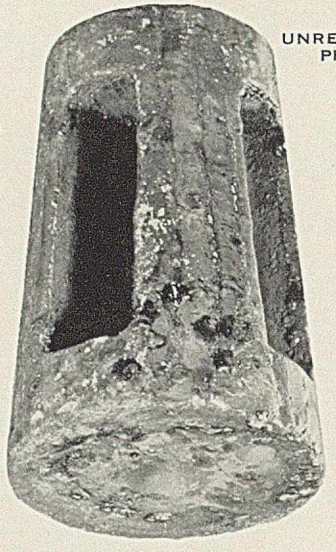
PATENT APPLIED FOR

A PROVEN ENGINEERING ACHIEVEMENT BY NORDSTROM

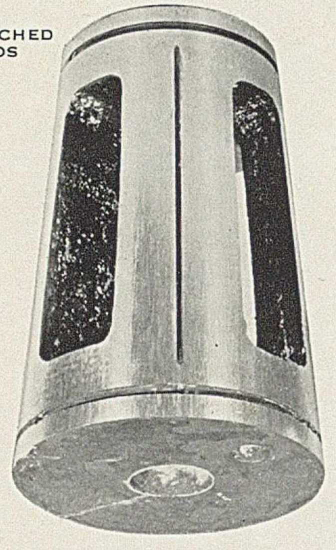
MERCHROMING

- —*a highly-technical metal alloy process.*
- —*an impenetrable coating on plug and body.*
- —*specially bonded to friction surfaces.*
- —*gains lowest coefficient of friction.*
- —*invulnerable to corrosion, erosion.*
- —*for temperatures as high as 1000° F.*
- —*prevents galling and scoring.*
- —*applicable to various Nordstroms.*

UNRETOUCHED PHOTOS



MERCHROMED PLUG *in the rough*

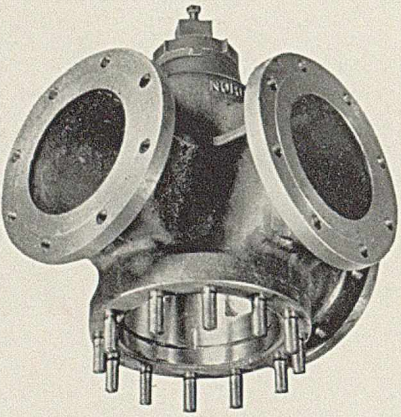


SAME PLUG *after machining*

Again reflecting the initiative of Nordstrom engineers in offering the most advanced methods of valve manufacturing, *MERCHROMING* is presented. It is a process in which a special welded coating is applied to the rotating, frictional surfaces of the plug and its contacting body. Merchroming provides a coating of extreme hardness, corrosion-resistant, capable of maintaining its properties at temperatures as high as 1000° F. The plugs are "hot-lapped" into the bodies at a temperature corresponding to the service for which they are intended, assuring the most accurate fit and extremely smooth operation. Further details upon request.

While Merchromed Valves may be unnecessary for your services, this new development in valve manufacturing indicates the ability of Nordstrom engineers to provide for every service. Only Nordstrom Valves meet every major valve need.

KEEP UPKEEP DOWN WITH NORDSTROMS



NORDSTROM HYPRESEAL MULTIPORT, SHOWING MERCHROMED BODY

After Merchroming is completed in the body and on plug by special welding, the rough surfaces are ground or machined to final dimension; then the plug is "hot-lapped" into the body. Contacting surfaces have a low-friction, super-finish; intensely hard and perfectly fitted.

Nordstrom

LUBRICATED FOR ALL-PURPOSE SERVICE **VALVES**

Sealdport Lubrication

MERCO NORDSTROM VALVE COMPANY—*a Subsidiary of* Pittsburgh Equitable Meter Company

WORLD'S LARGEST MANUFACTURERS OF LUBRICATED PLUG VALVES; GASOLINE, OIL & GREASE METERS

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SHARPLES ALCOHOLS

SHARPLES
TRADE
MARK
SOLVENTS

	PENTASOL*	n-AMYL ALCOHOL	iso-BUTYL CARBINOL	sec-BUTYL CARBINOL	DIETHYL CARBINOL	TERTIARY AMYL ALCOHOL REFINED
COLOR AND FORM	COLORLESS LIQUID	COLORLESS LIQUID	COLORLESS LIQUID	COLORLESS LIQUID	COLORLESS LIQUID	COLORLESS LIQUID
MOLECULAR WEIGHT	88.09	88.09	88.09	88.09	88.09	88.09
SPECIFIC GRAVITY AT 20°	0.815	0.82	0.815	0.815	0.82	0.81
POUNDS PER GALLON	6.79	6.83	6.79	6.79	6.83	6.75
DISTILLATION RANGE °C	112-140	134-139	128-132	125-131	113-118	99-104
FLASH POINT °F	113	136	132	122	102	75
REFRACTIVE INDEX AT 20°	1.4092	1.4113	1.4099	1.4097	1.4098	1.4049
ACIDITY, MG. KOH PER GM	Not over 0.06	Not over 0.06	Not over 0.06	Not over 0.06	Not over 0.06	Not over 0.15
NON-VOLATILE AT 100° C MAXIMUM /100cc	0.005 GM.	0.003 GM.	0.003 GM.	0.003 GM.	0.003 GM.	0.003 GM.
WATER CONTENT	NONE	NONE	NONE	NONE	NONE	NONE
SOLUBILITY IN WATER	SLIGHTLY SOLUBLE	SLIGHTLY SOLUBLE	SLIGHTLY SOLUBLE	SLIGHTLY SOLUBLE	SLIGHTLY SOLUBLE	PARTIALLY SOLUBLE
SOLUBILITY IN ETHER	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE
SOLUBILITY IN BENZENE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE
SOLUBILITY IN NAPHTHA	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE	MISCIBLE

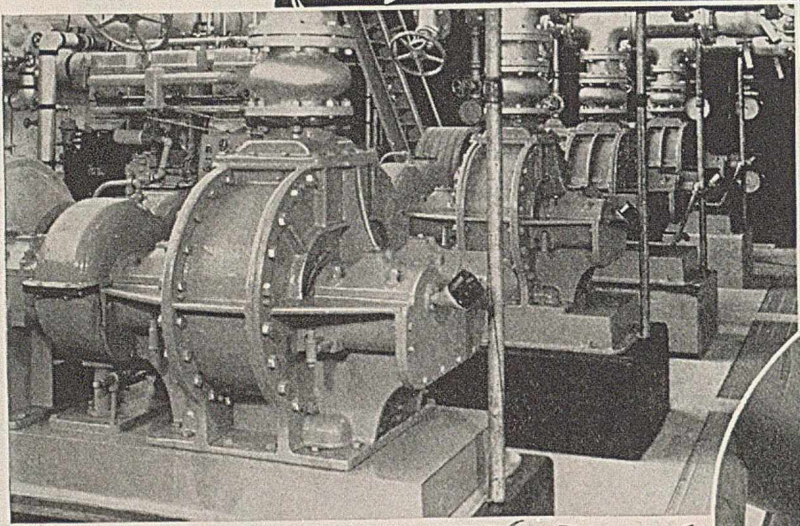
*** MIXED AMYL ALCOHOLS**

Sharples Amyl Alcohols are synthetic products, made in commercial quantities and contain only the Amyl group in its various isomeric forms. They find wide application in lacquer solvents, anti-foaming agents, pharmaceuticals, flotation reagents and organic syntheses. Send for Sharples Catalog of Organic Chemicals describing more than 125 new compounds.

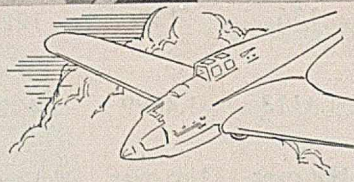
THE SHARPLES SOLVENTS CORP.

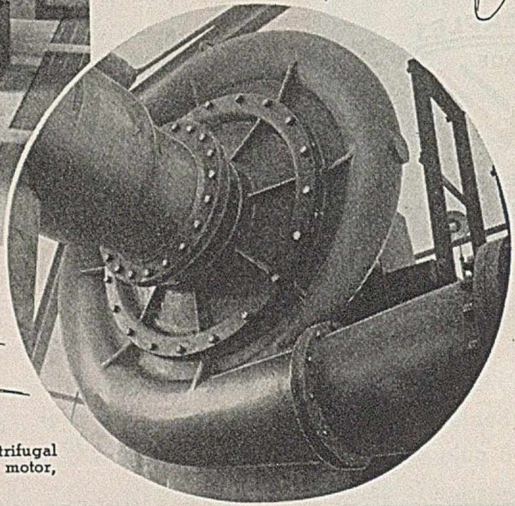
PHILADELPHIA CHICAGO NEW YORK

Your AIR Defense



Four 1800 CFM, 7½ lb. blowers, V-belt driven from motors, used for liquid agitation.





11,750 CFM, 3 lb. single stage centrifugal blower direct connected to 200 HP motor, in oil refinery service.

Control of the air by swarms of fast flying planes gets the headlines. But in a very real sense, national defense will also depend on complete mastery of air used in chemical processes and throughout industry.

In that field your own air defense can be safely entrusted to the skill and experience of Roots-Connersville blower craftsmen. The blower units they produce can be counted on for continuous service not only through the present period of stepped-up production but for long afterwards.

Standard and specially designed blowers, gas exhausters and boosters are built to meet all requirements for moderate pressures from 8 ozs. to 15 lbs., or higher in compound arrangement, and for volumes up to 50,000 CFM. There is an "R-C" sales engineer near you. Would you like to talk with him? No obligation, of course.

Roots CONNERSVILLE BLOWER CORPORATION

412 Georgia Ave. Connersville, Ind.

IN HANDLING AIR AND GAS *Experience Counts* SINCE 1854

NEW YORK CHICAGO POTTSTOWN, PA. SAN FRANCISCO DETROIT ST. LOUIS LOS ANGELES PITTSBURGH BOSTON


HERE'S MUD
IN YOUR EYE!

"They Just *Don't Break!*"

. . . . that's what users say about these Galvanometer Suspensions!

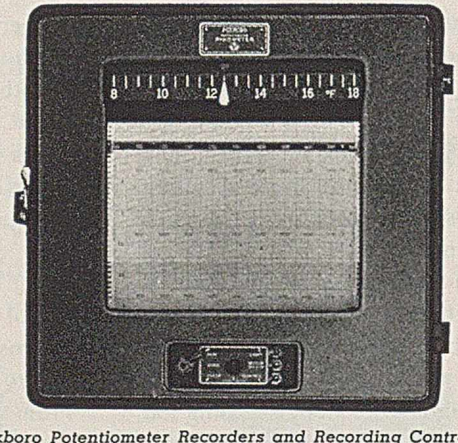
Did you ever see a year or more pass without a single galvanometer suspension replacement in a bank of operating pyrometers?

Several large-scale users of Foxboro Potentiometer Recorders and Controllers have reported this experience. They told us not to bother sending spare suspensions with new instruments on order!

Foxboro galvanometer suspensions are so designed that breakage practically never occurs. Their acid-proof gold strips are longer, heavier, stronger . . . spot-welded, instead of soldered in place. And their end-brackets are made with smoothly-crowned snubbing surfaces that stop destructive shear action.

Yet this is only one of numerous refinements that make Foxboro Potentiometer Instruments more sensitive and more economical to maintain. Other original Foxboro features make possible instant, accurate response with *slower* movement of elements and *fewer* moving parts to wear out!

Get the complete story on these trouble-free instruments. Write for Bulletin 190-4. The Foxboro Co., 40 Neponset Ave., Foxboro, Mass., U. S. A. Branches in principal cities of United States and Canada.



Foxboro Potentiometer Recorders and Recording Controllers are guaranteed accurate within 1/4 of 1% of scale range.

— RECORDING · CONTROLLING · INDICATING — **FOXBORO**

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Potentiometer Instruments

DAYTIME BLACKOUTS

A Case Where a Valve Menaced Plant Operation

SOLVED WITH PREVENTIVE MAINTENANCE

FROM his window the Superintendent of a chemical processing plant saw the stacks belching smoke that turned day into night. It happened before—just recently.

Suspecting boiler trouble, he became alarmed. "Maybe there's one reason for production delays!" He grabbed a phone. "Why the blackouts, Bill?"

"The forced draft blower is acting up," replied the engineer, "the valve in the steam line's gone out again!"

Only a short time ago this valve was repaired. Yet, again, it was causing irregular boiler operation and fuel waste; in fact, it might have crippled the boiler completely! That's how Preventive Maintenance—the modern way of protecting against trouble by stopping it at the source—entered the case.

The engineer knew that valves shouldn't behave that way. But he wouldn't risk ordinary repair again. And through the Crane Man, R. B. H., he would benefit from Crane's wide experience and knowledge in applying the best corrective measure.

The first step in applying Preventive Maintenance is making sure that the valves and fittings are right for working conditions.

Here was a renewable disc valve in the steam line to a turbine-type blower. It couldn't stand the "gaff" of constant throttling. The disc wouldn't last. No wonder the draft blower ran wild!

Preventive Maintenance counseled replacement with a Crane No. 14½P—a plug type disc valve designed for tough throttling jobs. Its materials and construction would safely resist the ravaging effects of throttled steam. It would give unvarying control of flow—keep the blower running evenly.

RESULTS: No more blackouts even after two years. The menace of interrupted boiler operation, fuel waste, even complete shutdown was eliminated with Preventive Maintenance. Another user of piping knows that the Crane Man can help get most for piping maintenance dollars. Because, Crane is not only the source of valves and fittings for every need, but of accurate information on their proper usage as well.

This case is based on the personal experience of R. B. H., a Crane Representative in our Minneapolis Branch.

TOUGH FLOW TAMED WITH CRANE BRASS PLUG DISC VALVES

In your boiler room—in any lines requiring severe throttling, you'll find these valves exactly right for the job. They're sound protection against trouble in blower, blow-off, and boiler-feed services, in drip and drain lines.

The unusual stamina of these Crane valves is in their plug-type disc and seat construction. Materials are just the right combination for highest resistance to the corrosion and erosion of actual working conditions. The wide seating area repels the damaging effects of wire-drawing and foreign matter; assures long-lasting tightness. The tapered disc provides easy, positive regulation of flow.

With Crane Plug Disc valves, you can apply money-and-trouble-saving Preventive Maintenance to all the *tough* spots in your piping. They're available in a complete range of pressure ratings. For 150 pound services, specify the No. 14½ P—in sizes up to 3 inches.

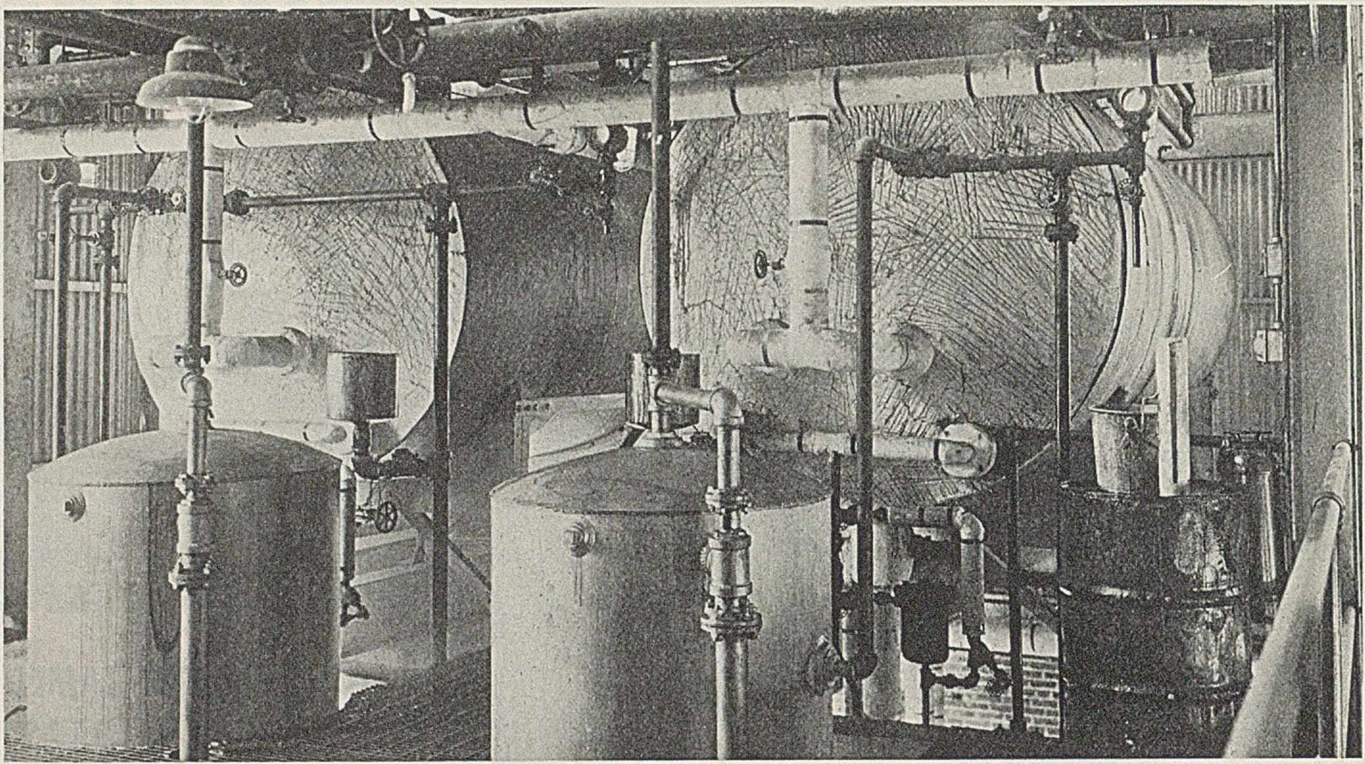
1940 OUR 85th YEAR

CRANE

CRANE CO., GENERAL OFFICES:
836 S. MICHIGAN AVE., CHICAGO

VALVES • FITTINGS • PIPE
PLUMBING • HEATING • PUMPS

NATION-WIDE SERVICE THROUGH BRANCHES AND WHOLESALERS IN ALL MARKETS

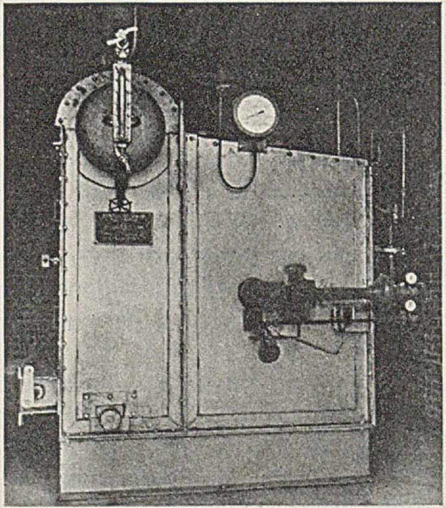


600° heat for these kettles is supplied by two Dowtherm vapor generators

Sixth Repeat Dowtherm Heating System

FOR ROSIN PROCESSING

Newport Industries, Inc., has recently ordered the seventh Dowtherm heating unit for high-temperature, low-pressure processing of resinous products. The first unit was installed at the Bay Minette, Alabama, plant less than five years ago, after other methods for obtaining high temperatures in processing vessels had been found inadequate. At that time, when less than 5% of the present total Dowtherm capacity was in service, this was the pioneer installation in its field. Hairline temperature control obtained by automatic firing of the Dowtherm vapor generator provided Newport Industries with uniform products, in close gradation and capable of accurate reproduction.



One of the 500,000 Btu per hour Dowtherm generators at Pensacola, Florida

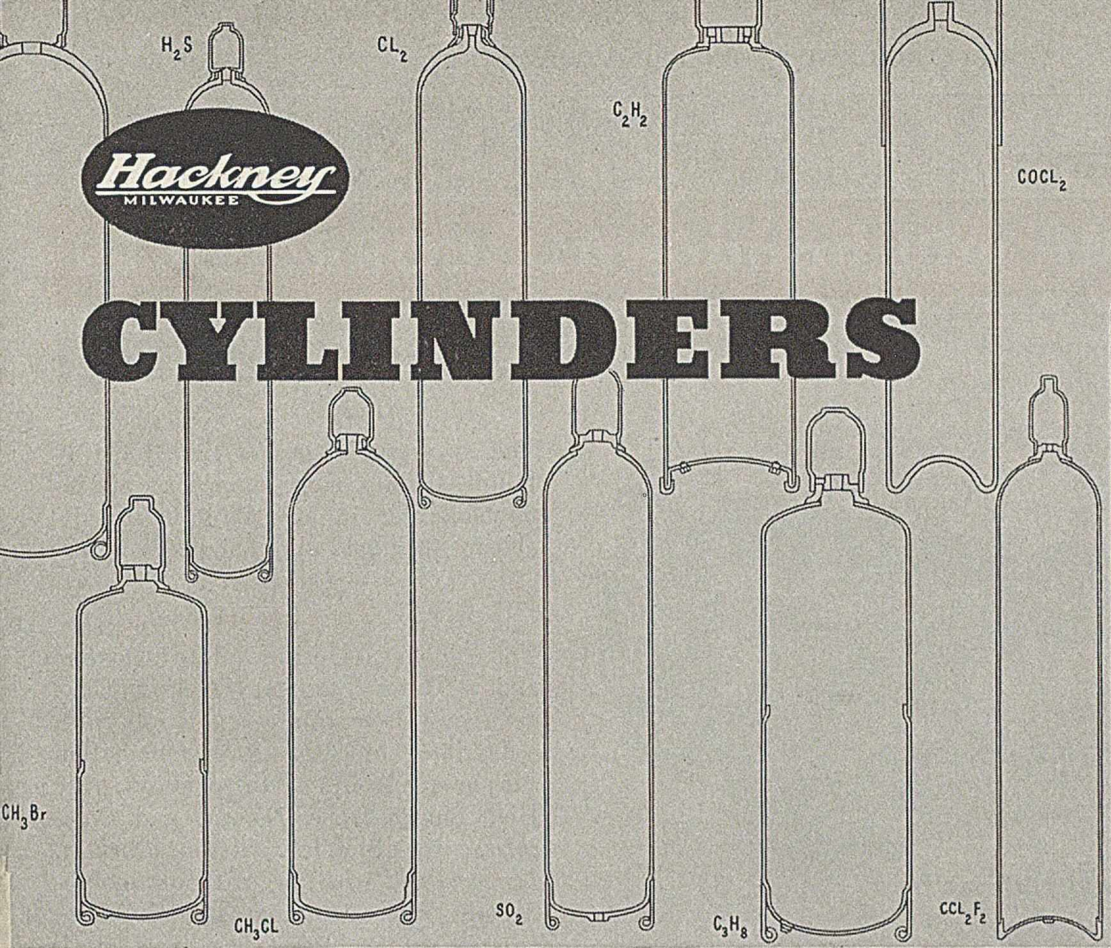
This simple, high temperature vapor system entailed no pressures above 60 lb. gage and provided automatic, scale-free operation at excellent efficiencies.

Within seven months, a duplicate Dowtherm unit was installed at the Pensacola plant. The third, fourth and fifth units were placed in the same plant while the sixth and seventh were installed at Dequincy, Louisiana.

Other Dowtherm heating systems by Foster Wheeler include distillation processes for toll oil, fatty acids and petroleum; continuous tinning; batch and continuous deodorization of vegetable oil; bodying of varnish; and processing of asphalt and plastics.

Foster Wheeler Corporation, 165 Broadway, New York, N. Y.

FOSTER FW WHEELER


H_2S
CL_2
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CH_3Br
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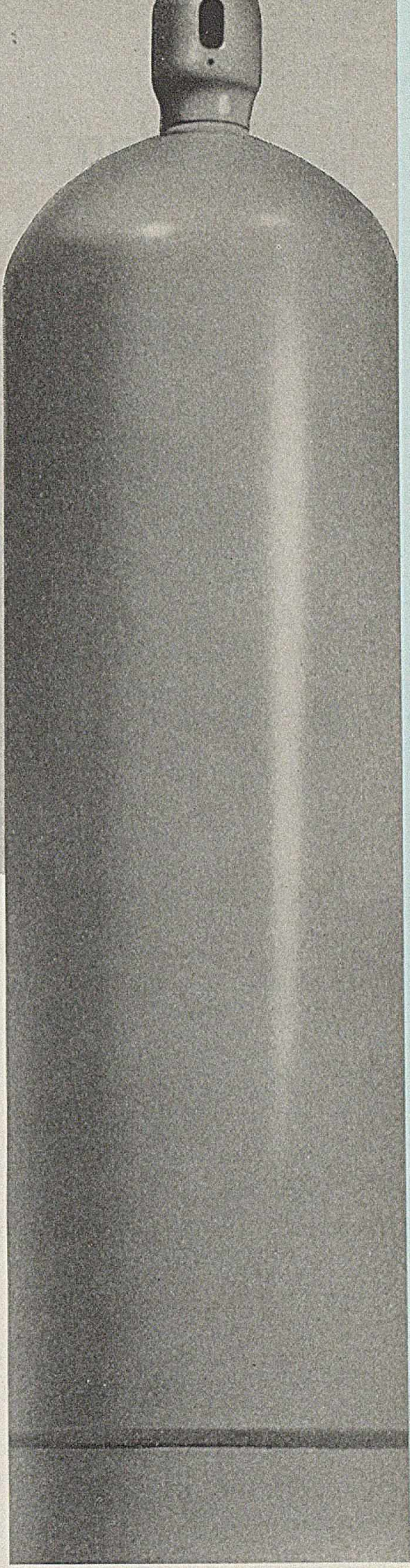
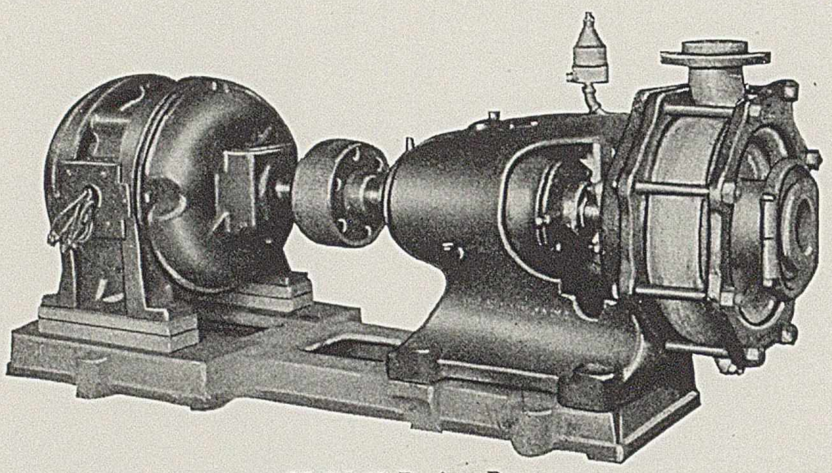


We *don't* say:

THIS PUMP will handle ALL CORROSIVES

. . . but we *do* say:



Model 40 Duriron Pump

The "wet end" parts of the Model 40 Pump—volute, cover, impeller—are interchangeable in any alloy most suitable for the liquid to be handled.

For instance

You can have a Duriron volute and cover and a Durco Stainless Steel impeller; or a cast iron volute and cover with a Durimet impeller. Any combination can be made up of these alloys: the High Silicon Irons, *Duriron* and *Durichlor;* the Stainless Steels, *Durimet, Durco 18/8* with or without molybdenum; the aluminum bronze, *Alcumite;* hard lead, cast iron, cast steel, or any of the special corrosion-resisting alloys.

From acids to caustics

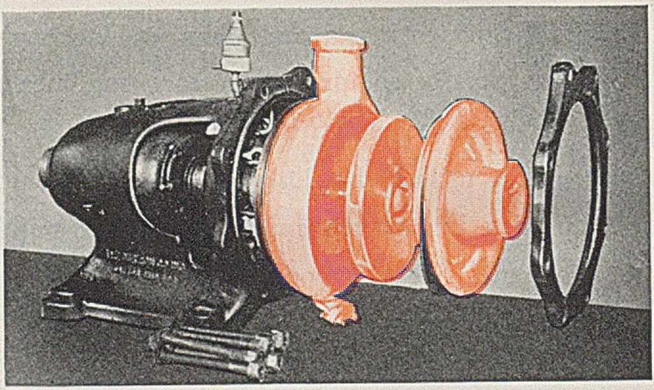
Because of this interchangeability, the Model 40 Pump made in *Duriron,* say, for use with sulfuric acid can be used later for caustics by replacing the essential parts in *Durimet.*

Or sulfuric to hydrochloric

You might be handling sulfuric acid now. Later, you may change over to using hot hydrochloric acid. A *Durichlor* volute, cover and impeller will equip your pump to handle hot hydrochloric acid without corrosion losses.

From plain to corrosive liquids

Your present liquors *may* not be corrosive but a small change in process may make them so. Or, a new process may prove a non-corrosive liquor based on pilot plant or laboratory data to be **corrosive** in the actual plant.



Interchangeable parts: volute, impeller, cover

Protect yourself with a cast iron, bronze or steel Model 40 Pump that can be later converted to the most suitable alloy for the purpose.

Space limitations prevent us from telling you the complete details about the Model 40 Pump and the various alloys in which it is procurable. Complete information will be supplied gladly. Write us today.

THE DURIRON COMPANY, Inc.

North Findlay Street Dayton, Ohio

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

U.S.I. CHEMICAL NEWS

December ★ A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries ★ 1940

See New Vanadium Source in Western Phosphate Rocks

Economical Recovery Possible By Solvent Extraction Process

LEONIA, N. J.—The phosphate deposits of Wyoming, Utah, Idaho, and Montana offer a source from which vanadium can be economically extracted, it is claimed in a patent granted jointly to inventors here and in New York. Efficiency of the process, it is said, depends on the use of solvents.

Western phosphate rock, it is said, has taken on greater importance as a source of phosphoric acid, as a result of increased demand for the acid in the manufacture of "double" and "triple" superphosphates. It is known that these rocks contain an appreciable amount of vanadium, which appears in the final phosphoric acid solution.

Converted to Pentoxide

The inventors propose to recover the vanadium content by a method that is described as simple and effective. The vanadium content of the acid solution is first converted to the pentoxide form by an oxidizing agent such as potassium persulphate. The vanadium content is then extracted, it is claimed, by the action of a selective solvent. Suitable solvents, according to the inventors, include ethyl ether, isopropyl ether, ethyl acetate,

(*Continued on next page*)

New Coating Makes Paper Moisture- and Odor-proof

WILMINGTON, Del.—A new composition that can be applied to paper in a continuous film makes the paper substantially proof against moisture, odors, and vapors, according to a manufacturer here.

Basis of the coating is said to be a granular white material, made by completely reacting chlorine and pure, pale crepe rubber. It is said that the material is soluble in many common solvents and that it deposits clear films.

For paper coatings, the material is usually mixed with a plasticizer such as dibutyl phthalate, it is reported. Dibutyl phthalate is chosen, according to the manufacturer, because it helps to develop excellent moisture- and vapor-proofness in the finished coating. In addition, it has the advantage of being free from odor.

Dibutyl Phthalate is produced by U.S.I.

Report Ethyl Cellulose Improves Spirit Varnish

LOUISVILLE, Ky.—Moisture resistance, hardness, and abrasion resistance of spirit varnishes can be substantially improved by substituting ethyl cellulose for small percentages of the resin content, it is indicated by investigations carried on here.

Studies were made of pontianak and Manila resins, using a solvent consisting of 75% alcohol and 25% toluene. All qualities investigated showed substantial improvement, it is claimed, when ethyl cellulose was added.

New Acetone Uses Found, Sales Volume Continues on Up Trend

Demand Continues Strong in Existing Fields, Many Additional Markets Seen in Novel Solvent and Raw Material Applications

Uncovery of many novel applications for acetone is combining with continued demand in established fields to maintain sales at a high level for this widely used U.S.I. product. Export markets are up, as well as domestic, and acetone exports for the first half of the current year jumped to 12,128,410 pounds from a figure of 8,159,890 pounds for the same period last year. Many of the newer uses of acetone make use of its solvent properties; in other cases it is employed as a raw material for chemical manufacturing processes.

The rayon industry remains one of the largest users of acetone, and it is estimated that the consumption in rayon and allied fields in 1940 will reach a figure of 32,000 tons. Even in such well established fields as this, new acetone applications are coming to light, and a recent patent described a method for producing rayon yarns of improved extensibility, employing acetone.

Applications in Cellulose Field

Moistureproofing of regenerated cellulose sheets can be effected, it is claimed, by treating the sheets with acetone, which is said to displace existing liquids in the surface layers of the sheets. The sheets are then impregnated with a succinic acid-glycerol resin dissolved in acetone. A process for dyeing cellulose derivatives is said to consist in dissolving them in acetone with a diazogene compound and a coupling component.

Among the established uses of acetone, its application as a solvent for acetylene is a very important one. It is the most economical solvent known for this purpose, dissolving 25 times its own volume at ordinary temperatures and pressures. Other solvent uses include dry cleaning fluids, paint and varnish removers, natural and synthetic resins, bituminous paints, smokeless powder, TNT, artificial leather, lacquers, and dopes. A novel use is in the recovery of copper in the wire drawing process. The oily sludge

(*Continued on next page*)

U.S.I. Widens Its List Of Acetoacet-arylides

U.S.I. announces that the following acetoacet-arylides are now in regular production:

Acetoacet-anilide
Acetoacet-ortho-chloranilide
Acetoacet-ortho-toluidide
Acetoacet-para-chloranilide
Acetoacet-ortho-anisidide

Laboratory or pilot plant samples have been prepared of these additional items, which can be made in larger quantities if sufficient demand appears:

Acetoacet-para-phenetidide
Benzoylacet-anilide
Biacetoacetyl-meta-toluylenediamine
Biacetoacetyl-para-phenylenediamine
Acetoacet-para-nitroanilide
Acetoacet-2,5-dichloranilide
Acetoacetyl-alpha-naphthylamine
Acetoacet-cumidide (pseudo)
N, N'-Biacetoacetbenzidide

In addition to these products, on which inquiries are invited, U.S.I. is in a position to make laboratory samples of other acetoacet-arylides at the suggestion of prospective customers.

Produces "Synthetic" Hardwood

RIDGEFIELD PARK, N. J.—A product similar to hardwood can be prepared by a process for injecting natural or synthetic resins into green wood, at the same time extracting the sap and moisture, it is reported here.

The "synthetic" hardwood, it is claimed, is resistant to warping, rotting, and fire, and can be produced at lower cost than the natural hardwoods it is intended to replace.

Solvent in the manufacture of artificial textiles, vehicle in liniments—these represent two of the extraordinarily diversified uses of acetone.

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

U.S.I. CHEMICAL NEWS

December ★ 1940

Drying Components of Marine Oils Extracted By Ethyl Acetoacetate

MILWAUKEE, Wis.—A novel application for ethyl acetoacetate in extracting the drying constituents of fish oils is revealed in a patent granted to an inventor here.

Ethyl acetoacetate is particularly valuable in refining raw oils such as sardine or menhaden, according to the inventor, because it dissolves most of the unsaturated components which are useful in paints and varnishes, while at the same time it has low solvent powers for the undesirable "break" and color constituents.

Ethyl Acetoacetate is produced by U.S.I.

Acetone Sales Volume Up

(Continued from previous page)

resulting in the drawing process is extracted with acetone, it is said, removing the oil and leaving a residue of fine copper powder. A patented plastic wood composition is said to incorporate vinyl resins and acetone.

As a raw material for chemical manufacture, acetone has exceptional potentialities. Benzylidine, bromoform, chlorbutanol, chloracetone, diacetone, chloroform, iodoform, indigo, ionone, isoprene, and mesityl oxide are among the more familiar compounds that can be produced from acetone. Oxidation inhibitors for rubber are commonly prepared by the reaction of acetone with an aromatic amine. A recent patent in this field covers an inhibitor prepared by heating acetone and a *p*-amino-substituted diaryl thio ether in the presence of iodine. A new gum inhibitor for oils and cracked gasoline is described as a reaction product of acetone and pyrocatechol.

Preparation of Bis-phenols

Still other uses for acetone include a process for preparing bis-phenols by treating phenols with acetone in the presence of an inorganic acid; manufacture of ketene and its homologs by pyrolysis of acetone in contact with copper; preparation of fusible resins by treating an aldehyde with acetone in the presence of a catalyst.

In the medical field, acetone is extensively used as a vehicle for liniments and in the treatment of purulent wounds. This, of course, is in addition to the medical use of many of the compounds already mentioned, in which acetone is used as a raw material.

As a leading producer of solvents, U.S.I. supplies acetone of the highest quality for these diversified requirements.

Here's Pleasant News For Cigarette Smokers

SOUTH ORANGE, N. J.—No loose shreds of tobacco will find their way into your mouth if the end of your cigarette is impregnated with a solution of ethyl cellulose in anhydrous ethyl alcohol, it is claimed by an inventor here. The solution, it is said, stiffens and waterproofs the paper at the mouth end of the cigarette, and binds the tobacco shreds together so that they do not become loose.

The inventor also claims that the composition is non-toxic and has absolutely no effect on the taste or odor of the smoke. Best news of all is the claim that absent-mindedly lighting the wrong end produces no ill effects.

U.S.I. is a leading producer of Anhydrous Ethyl Alcohol.

Claims Pipe Seal Immune To Alcohol, Oils, Steam

BROOKLYN, N. Y.—Use of blown castor oil, produced by oxidizing or polymerizing raw castor oil, is desirable in packing and sealing compounds exposed to heat, vibration, and chemicals, it is claimed in a patent granted to an inventor here.

The blown castor oil, the inventor claims, is substantially insoluble in gasoline, gasoline-alcohol mixtures, fuel oils, and alcohol-containing preparations, such as anti-freeze. Moreover, it is said that the seal is not affected by heat, hot water, or steam.

A typical composition is said to have the following proportions:

Philippine gum	6 lbs.
Ethyl alcohol	1 gal.
Blown castor oil	1½ gal.
Talc	25 lbs.

Vanadium Recovery Process

(Continued from previous page)

butyl acetate, and a number of other organic compounds.

Several methods have been proposed for recovering the metal values from the organic solution. For example, it is said that the solution may be brought in contact with water, allowing a certain quantity of the metal value to pass into the aqueous phase. The vanadium in the water phase can then be reduced to the tetravalent state, in which it is largely insoluble in the organic solvent, and the water phase can be recycled.

Ethyl Ether, Ethyl Acetate, and Butyl Acetate are produced by U.S.I.

TECHNICAL DEVELOPMENTS

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

New rust preventives are said to incorporate an ingredient that provides a homogeneous, non-crystalline film, with a high degree of cohesion and adhesion to metal. It is reported that products can be supplied to meet industrial specifications. **(No. 400)**

U S I

A transparent floor finish is unaffected by extreme conditions of acidity or alkalinity, according to the maker. It is claimed that dried films of the product have been immersed in dilute sulphuric acid, carbolic acid, and sodium hydroxide solutions without damage to finish or gloss. **(No. 401)**

U S I

Fugitive tints for identifying cotton, viscose, and acetate staple fibers are described as oil-soluble dye concentrates to be added to the oil used in conditioning cut staple fibers. Eight colors are said to be available. **(No. 402)**

U S I

Sodium chlorite is said to be strong enough to bleach cotton, rayon, wood pulp and other cellulose fibers, without attacking the fibers themselves. It is claimed that the sodium chlorite will bleach in both acid and alkaline solutions. **(No. 403)**

U S I

Textile colors can be applied directly to cotton, rayon, acetate, and other fabrics by standard textile printing machinery, and require no after-treatment, it is claimed. It is said that the colors have excellent fastness to light and to repeated washings. **(No. 404)**

U S I

A mildew preventive is said to be especially designed for incorporation in paints and plastic materials to prevent the growth of mold, mildew, spores, and algae. It is also claimed that the product promotes even spreading, increases adhesion and flexibility of paint film. **(No. 405)**

U S I

A new ink that is said to be especially suitable for laundry marking is described as resistant to soap, lye, bleaching fluid, and oxalic acid. **(No. 406)**

U S I

Stable emulsions of mineral oil, pine, oil, toluol, and other oils and waxes, containing as high as 6% hydrochloric acid and other strong electrolytes, have been prepared with the aid of a new emulsifying agent, it is claimed. Applications are said to include paper, leather, textile, and cosmetic industries. **(No. 407)**

U S I

Water-treating equipment is said to have been developed for removing carbon dioxide from water that has been treated in carbonaceous hydrogen zeolite softeners. It is claimed that the treatment also oxidizes any soluble iron present, so that it can be filtered out. **(No. 408)**

U S I

A deep black finish can be produced on steel by a new low-temperature process, it is claimed. It is said that the dimensions of treated parts remain unchanged, and that the finish is resistant to rust and wear. It is also reported that temperatures used are not high enough to affect heat-treated parts. **(No. 409)**

U.S. INDUSTRIAL CHEMICALS, INC.

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

A SUBSIDIARY OF U. S. INDUSTRIAL ALCOHOL CO.

ALCOHOLS
- Amyl Alcohol
- Butyl Alcohol
- Fusel Oil—Refined
- Methanol

Ethyl Alcohol
- Anhydrous
- Absolute
- C. P. 96%
- Pure (190 proof)
- Specially Denatured
- Completely Denatured
- U. S. I. (Denatured Alcohol Anti-freeze)
- *Super Pyro Anti-freeze
- *Solox Proprietary Solvent

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

ESTERS, ACETATES
- Acetic Ether
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

ESTERS, ETHYL
- *Diatol
- Diethyl Carbonate
- Diethyl Oxalate
- Ethyl Chlorocarbonate
- Ethyl Formate
- Ethyl Lactate

*Registered Trade Mark

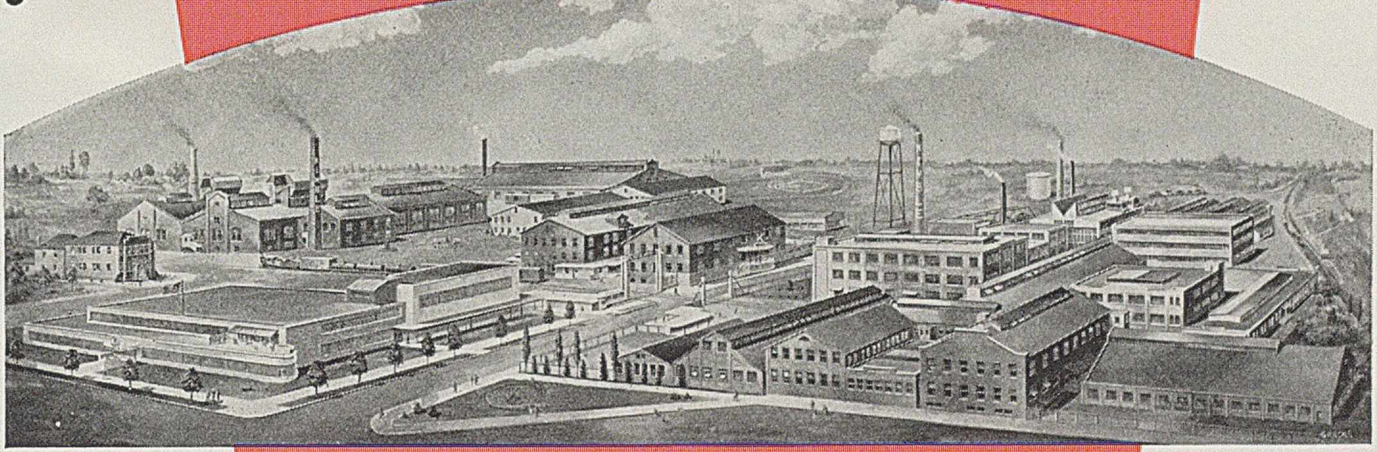
ESTERS, PHTHALATES
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate
- Dimethyl Phthalate

OTHER ESTERS
- Amyl Propionate
- Butyl Propionate
- Dibutyl Oxalate

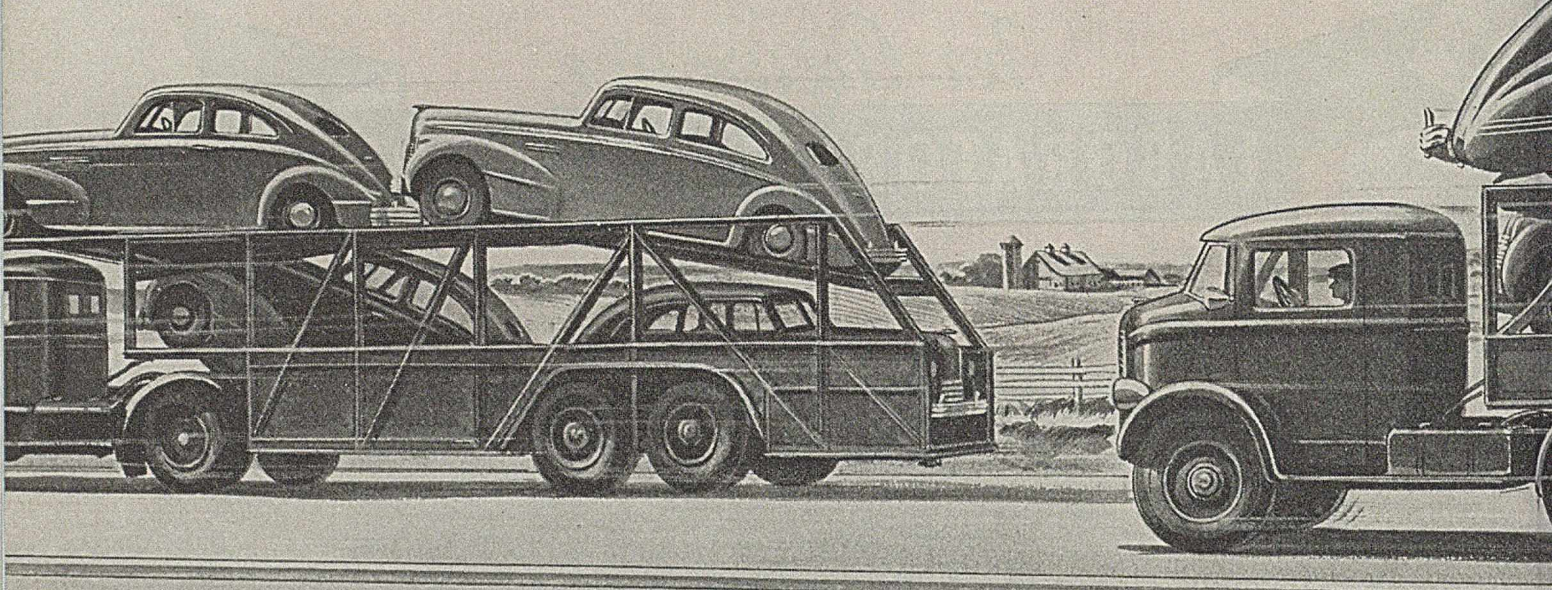
INTERMEDIATES
- Acetoacetanilid
- Acetoacet-o-chloranilid
- Acetoacet-o-toluidid
- Ethyl Acetoacetate
- Sodium Ethyl Oxalacetate

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

OTHER PRODUCTS
- Acetone, C.P.
- Collodions
- *Curbay Binders
- *Curbay X (Powder)
- Derex
- Ethylene
- Methyl Acetone
- Nitrocellulose Solutions
- Potash, Agricultural
- *Vacatone
- *Curbay B-G



New Cars Reflect



1941 MODELS SHOW CONTINUATION OF TREND IN ENGINE DESIGN TO UTILIZE HIGHER ANTI-KNOCK GASOLINE

THE MARKED INCREASE in the compression ratios of 1941 cars—the sharpest rise in five years—is ample evidence that automobile manufacturers are keeping pace with advances in gasoline anti-knock quality. The compression ratios for all makes and models of 1941 cars average 6.66 to 1, as against 6.43 to 1 for 1940. At least twenty-five of the new models have higher compression ratios than they did last year, and some manufacturers who have not increased their already high compression ratios have made other changes in engine design to obtain additional horsepower from today's greatly improved fuels.

How closely increases in engine efficiency have paralleled gains in gasoline anti-knock value in recent years is shown in Figures 1 and 2. Improvements in motor fuel have made it possible for automotive designers to stress efficiency rather than size—a trend which in all likelihood will continue. Future developments in automotive engine designs will probably follow lines already successfully established in both automotive and aviation practice: the improvement of performance and fuel economy through further increases in compression ratios or by supercharging or both.

Figures 3 and 4, based on laboratory tests made on a 1940 model vehicle, show the gains in fuel economy, car speed and acceleration made possible by simultaneously raising the compression ratio from 6.1 to 1 to 8.6 to 1 and the fuel octane number from 78 to 95. And Ethyl research workers are now experimenting with engines having compression ratios above 11 to 1 and requiring fuel of over 100 octane number. Tests with supercharged engines also are being conducted. (Fig. 5.)

Engines and fuels are so closely related that their development is a joint responsibility of the automotive engineer and the petroleum technologist. Through their cooperative efforts, suitable fuels of higher anti-knock quality will be produced economically for engines which will utilize them with greatest efficiency.

We of the Ethyl Gasoline Corporation, through our research laboratories in Detroit and San Bernardino, are actively cooperating with engine designers in making the best possible use of tomorrow's fuels and with fuel refiners in producing gasolines best suited to the engines of tomorrow.

ETHYL GASOLINE CORPORATION, *Chrysler Building, New York, N.Y.*

Progress in Fuels

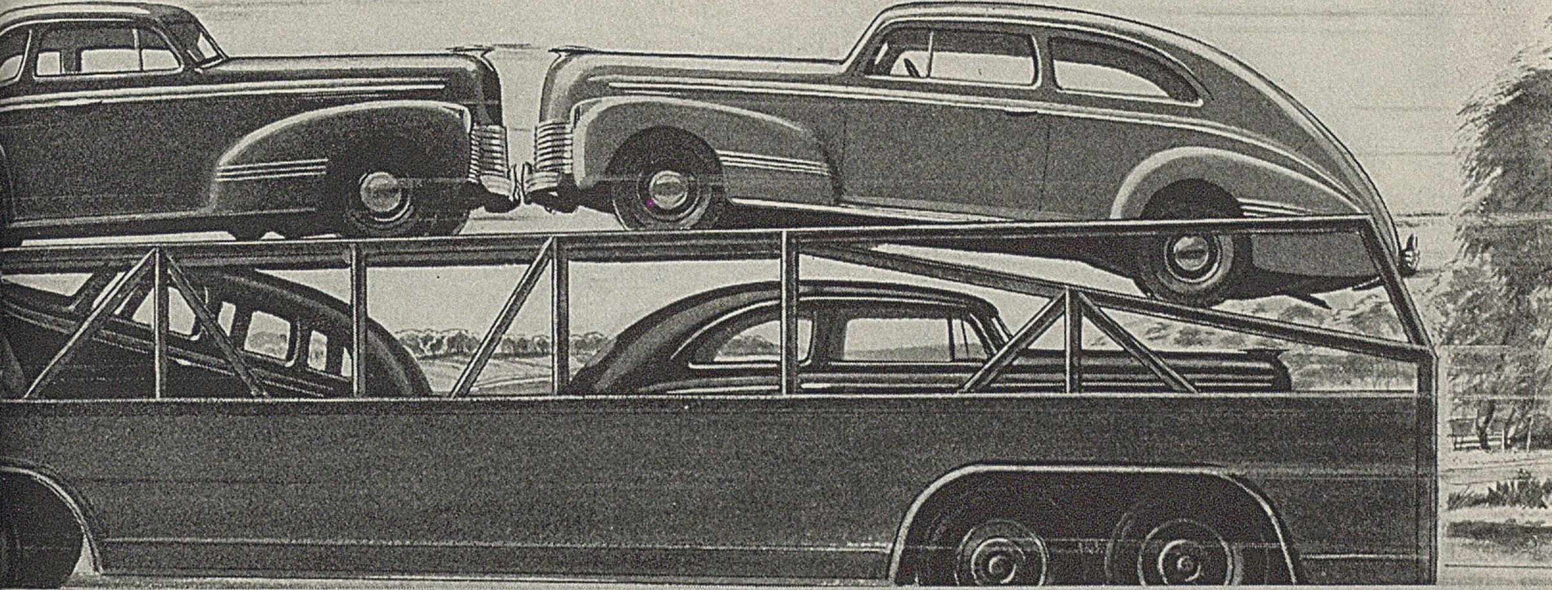


FIG. 1 (*below*) Octane numbers of automotive fuels have risen steadily over the past ten years. It is interesting to note that the regular gasoline being marketed today is superior in anti-knock quality to the premium gasoline of 1933.

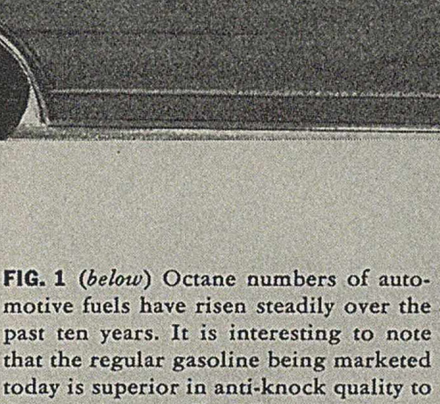


FIG. 5 (*right*) In laboratory tests on an eight-cylinder valve-in-head engine, supercharging to the limit permitted with 90 octane gasoline resulted in maximum brake horsepower of 145, as compared with 80 horsepower and an octane number requirement of 78 unsupercharged. Specific fuel consumption was substantially unchanged by supercharging.

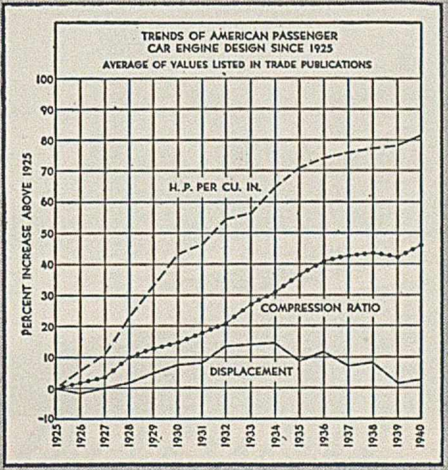
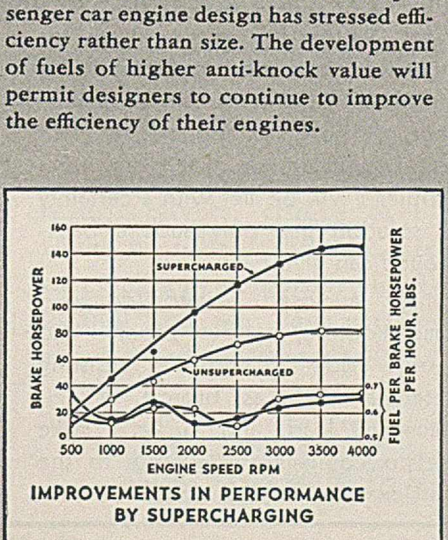


FIG. 2 (*above*) The trend of American passenger car engine design has stressed efficiency rather than size. The development of fuels of higher anti-knock value will permit designers to continue to improve the efficiency of their engines.



IMPROVEMENTS IN PERFORMANCE
BY SUPERCHARGING

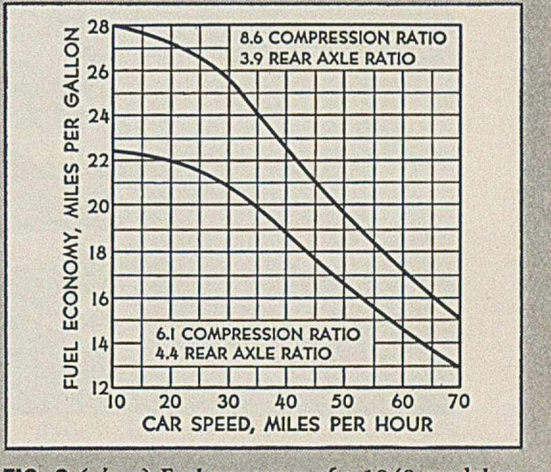


FIG. 3 (*above*) Fuel economy of a 1940 model vehicle at 6.1 compression ratio and 4.4 rear axle ratio compared with fuel economy at 8.6 compression ratio and 3.9 rear axle ratio. Maximum power ignition timing was used with each compression ratio. Accelerating ability at 8.6 compression ratio and 3.9 rear axle ratio is equal to that of the other combination at low speeds and is much better than the other at high speeds.

IMPROVEMENT IN FULL THROTTLE ROAD PERFORMANCE
OF A 1940 MODEL CAR WITH 8.6 COMPRESSION RATIO
AS COMPARED WITH THE SAME CAR WITH
6.1 COMPRESSION RATIO

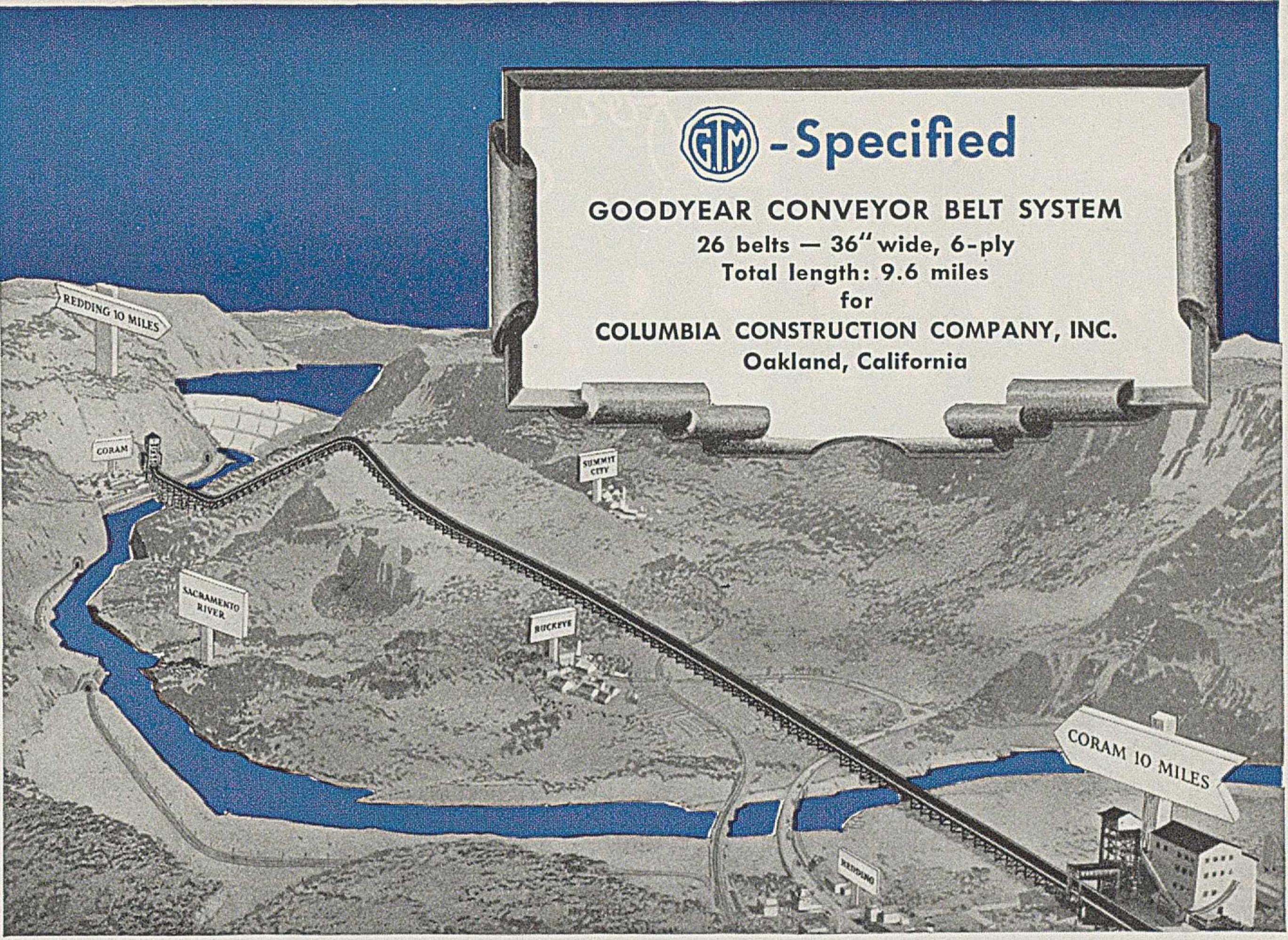
ALL DATA OBTAINED WITH SPARK ADVANCE FOR MAXIMUM
PERFORMANCE AND WITH A 4.4 REAR AXLE RATIO

ACCELERATION ON LEVEL ROAD	PERCENT IMPROVEMENT
10 TO 30 M. P. H.	17.2
10 TO 60 M. P. H.	18.0
ACCELERATION ON 11.6 % GRADE	
TIME REQUIRED TO CLIMB GRADE	25.8
SPEED AT TOP OF GRADE	67.6
TOP SPEED	5.4

THE FUEL OCTANE NUMBERS FOR "TRACE" KNOCK
WITH 6.1 AND 8.6 COMPRESSION RATIOS
WERE 78 AND 95 RESPECTIVELY

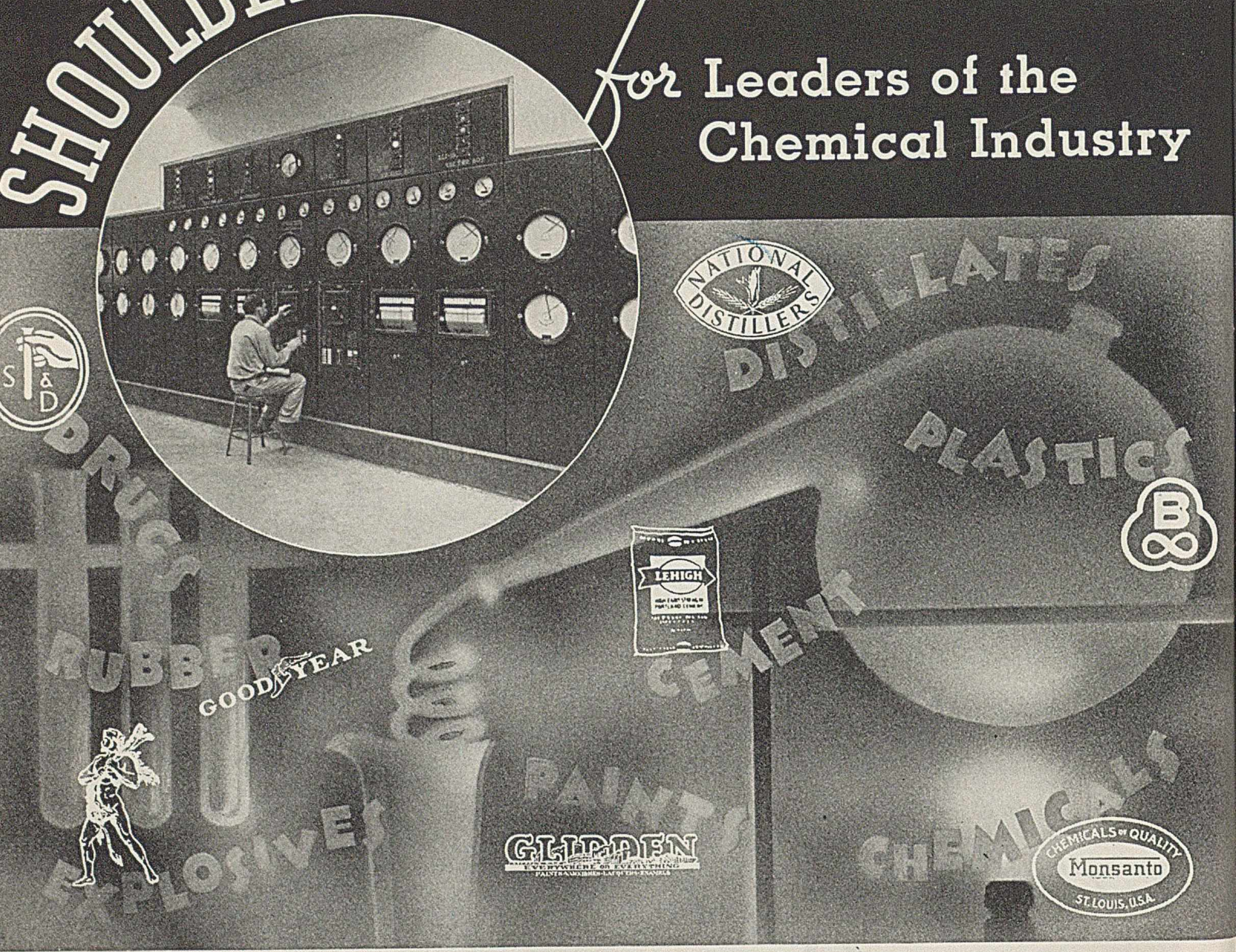
FIG. 4

NETTCO
We know when we have been well served and will not hesitate to call upon you again when we require equipment in your line



G.T.M. -Specified
GOODYEAR CONVEYOR BELT SYSTEM
26 belts — 36" wide, 6-ply
Total length: 9.6 miles
for
COLUMBIA CONSTRUCTION COMPANY, INC.
Oakland, California
REDDING 10 MILES
CORAM
SUMMIT CITY
SACRAMENTO RIVER
BUCKEYE
CORAM 10 MILES

SHOULDERING RESPONSIBILITY for Leaders of the Chemical Industry



THE Chemical Industry includes many lines, which, upon first thought, seem to be unrelated to it. So important are these various phases of the Chemical Industry, however, that we are in daily contact with this industry in some form or another.

Here again we find Brown Instruments "Shouldering Responsibility" for leaders of an industry where accurate measurement and control of temperatures, pressures, flows and liquid levels are major factors in the production of chemicals, plastics, explosives, paints, and other products comprising this industry. Brown Instruments produce facts and figures which enable engineers, operators and executives to maintain quality at its highest standard and costs at a minimum. They provide a constant checking and control service, indispensable to management. Regardless of the product you manufacture, or process, Brown Instruments will enable you, too, to improve your quality and reduce production costs. The services of the Brown Engineer are available to give you unbiased counsel on the application of indicating, recording and controlling instruments. Call him in. There is no obligation.

THE BROWN INSTRUMENT COMPANY, *A division of Minneapolis-Honeywell Regulator Company,* 4480 Wayne Ave., Philadelphia, Pennsylvania . . . Branch and distributing offices in all principal cities. Toronto, Canada: 117 Peter Street — Amsterdam - C. Holland: Wijdesteeg 4 — England: Wadsworth Road, Perivale, Middlesex — Stockholm, Sweden: Nybrokajen 7.

Learn what Brown Instruments are doing for others and what they can do for you. Our Booklet, "Instruments From the Executive Viewpoint" explains how. Write for it.

INCREASED INDUSTRIAL EFFICIENCY IS THE KEYSTONE OF PREPAREDNESS

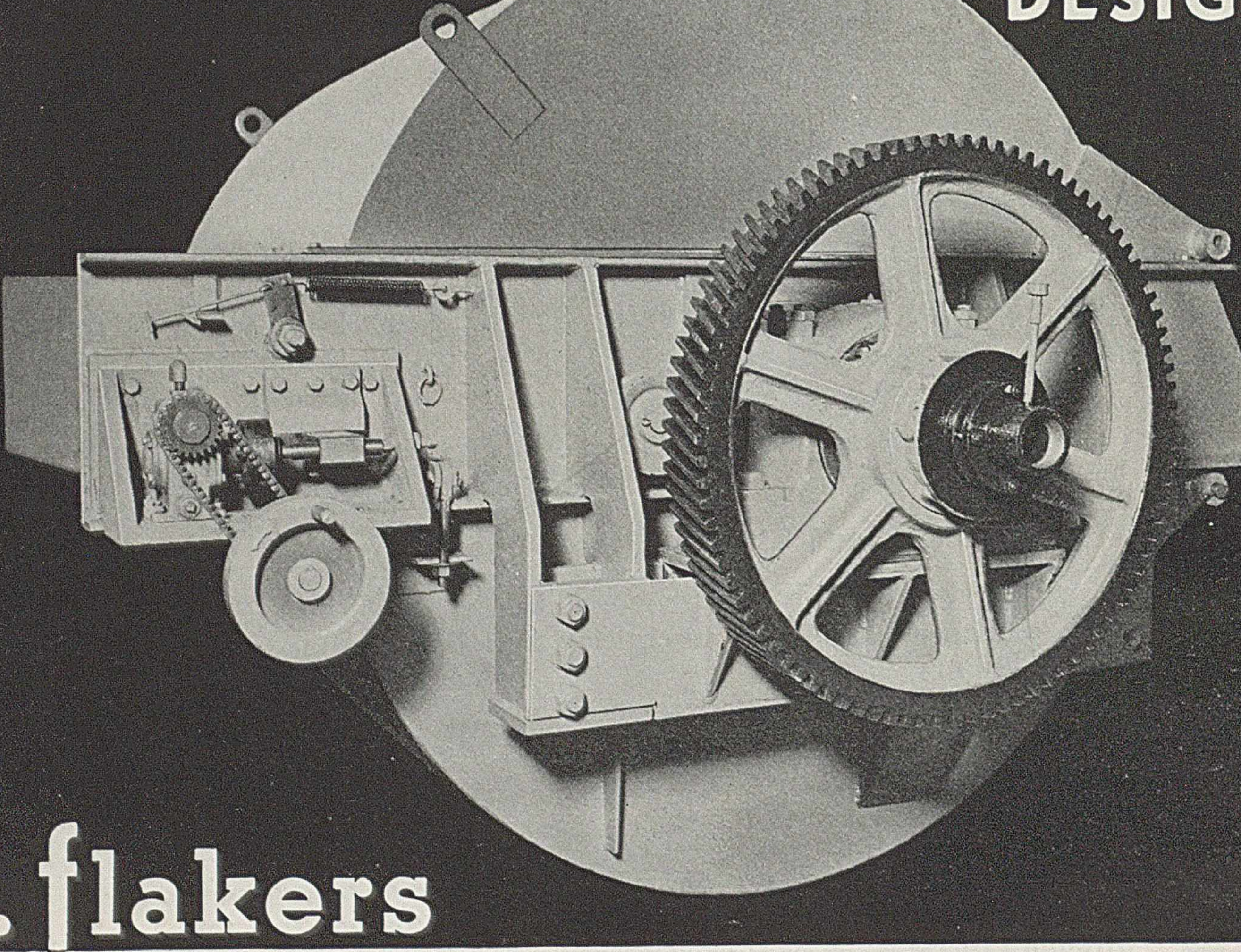
BROWN INSTRUMENTS

AND MINNEAPOLIS-HONEYWELL CONTROL SYSTEMS

For Temperatures . . . . Pressures . . . . . Flows . . . . . Liquid Levels
Speed Up Production — Keep Costs Down

Inset, Brown Instrument Centralized Control Board installed in the plant of one of America's largest oil refineries.

Typical of BLAW-KNOX PROCESS EQUIPMENT DESIGN



...flakers

Blaw-Knox has designed and manufactured the very effective flaking drum shown in the photograph, to enable chemical products to be economically supplied in flake form. This equipment chills the liquid on a highly polished stainless steel drum and scrapes off the flakes with an adjustable knife.

Blaw-Knox engineers are constantly designing new equipment to shorten production time and increase the quality of many of the product groups in the process industries.

BLAW-KNOX DIVISION
OF BLAW-KNOX CO.
FARMERS BANK BUILDING, PITTSBURGH, PA.

BLAW-KNOX PROCESS EQUIPMENT INCLUDES: Inclined High Velocity Evaporators . . . Vertical High Velocity Evaporators . . . Forced Circulation Evaporators . . . Rotary Dryers . . . Autoclaves . . . Vacuum Rotary Dryers . . . Extraction Apparatus . . . Distillation Equipment . . . Hot Oil Circulation System . . . Vulcanizers . . . Absorbers . . . Impregnating Equipment . . . Solvent Recovery System . . . Heat Exchangers . . . Condensers . . . Mixing Equipment . . . Distilled Water Evaporators

TRICRESYL PHOSPHATE

Fire-Retarding Plasticizers

TRIPHENYL PHOSPHATE

TRICRESYL PHOSPHATE is a practically colorless, odorless liquid weighing about 9.7 pounds per gallon. It has a high boiling point and an evaporation loss of only 0.2% in 100 hours at 100°C. It is the standard fire-retarding plasticizer for nitrocellulose and is compatible with most lacquer resins, giving tough, firm, flexible films of excellent weathering qualities. The ortho isomer has been removed, thereby reducing toxicity dangers to a minimum and making the product more suitable for many applications.

USES

Plasticizer in cellulose ester varnishes, lacquers and plastics; fire retarder in nitrocellulose.

SPECIFICATIONS

Form	Clear, oily liquid
Color	Essentially colorless
Specific Gravity at 20°/20°C.	1.165 ± 0.005
Refractive Index at 20°C.	1.556 ± 0.001
Acidity (as H_3PO_4)	0.01% max.
Free Phenols (Permanganate Test)	A distinct purple color to be present after 30 minutes. (10 gram sample—40 c.c. N/100 $KMnO_4$.)

TRIPHENYL PHOSPHATE is a white crystalline compound melting at about 48.5°C., and boiling at 245°C., at 11 mm. pressure. Its evaporation rate is of the same order as Tricresyl Phosphate. It is miscible with the common solvents and thinners and with vegetable oils.

It is the most suitable flame retarder for cellulose acetate, and in addition imparts good flexibility and high tensile strength. Acetate films containing about 20 parts Triphenyl Phosphate by weight per 100 parts acetate show satisfactory flame-resistance.

USES

For rendering acetyl cellulose, cellulose formate, airplane dopes, etc., non-inflammable; as lubricant; as plasticizer for cellulose acetate and ethyl cellulose.

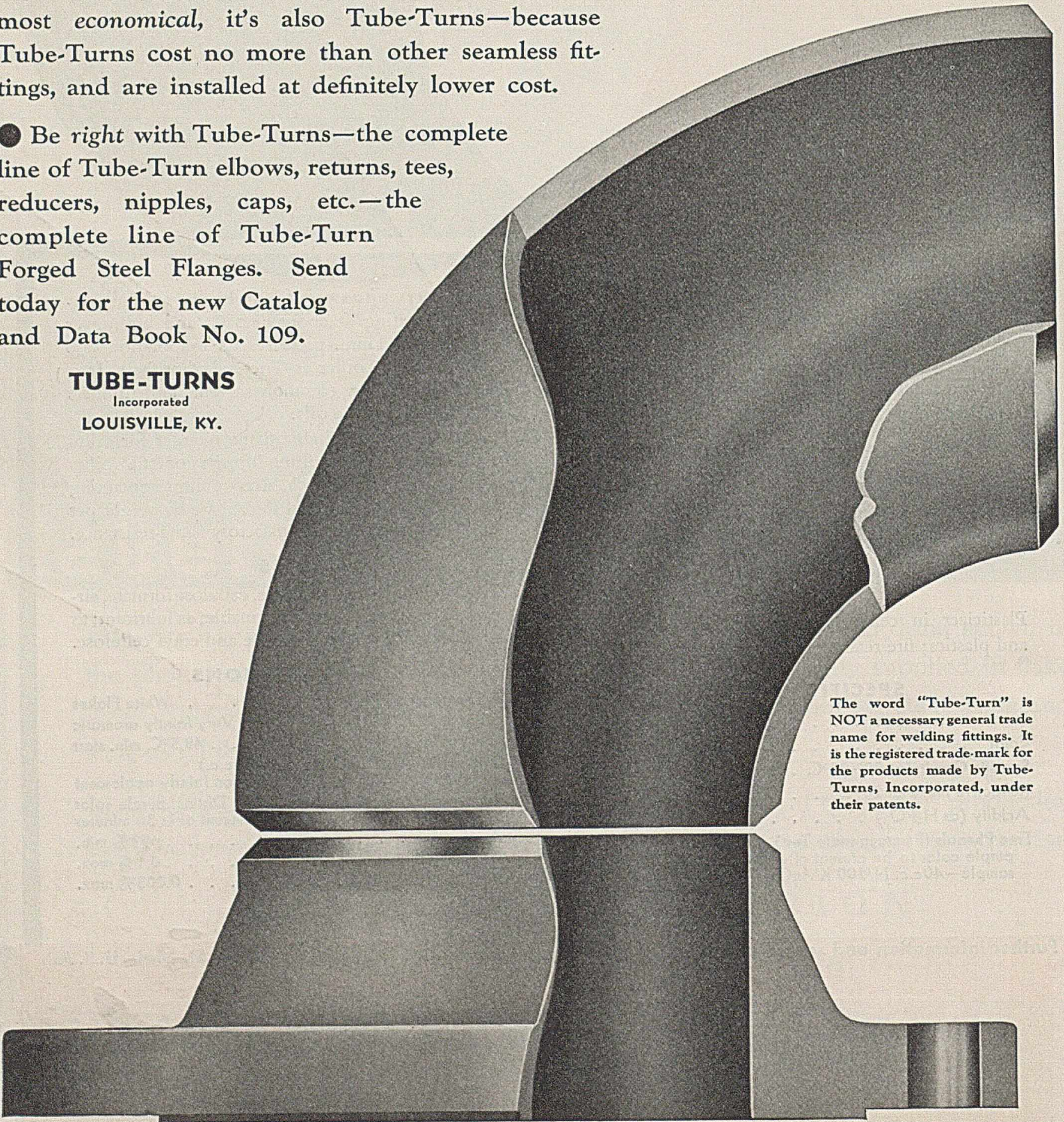
SPECIFICATIONS

Appearance	White Flakes
Odor	Very faintly aromatic
Melting Point	48.5°C. min. start
Solution in Alcohol (10 gms. in 50 c.c.) Turbidity	Not more than faintly opalescent
Permanganate Test	Distinct purple color to be present after 30 minutes
Assay	99% min.
Free Phenol	0.1% max.
Acidity (as H_3PO_4)	0.003% max.

Further information and samples sent on request. Inquire: MONSANTO CHEMICAL COMPANY, St. Louis, U. S. A.

MONSANTO CHEMICALS

SERVING INDUSTRY... WHICH SERVES MANKIND



99.63% EFFICIENCY IN RAYON SOLVENT RECOVERY PLANT*

"Columbia" Activated Carbon System Proves Effective, Economical, and Safe

RECENT tests over a 19-week period on a "Columbia" Activated Carbon solvent recovery plant for recovering acetone in the manufacture of rayon showed an average efficiency of 99.63 per cent.* Such performance explains why the rayon industry is swinging so strongly toward the "Columbia" Activated Carbon process.

Smaller Utility Requirements— Greater Flexibility

The "Columbia" Activated Carbon system has replaced the water absorption system in a number of large rayon plants because it costs less to operate. One report indicates only half the steam and water consumption and less than one-third the electric power per pound of recovered acetone. In addition, the "Columbia" Activated Carbon system is more flexible because it will efficiently recover practically any low-boiling solvent under widely varying conditions of temperature, humidity, and vapor concentration.

Low-Cost, Safe Solvent Recovery

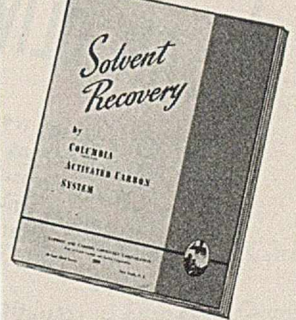
A plant producing plastic products replaced the condensation process of acetone recovery with the "Columbia" Activated Carbon system and reports the following advantages: "Lower original cost, greater overall efficiency, lower recovery expense per unit of recovered solvent, somewhat less building space required, and indicated low maintenance cost." In addition, the activated carbon system is safe because it effects efficient solvent recovery at vapor concentrations far below the explosive range.

Why Not Save Your Solvent Dollars?

We can design and supply a complete "Columbia" Activated Carbon plant with guaranteed operating characteristics to recover such volatile solvents as alcohols, chlorinated compounds, esters, ethers, hydrocarbons, and ketones. If you vaporize solvents in your operations, give us specific data and let us help you determine what and where you can save.

*Only 0.37% of the solvent vapor in the air passing to the recovery plant was lost, even though the plant was operating 15% over design load during the last 7 weeks of the test period.

WRITE FOR THIS BOOK!



This book, which contains 32 pages and 26 illustrations, describes the "Columbia" Activated Carbon solvent recovery system and tells how and where it can be used profitably. A request on your company letterhead will bring you a copy, without obligation.

The word "Columbia" is a registered trade-mark of Carbide and Carbon Chemicals Corporation.

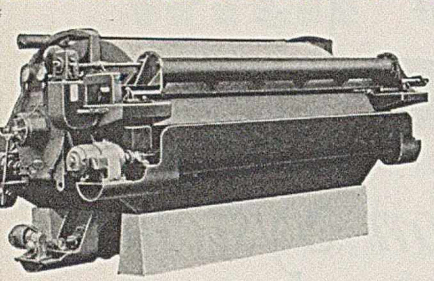
Representative Industries For Which We Have Designed and Supplied Complete Solvent Recovery Plants Include—
Rayon . . . . Artificial Leather
Lacquer Coatings . . . . Rubber
Rotogravure Printing . . Plastics

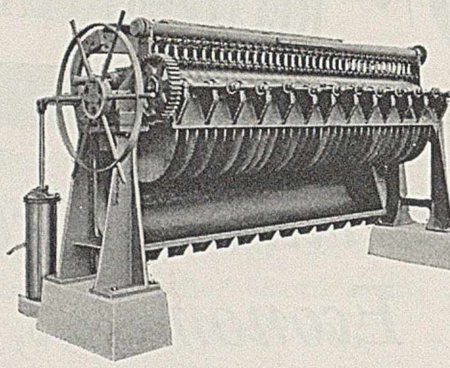
For information concerning the uses of "Columbia" Activated Carbon, address:

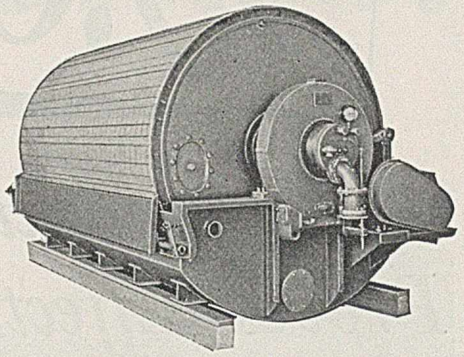
CARBIDE AND CARBON CHEMICALS CORPORATION
Unit of Union Carbide and Carbon Corporation
UCC
30 East 42nd Street, New York, N. Y.

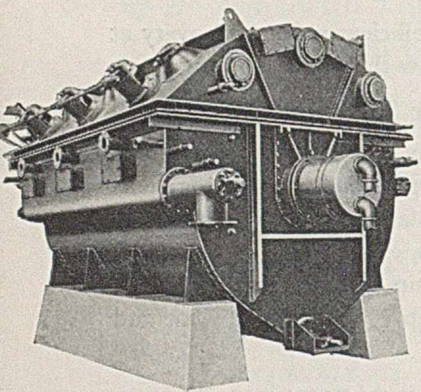
PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

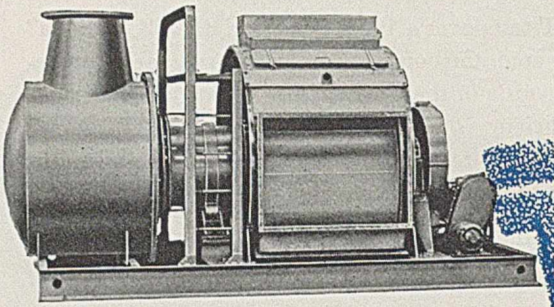
Your Best Defense

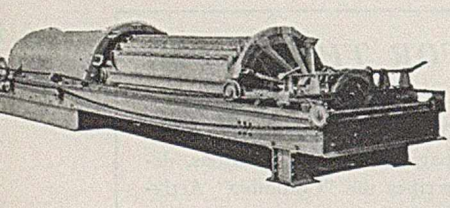












Special Filters

AN OLIVER UNITED SPECIALTY

Of course, we design and construct those well-proved standard filters such as Olivers, Americans, Dorrcos, Sweetlands, Kellys, Oliver Pressures, but to the processing plants stepping up their programs and enlarging their activities it may well be that the special filters carrying the name "Oliver United" will be more important.

For filtration problems involving corrosion we can provide filters protected by

Rubber
Silicon Bronze
Lead

Stainless Steel
Monel
Wood

and other materials

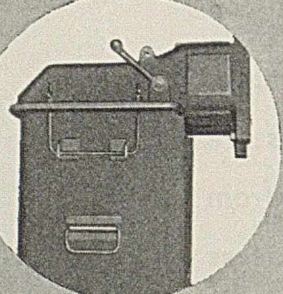
For handling products giving off gases or vapors, we can provide hooded filters; for maintaining high or low temperatures, we have jacketed filters.

We have filters such as the Oliver Top-Feed Filter designed especially for crystalline materials; filters such as the open and hooded Oliver Precoats for materials carrying slimy or gummy solids; filters such as the Kelly for extremely high pressure operations.

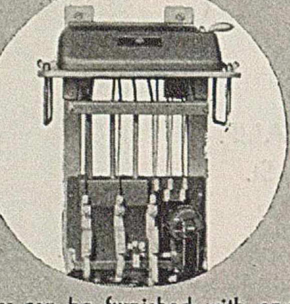
All evidence points to Oliver United as the best source for
clarifiers not only for routine operations but for special
special filters.

Announcing The NEW

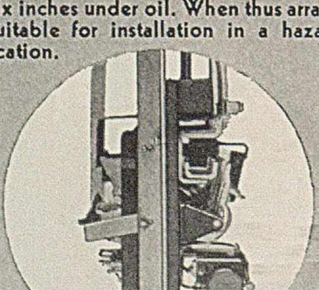
3 IMPORTANT FACTS ABOUT THIS G-E OIL-IMMERSED STARTER



he corrosion-resisting cast-iron head is designed for making conduit connections from op, bottom, or either side. Installation is asy, expense is low.



he starter can be furnished with operating arts six inches under oil. When thus arranged, is suitable for installation in a hazardous as location.



he circuit breaker can interrupt a short circuit f 10,000 amperes. The breaker and the magetic switch are mounted back to back. This rrangement is compact and is better able to ithstand the mechanical stresses that a short ircuit on the line might cause.

EASY TO INSTALL

The CR7008 oil-immersed starter consists of a magnetic switch for motor starting and a circuit breaker for disconnecting and for short-circuit protection. They come to you in one "package," to be installed as a unit—saving you time, trouble, and expense.

This starter is designed for wall mounting. It needs only four bolts. The cast-iron head, a new feature, keeps the case from the wall and enables you to make rigid conduit connections from *top, bottom, or either side*. The incoming and outgoing terminals have solderless connectors. The control terminals are furnished with a binding screw. All this makes for easy wiring. Two stainless-steel tank holders provide a simple means for attaching the tank.

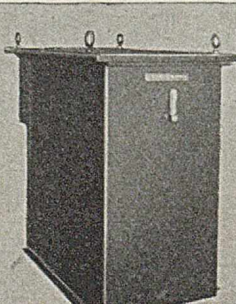
ASSURES LOW MAINTENANCE, DEPENDABLE SERVICE

All operating parts, including the overload relays and the circuit breaker, are immersed in oil. Corrosive fumes cannot get at them. The cast-iron head, mentioned above, resists corrosive moisture that may condense on it. The case is of copper-bearing steel, painted with aluminum paint. The contactor tips are extra heavy and are reversible in the Size 2 and Size 3 starters, thus being good for twice the usual length of service. Flamenol wire, which is resistant to oil, is used thoroughout the switch in making connections.

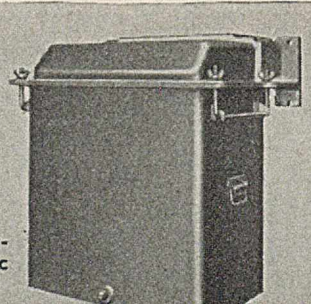
EASY TO INSPECT

The operating devices are easily accessible. A special track arrangement on the inside of the tank facilitates moving the tank up and down. Hooks on which to hang the tank after it has been lowered are provided. You don't have to set the tank on the floor and run the risk of its being upset and spilling the oil.

THE G-E LINE OF OIL-IMMERSED CONTROL MEETS



Type C4, high-voltage, high interrupting capacity



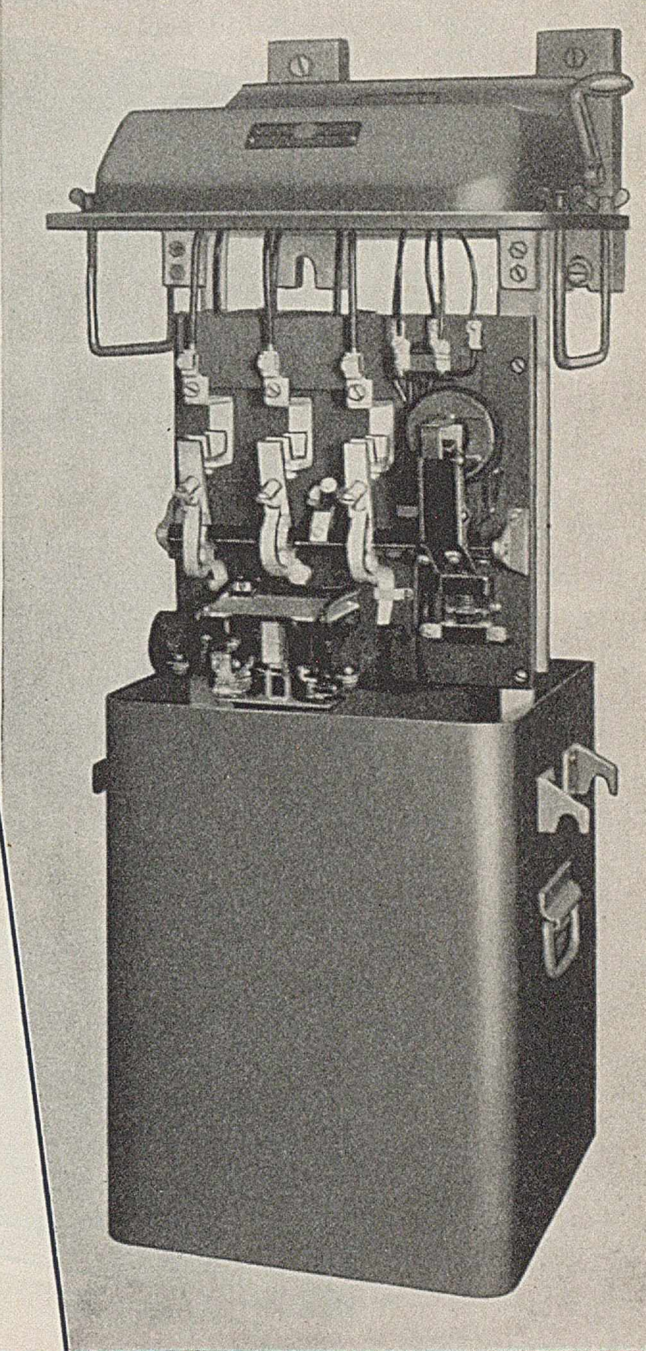
Type CR7006, low-voltage magnetic starter

G-E OIL-IMMERSED COMBINATION STARTER for Low-voltage Service

PROTECTS MEN AND EQUIPMENT

Thermal overload relays, specially designed for operation in oil, protect the motor against damage from excessive overloads. They are mounted with contacts at the bottom or side to prevent the possibility of oil sludge's interfering with their action. Undervoltage protection safeguards machines and operators from danger of unexpected restarting after a power interruption. The incoming terminals and the wires to the top of the circuit breaker are completely shielded so that an operator cannot make accidental contact with these live parts.

The new type of circuit breaker has a rating of 10,000 amperes and will interrupt short circuits up to that value. It is operated by means of a handle extending through the switch cover. The tank cannot be lowered unless this handle is in the "off" position, and power cannot be turned on until the tank is in place—an important safety feature.



HERE'S the oil-immersed control you've been asking for! This G-E CR7008 combination starter is now available for service with motors up to 30 hp at 220 volts, and 50 hp at 440 volts. It's packed with the features you want—new ones to meet the latest ideas and suggestions of operating men, old ones that have thoroughly proved themselves under actual operating conditions in refineries and chemical plants.

Decide now to install these new starters in your plant or refinery. Our nearest representative will be glad to go over your requirements with you. General Electric, Schenectady, N. Y.

ALL YOUR REQUIREMENTS!

Type R1AA, high-voltage, normal interrupting capacity

GENERAL ELECTRIC

INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY • HARRISON E. HOWE, EDITOR

EDITORIALS

Foreign Control

NOT until after the United States entered the World War did we begin to learn to what extent individuals and corporations in other lands exercised control over American products and some processes operated here. This control and its exercise in the effort to prevent the full use of our facilities and resources caused the Alien Property Custodian to take steps which led to the formation of the Chemical Foundation, Inc.

It was not to be expected that the owners of the property thus acquired for the benefit of the United States would be willing to undergo a repetition of the experience. Consequently, various plans have been set up and put into operation intended by the legal mind to make difficult or impossible a similar transfer of property should the occasion arise. One device is for trustees to vote stock of undisclosed owners sometimes resident in different parts of the world. There are doubtless many other methods. Now, it is well to know the facts in advance of need. Senate Resolution 309, Seventy-Sixth Congress, third session, authorizes a committee to investigate interstate commerce conditions affecting national defense. The current impression is that this committee will begin its hearings shortly after the first of January, with the announced purpose of learning the ownership of stock, influence in, control of, and power over domestic business and production related to national defense, by any firm, person, partnership, association, corporation, foreign government, or agents or instrumentalities thereof.

The Committee on Interstate Commerce or a duly authorized subcommittee thereof has been directed to make the investigation and to report. This committee can be of great value to the country if it strictly follows its terms of reference and does not conduct a little fishing expedition into the affairs of corporations having no bearing on the main question. Let us hope, in this instance at least, the investigation can be confined to those questions affecting national defense in fact.

Serious Monkey Business

MONKEY business is not a laughing matter when you can't buy monkeys to save your life! For monkeys do save lives as test animals for new drugs before clinical tests are made on human beings. Only one monkey out of seven or eight imported into this country finds his way into a zoo or circus. All the others fulfill a useful purpose in scientific tests for which their similarity to humankind particularly adapts them.

Normally, some 15,000 monkeys a year are brought to the United States from British India, which for humane reasons enforces an embargo on their export during the hot, rainy summer months. This spring shortage of ships and war restrictions prevented importers from bringing in enough to meet the demand over the summer. War continues to hamper imports.

We face a serious shortage of animals because of the active development of new drugs. Especially important at present are the large numbers of derivatives of sulfanilamide, sulfapyridine, sulfathiazole, and others coming out of chemical research laboratories which must be tested on monkeys before they can be used clinically on human beings. The search for substitutes for quinine now being pushed by a committee of the National Research Council will also require large numbers of monkeys. Research on poliomyelitis is being impeded now for lack of monkeys, since no other test animal will contract the human form of this disease.

The monkeys used are members of the family *Macaca rhesus* and grow wild in the jungles of India. They are the kind commonly shown in zoos and circuses. Attempts to breed them elsewhere have failed, although efforts are now being made to grow them in Puerto Rico. Cebus monkeys, native to South and Central America, are not satisfactory test animals.

Until rhesian monkeys are raised in or near the United States, manufacturers of synthetic drugs here must continue to watch and hope for imports.

Chemistry and Preparedness

CHEMISTS and the chemical industry occupy such a place that a preparedness program without their contributions is impossible. The products of chemistry must be available in vast quantities if a defense program is to be effective. We can think of no basic industry, no article of commerce, no requirement of defense, that in some way does not involve the products of chemistry. Happily our position is vastly different than in 1917. Harry L. Derby, president of the American Cyanamid and Chemical Corporation, in a recent address made some comparisons.

In 1914 the chemical industry of the United States represented an investment of $369,000,000, an annual business of $261,000,000, and had 47,681 employees. Its federal corporate taxes were about $3,000,000.

In 1937 the investment had reached $2,000,000,000, the annual business $1,250,000,000, and there were 150,000 employed. Taxes were over $56,000,000. At the present time it is estimated that $35,000,000 is spent annually for research and even more for development of new products. Today the chemical industry is far ahead of many other essential industries in its capacity for production and could provide increased facilities in a relatively short time if necessary.

In addition to all this the chemist may be called upon for such a variety of work that plans should be made accordingly. Some two or three thousand active chemists hold reserve commissions, most of them in technical branches of the Army. Mobilization is based upon the use of these men in government service should they be required, and most of them have been trained for specific assignments in line with their professional work. This includes the manufacture of some materials which can be produced more economically and with greater safety in government arsenals, as well as possible assignment to plants for particular activities in connection with government orders.

In many cases peacetime industry should be prepared to share its trained and experienced personnel with the Government and arrange to begin training those who might take the places of the men called. Reserve officers and consultants, who have given their time to prepare themselves to serve in case of need, should be able to return to their present employment after emergency service. To provide for their temporary absence would be expected of any progressive management.

Should a real emergency arise beyond any now foreseen, a tremendous burden will fall on the chemical industry. The production of large quantities of material will mean careful checking at every stage. Sometimes the discovery of substitutes and even research and development as new problems arise will claim attention. Many manufacturers know what they are expected to produce in a crisis and have carefully studied plans and specifications. All too often, commercial concerns have taken government contracts with the hope of beating down the quality of the article specified. Present specifications have been prepared and approved by the industry concerned with a view to production of articles of definite quality under wartime conditions. Military operations are based upon the receipt of adequate quantities of standard quality materials. The problem therefore becomes that of meeting specifications on large outputs. This program calls for the coordination of a program of manufacture with a plan for personnel. A part of present activity should certainly be the careful study of all the processes and products involved and planning the use of suitable personnel so that nothing will interfere with an even, steady flow of acceptable products.

Many will remember the difficulties of the past when a large percentage of production in some cases had to be refused. To prevent these and other errors advance study of all factors is necessary and should be under way. We are hopeful that "It is later than you think" is an overstatement but we had better act and work as if it were an understatement.

Incomplete

BEGINNING with the October 25 *News Edition* we print paragraphs from a report of the Scientific Advisory Service, maintained by several leading banks in an effort to spread the benefits of science as applied to industry. These statements of what industry now expects of research indicate much work remaining to be done; n some cases there may be a product or process ready but unknown to the inquirer, so that actual business may result.

The change in attitude on the part of some banks and bankers is significant. Too often they have come into the management of an industry in financial distress, only to discontinue scientific work. Time and again the banker has looked upon research as an unjustifiable extravagance and a place where a few pennies might be saved. What was really needed in many instances was an increase in research and the application of its results to put a new breath of life into an exhausted enterprise. But here is a group of banks not only assisting their clientele to make the acquaintance of scientists who might help them, but obtaining from over a thousand industries indications of what they would like to have scientists do.

More than that, this list of wants reaffirms a declaration often made by scientists that our work is incomplete. The world is far from finished. We have yet to find a scientist of experience who shares the defeatist attitude too common among economists, social workers, and politicians, who see no opportunity for youth.

Youth itself does not always share this attitude. One out of many possible examples is presented by the efforts of some college boys who have provided themselves with good jobs by tapping a valuable natural resource that but few had noticed. Beginning in a very small way indeed, three young men have been collecting and preparing for sale sea moss which grows along the New England coast. A similar moss has been imported for years from Europe, but now we have a domestic source with prospects of higher quality as improvements are made in the old-fashioned method of handling it. By recognizing an opportunity, a good livelihood has been made when expected jobs did not materialize.

Does it not seem strange that with so much to be done and so many anxious to do the work, present-day society finds so many obstacles to put in the way?

NEW TEXTILE FIBERS, FABRICS, AND FINISHES

Presented before the Division of Industrial and Engineering Chemistry at the 100th Meeting of the American Chemical Society, Detroit, Mich.

Resins and Plastics for the Modification of Textile Fabrics

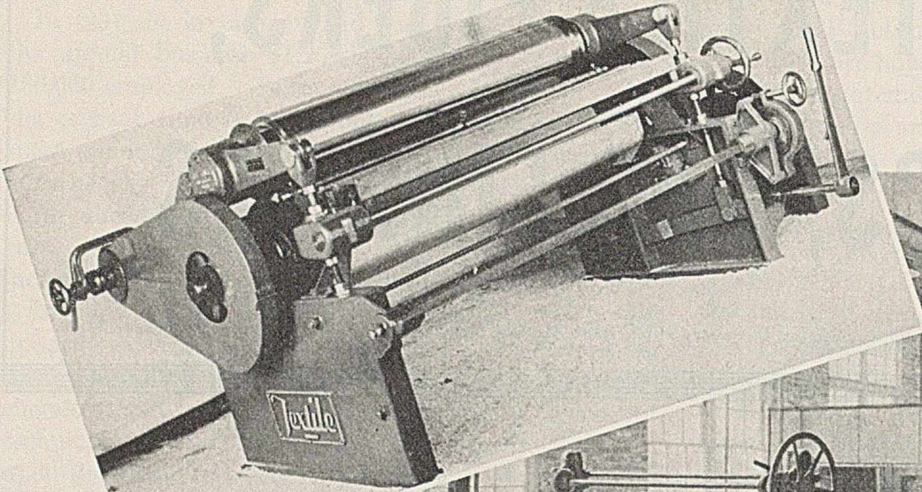
D. H. POWERS, Röhm & Haas Company, Inc., Philadelphia, Penna.

Recent years have seen the development of clear, colorless synthetic resins for textile fabric modification. These resins are applied as aqueous solutions or dispersions. In contrast to the older textile-coating resins for producing artificial leather and similar types of coated fabrics, these impregnating resins do not alter the surface appearance. However, they may greatly improve the tensile strength, resilience, durability, luster, and firmness of the fabrics. They impart to vegetable fibers many of the properties of animal fibers. Data are given to show the effect of applying different types of resins as well as of varying polymers of the same resin. The use of these water-dispersed synthetic resins is of increasing value and importance in the development of new and unique textile and industrial fabrics.

SYNTHETIC resins have been used for many years in coating lacquers applied to textile fabrics to produce oilcloths, tarpaulins, bridge-table covers, artificial leather, etc., and in each case the fabric merely acted as a backing or supporting material for a continuous, heavy lacquer film. In the last few years, however, an entirely new use of resins and plastics for the modification of textile fabrics has grown up. In this application the resins are not used as coating materials but are impregnated into the fiber and may impart to the fabric improved properties of luster, strength, or resilience, but in each case the appearance of the fabric is not destroyed and the resin-treated fabric retains all of the properties of a textile with its characteristic porosity, absorbency, elasticity, flexibility, and serviceability. While this new method of modifying fabrics with resins frequently uses relatively low percentages of resins on the weight of the fabric, because of its far wider range of application, the total resin consumed in this field has grown to a point where it far exceeds the volume of coating resins previously used.

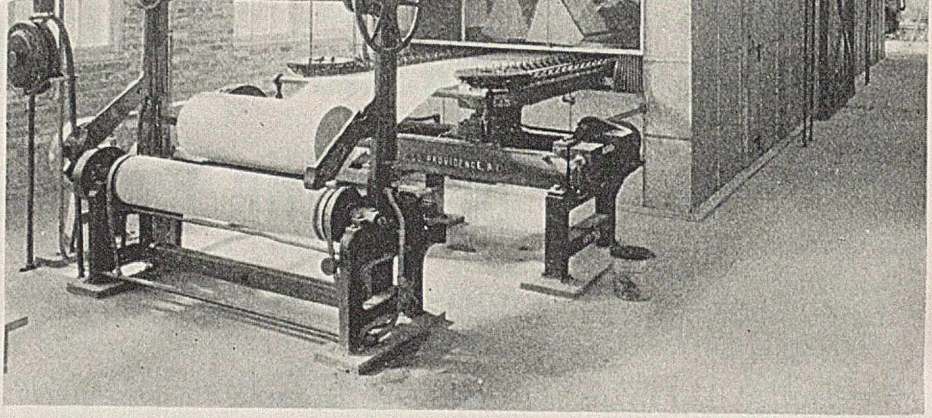
With this development of a new technique for the resin modification of textile fabrics, the object has been to improve or change some of the physical characteristics of the fabric without changing the appearance of the fabric. This development has proceeded so widely and so successfully that today there are fabrics which consist of 30 per cent synthetic resin and 70 per cent fiber, and yet they retain all of the appearance, feel, and even microscopic characteristics of a textile fabric made exclusively of natural or synthetic yarns. In other words, the resins are being impregnated into the individual fibers, and while they are modifying the properties of the fibers, they are not being used to coat the fibers like a lacquer or varnish. This new type of resin application is adaptable to all types of fibers and fabrics, and today there are millions of yards of cotton, rayon, wool, and silk fabrics which have been modified and whose serviceability has been improved by the addition of 1 to 30 per cent of specially developed synthetic resins.

The types that have been most successfully developed for this modification of textile fabrics are the clear, colorless, light-stable resins which can be dispersed or dissolved in water solution. It is necessary that resins of this type be



(*Left*) Two-Roll Roll Padder Used for Application of Resin Finishes to Fabrics

Courtesy, The Textile-Finishing Machinery Company



(*Right*) Delivery End of a Tenter Range Used for Drying in the Finishing Process and for Curing Fabrics Treated with Urea-Formaldehyde Resins

Courtesy, The Textile-Finishing Machinery Company

used, for they must not alter the shade of the most delicate tint and must be applied from water to ensure thorough penetration and to avoid coating and lacquer effects. The same resin may be applied either as a surface coating from a solvent or from a water dispersion to give a lustrous finish, or from a water solution to give resilience and produce three entirely distinct effects, even though the composition of the deposited resin may be substantially the same. The important point is the location, distribution, and concentration of this deposited resin. Effects have been obtained by applying unpolymerized resins in aqueous solution and polymerizing them within the fiber that cannot be matched or duplicated by any other method of impregnating or treating, and it is this permeation of the low-polymer resins into the fiber that has opened up a new and large field for resin application.

Resins to Change Character of Fabric

It is possible to obtain a great variety of effects by the proper selection of resins and by varying the method of application. It has reached the stage today where a fabric may be modified or changed in as many ways with resins as it is possible to change it by varying the count, the twist, the type of fibers used, and the method of finishing. Resins are being used in large quantities to give rayon fibers the resilience of wool, cotton fibers the luster of silk, cotton fabrics the stability of a high-grade worsted, spun rayons the character and quality of high-priced woolens, and cottons and rayons the coolness and absorbency of linen. In addition to these effects, it is possible to improve the tensile strength, double or triple the wearing properties of the fabric, increase or decrease the elasticity and elongation of the yarns, increase or decrease the luster of the fabric, and improve the washability and serviceability of the garments. The modern fabric designer must consider the use of resins in developing new and novel fabrics, for they are just as important today as the designer of twenty years ago considered the blending of animal and vegetable fibers and the variation of twist and yarn count. The use of synthetic resins in the modification of spun rayon fabrics has tremendously assisted the promotion of this fiber to the point where it is the most important development today in the suiting and dress goods field. Further application of resins will greatly increase the range of application of these spun rayon fabrics into new and unexplored fields.

These synthetic resins are being used as a part of the warp sizing to impart better wearing properties to the finished fabric. They are being used as binders for bright pigments to give better light fastness to the finished fabric. They are being used as finishing agents to improve the wearing and washing properties of all types of fabrics from the sheerest lawns to the heaviest drills.

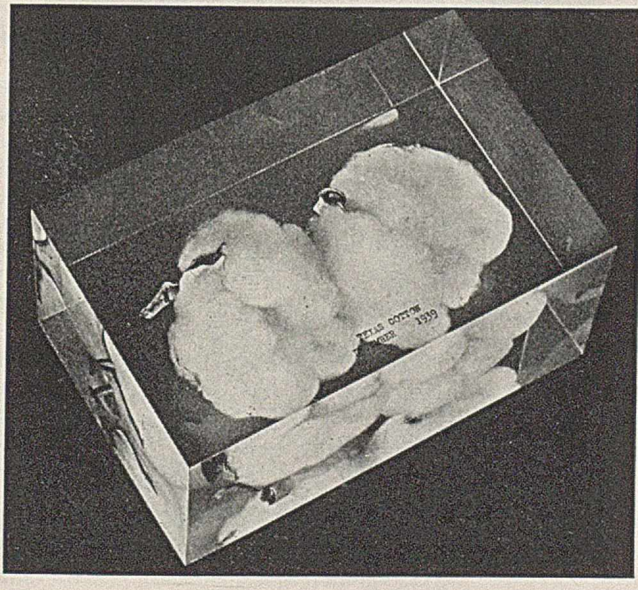
Development of Resin Modification

In tracing the development of synthetic resins for textile finishing, a great deal of credit goes to the Tootal Broadhurst Lee Company of Manchester, England, for the pioneer work in applying phenol-formaldehyde and urea-formaldehyde resins to cotton fabrics. They showed that unpolymerized urea-formaldehyde and phenol-formaldehyde resins could be impregnated and squeezed into the core of cotton and linen fabrics and, when polymerized in this position, produced fabrics with tremendously improved resilience. They further showed that if the surface or coating resin could be removed before it was polymerized, the resulting fabric was not stiffened and retained all of its initial suppleness, fullness, and drape. Their work goes back nearly fifteen years, but it was not until about seven years ago that they came to the United States with their anticrease process in an effort to license all of the large textile mills. While the development of this process has been slow in this country, there is no question but that it was the first successful application of resins to the modification of textile fabrics. This work was originally done on cotton fabrics, but it proved to be of tremendous value to the spun rayon fabrics which were developing for women's wear in 1935. Millions of yards of fabrics containing 10 to 15 per cent of urea-formaldehyde resin are on the market today. In no case does the fabric or fiber show any evidence of resin coating, and the treated fabric is as soft as, and occasionally softer than, the untreated and less attractive type.

In a study of the effect of some of these resins, we have treated a standard-construction cotton sheeting and a standard-construction spun rayon dress fabric with varying percentages of resins from aqueous solution or dispersion. In every case the resulting fabric has the same color and appearance as the untreated fabric. In every case the shade is unchanged. On the other hand, the resilience of the fiber in certain cases was more than doubled. The abrasion resistance in some cases is increased fivefold. The firmness of the fabric is decreased in some cases and tripled in others. The elongation is decreased as much as 50 per cent and may be increased by the same figure. Some of the results obtained are tabulated here; we should emphasize that in each case the resulting fabric, when handled and examined in a cursory way, would show no superficial variation in spite of large changes in elongation, wear resistance, and durability.

Application of Urea-Formaldehyde Resins

Urea-formaldehyde resins are of particular interest for textile application because of their clarity and light stability and because of the ease of their application from aqueous solutions. However, it is important that they be applied in exactly the right way, since their extreme brittleness will stiffen and tender a fabric and greatly reduce its wearing qualities if it is not correctly impregnated. Brittle surface resin will ruin the appearance and handle of any fabric, and only after years of experimenting can the textile mills now handle these stiff resins without fabric embrittlement.


Cotton Bolls Embedded in Acrylate Resin by Process Developed by Charles E. Sando of the U. S. Department of Agriculture

Effect of Squeeze. Fabrics were treated with a 9 per cent aqueous solution of low-polymer urea-formaldehyde resin and with an 18 per cent solution of this same resin. The fabrics were run through the 9 per cent solution with a light squeeze and through the 18 per cent solution with a tight squeeze so that the actual resin content of the fabrics was the same in both cases. After impregnation, the fabrics were dried and cured for 5 minutes at 300° F. to insolubilize the resin. The following table shows the differences obtained in these two fabrics having the same resin content:

	Tensile Strength[a], Lb./Sq. In.	Elongation[a], %	Crush Resistance[b]	Abrasion Resistance[c]
Original fabric	120	23	2.5	2100
9% soln., light squeeze	121	20	3.0	960
18% soln., tight squeeze	131	24	3.3	1460

[a] Tensile strength and elongation were tested on a Scott machine. Figures are averages of five breaks using 1-inch jaws and a 3-inch gap.

[b] Tested according to Tootal Broadhurst Lee specifications; results are a mean of three tests. All fabrics were tested after conditioning for at least 8 hours at 76% relative humidity. A good worsted will have a crush resistance value of 2.8–3.2.

[c] Tested in accordance with Tootal Broadhurst Lee standard; test piece rotated under a given load at high speed against a heavy worsted fabric of standard construction.

Effect of Concentration. Where the fibers are impregnated with a low-polymer resin, the concentration applied is extremely important. Each fiber or fabric seems to have a saturation point or limiting concentration which it will hold. When applying higher concentrations, the excess seems to spill over and thus give brittle surface effects, poor abrasion, and fabric stiffness. This saturation point seems to be dependent on a great many factors, such as the twist of the fiber, the tension on the yarn during weaving, and the depth of shade to which it has been dyed. Yarns which have been dyed in heavy shades, particularly with sulfur colors, take much less resin into the fiber. As a rule, mercerized yarns will hold more resin than unmercerized yarns, and rayons will consistently hold more resin than cottons or linens. The use of penetrating or wetting agents frequently improve resin pickup by the fibers, since they undoubtedly cause a swelling of the fibers.

The following table shows the effect of increasing resin concentration; in each case, a point of maximum value is noted and higher concentrations give a sharp reduction in effects and tend to coat and embrittle the fabric:

Stiffness of Fabric[a]		Resin Content of Fiber, %	Tensile Strength, Lb./Sq. In.	
Cotton	Spun rayon		Cotton	Spun rayon
2.0	2.0	0	118	120
2.1	2.2	1.0	114	124
2.1	2.4	3.0	112	127
2.4	2.5	8.0	98	130
9.4	3.6	20.0	86	114

[a] Calculated on basis of the original fabric having a value of 2.0 (1.0 in the warp and 1.0 in the filling). The values are l^4/t ratios compared with the l^4/t ratio of the original fabric, where l is the distance between supports and t is the amount of sag of sample. A difference of 0.2 is detectable in touching the fabrics.

Effect of Nature of Resin. It would be expected that entirely different effects could be obtained with different types of resins; but it is still more interesting to note that when urea-formaldehyde resins are applied in different degrees of polymerization or dispersion, they will give entirely different effects when used in the same concentration. The following table shows the effect of applying identical resin concentrations, but a variation of physical form of the resin and consequently a variation in the location of the deposited

Velvet Finished with Urea-Formaldehyde Resin for Increased Resilience and Resistance to Crushing

and polymerized resin. In each case the resin was applied from aqueous solution or dispersion, squeezed into the fabric with a tight nip, and dried and cured in the usual way:

Type of Urea-Formaldehyde Applied	Abrasion Resistance Cotton	Abrasion Resistance Spun rayon
Control	3,000	2300
True water soln.	3,500	2200
Intermediate polymer in true soln.	2,200	2700
Intermediate polymer in colloidal soln.	1,000	4100
Higher polymer in colloidal dispersion	7,000	3100
Very high polymer in colloidal dispersion	14,000	2800

All of the other properties of the cotton and spun rayon fabrics changed markedly with the different types of resin used, but the relative resistance to abrasion of the treated fabrics offers a single value showing the great variations possible with the same concentration of the same resin. It should also be emphasized that each type of fiber and each fabric offers a separate problem, and so general conclusions cannot be drawn regarding the effect of any one type of resin on all types of fabrics or fibers.

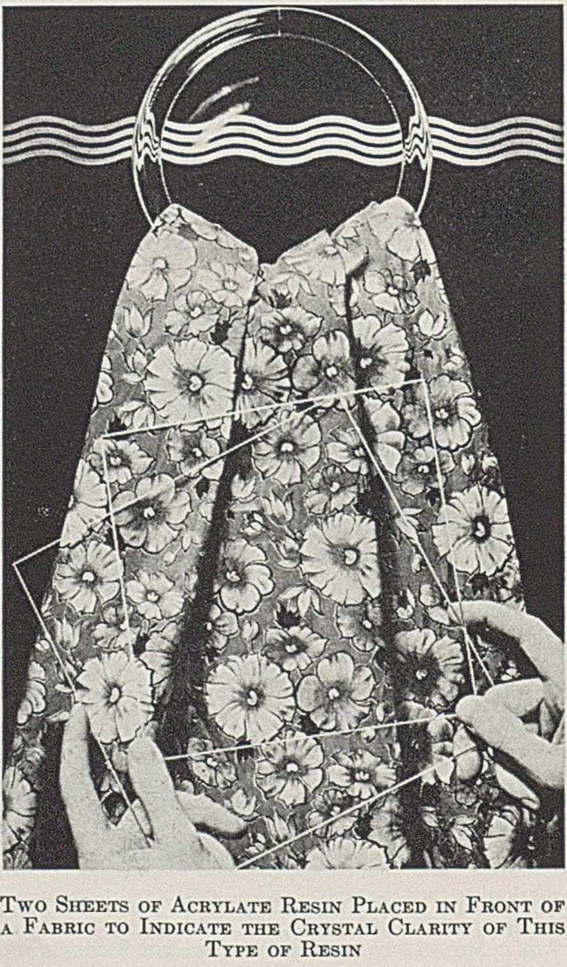
Application of Acrylate Resins

While the urea-formaldehyde type resins are interesting because of their ease of application from aqueous solution in low or high degree of polymerization, other resins are finding general application for the modification of textile fabrics. One of the most important classes is the acrylates. These resins are valuable because of their clarity, freedom from color, and stability to oxidation and aging. The general use of these acrylates for textile processing has been made possible by a unique method for their polymerization and dispersion in aqueous solution in the absence of any organic solvents or plasticizers. As a result of this process it is possible to prepare an extremely fine colloidal dispersion of an acrylate resin which is very hard and tough or very soft and plastic. These dispersions are unique and entirely different from the emulsions which may be prepared by emulsifying solvent solutions of highly plasticized resins in the presence of large percentages of emulsifying and stabilizing agents. Impregnating a textile with a solvent-free dispersion of a hard acrylate resin has no stiffening action whatsoever. It gives the same effect as treating a fabric with a 5–10 per cent dispersion of kaolin, with the tremendous difference that the resin is clear, colorless, and transparent, and may be embedded between the fine filaments to improve their tensile strength, durability, and wearability. They may improve resilience, but since the resins themselves are not brittle one does not encounter the problem of embrittlement which must be constantly guarded against when working with urea-formaldehyde resins.

The following table shows the influence of varying the hardness of the acrylate resin dispersed in water. Here again the effects are different on cotton from those on spun rayon, and no general conclusions should be made as to the results obtained with any given resin:

	Tensile Strength, Lb./Sq. In.		Abrasion Resistance		Stiffness of Fabric	
Resin Type	Cotton	Spun rayon	Cotton	Spun rayon	Cotton	Spun rayon
Control	131	121	3,000	2000	2.0	2.0
Hard acrylate	132	128	10,000	3000	4.0	4.0
Medium acrylate	130	141	9,000	5000	2.8	3.6
Soft acrylate	121	134	15,000	4000	2.3	2.1

In each series the same concentration of resin was deposited in the fabric. These changes were produced with resin concentrations as low as 2–3 per cent. In general, it has been found that low concentrations of the acrylates have more



Two Sheets of Acrylate Resin Placed in Front of a Fabric to Indicate the Crystal Clarity of This Type of Resin effect on the properties of the fabrics. On the other hand, it is usually possible to incorporate higher percentages of the urea-formaldehyde resins without stiffening or firming the handle of the fabric.

Other Resin Types

While the urea-formaldehyde and acrylate resins are the most important and most generally used on textiles because of their clarity and ease of application, other types, such as the alkyds, vinyls, and styrenes, are finding an increasing application, particularly where they produce certain specific effects. The following table gives a general comparison of the effects which may be obtained with the same concentration of different type resins on textile fabrics:

Type of Resin	Stiffness[a]	Resilience[b]	Durability[c]	Tensile Strength[d], Lb./Sq. In.
Control	2.0	2.3	10	51
Urea-formaldehyde soln.	2.4	3.2	11	47
Urea-formaldehyde dispersion	4.0	2.7	45	61
Hard acrylate dispersion	11.7	2.6	36	62
Soft acrylate dispersion	2.3	2.7	48	64
Hard alkyd dispersion	2.2	2.5	42	61

[a] Directly proportional to the control, which is given a value of 1.0 for warp stiffness and 1.0 for filling stiffness. The values are l^4/t ratios.

[b] Measured by Tootal Broadhurst Lee procedure on a fabric which has been conditioned at 76% relative humidity for 8 hours.

[c] Relative resistance to rubbing at high speed as compared with a standard untreated test piece.

[d] Tested on a Scott machine with a 1-inch jaw and a 3-inch gap.

Here again no general conclusions can be drawn as to which resin is the best suited for any particular purpose. It is, however, increasingly clear that resins may be used to improve the physical properties of textile fabrics greatly. For industrial application the use of resins is particularly important as it makes possible the development of fabrics to fit a wide range of specifications at a minimum cost. Since the resins are permanent and durable, they will usually last the life of the fibers themselves and in a great many cases greatly prolong the life of the fibers. As we learn more about the factors contributing to the tensile strength of yarns, we can reasonably expect to produce from cotton, rayon, or spun rayon, fabrics with all of the properties of woolens and worsteds and none of their susceptibility to attack by alkalies or moths. By the same token the use of resins on wool is similar to its action on spun rayon, and correspondingly improves the durability without imparting harshness or brittleness.

The year 1940 has seen the production of a number of fabrics which could never have been sold in the particular markets which they captured without the use of synthetic resins as a necessary part of their fibers. It is reasonable to expect that the next decade will see resin-modified fabrics competing and replacing on rapidly widening fronts the conventional textile fabrics whose properties were determined by their thread count, fiber length, and yarn twist. Today it is possible to alter a fabric as greatly by resin treatment as formerly required a fiber substitution of wool for cotton or silk for rayon.

Natural Protein-Base Spun Fibers

F. C. ATWOOD, Atlantic Research Associates, Inc., Newtonville, Mass.

THE technical literature of the past few years has contained numerous references to casein fibers, to soybean fibers, to fibers from zein and other proteins. Sometimes it is referred to as casein wool. Again we read of synthetic wool, of artificial wool, and other equally misleading terminology. This confusion of words is disconcerting to a chemist who approaches this field of man-made fibers for the first time. What is he to call the product when he starts with casein from milk or soybean and ends with a textile fiber, and why?

In writing this paper, I was confronted with the problem of a title. I could have continued the use of "casein wool". Everyone knows what is meant. But is the term accurate? Obviously, it is no more so than the term "artificial silk". Then why continue the use of these words and be confronted later with the job of coining a word like "rayon"?

Protein fibers do not fall under the definition of rayon. Swartz has suggested the name "natural protein fibers" for this class. But wool and silk would fall in such a grouping. Casein is a natural protein but is used only as the base for a fiber; it is no longer casein in a satisfactory textile fiber but is combined with other materials. In a low-grade fiber the combination is very loose and may be easily hydrolyzed. But the fiber is not a simple regenerated protein in the way that rayon is regenerated cellulose. Therefore, we find the fiber we are discussing is a protein-base fiber.

WHAT about the terms "synthetic", "artificial", or any other similar term? "Synthetic" has to do with the putting of different things together, the combination of separate substances. "Artificial" means made to resemble a raw material, counterfeit, produced by art rather than by nature. I do not think a protein-base fiber is included in those definitions. This fiber is actually formed or spun before there is a combination of substances. All commercially known protein-base fibers are treated or combined with formaldehyde after being spun. Moreover, it is unfair to say that the fiber is artificial. It happens to act like wool in some cases. It resembles silk and fur in other cases. Protein-base fibers are distinct entities by themselves and should be so considered.

The actual operation by which fibers are formed is neither synthetic nor artificial. "Spinning" is a true and accurate term, meaning to form by extension of a viscous liquid, to shape in manufacture into threadlike form. And that is what is done in the manufacture of protein-base fibers. My subject accurately deals with natural protein-base spun fibers.

After justifying the title of this paper, it is much too unwieldy to use. A new name is still needed to classify the fiber under discussion. Assume also that we may dissolve wool and silk waste and spin it, or use protein from a number of other sources. The end products will be similar and their value determined by the quality of the finished fiber, the economies of the raw material, and the simplicity of the required process. These products would all be natural protein-base spun fibers.

The name "protex" has been suggested for this group of man-made protein textile fibers. But generic names such as rayon and nylon which end in "on" are euphonious and more easily remembered. For want of a better name, I suggest "prolon" for the class of natural protein-base spun fibers.

DO THE properties of these fibers justify a class name? Is their commercial success likely to warrant serious consideration by textile chemists? Are raw material sources available in quantity and at a price to furnish large volumes of fiber if the fiber is commercially useful? If the protein-base fibers are not now of high quality, is it possible for their required qualities to be improved? I believe a study of this field during the past few years will result in a favorable answer to these questions. In countries forced by circumstances to accept substitute materials, the use of such fibers is already growing. Improvement in quality is sure to come with increased production.

Your guess is as good as mine about what is happening in foreign countries in regard to the production of protein fibers which had been started prior to the war. I know of a few imports of staple fiber within the year from Italy, Holland, and Japan. The Italian product, lanital, was of fair quality and showed some improvement over the first imports. The Dutch material appeared superior to the Italian product. The Japanese fiber was of good appearance but very poor in quality. The Japanese product is the only foreign material now available and is not suitable for domestic textile uses, although attempts will probably be made by Japanese interests to import it. These products were all made from milk casein. Some Japanese soybean casein fiber is expected soon, but the best information available indicates that the quality will be materially below that made from milk casein.

Some casein fiber was made in this country by the Italian process a few years ago and tried out on the trade. It was not good enough for American users and has now all been destroyed.

In 1939 factories were in commercial production of protein fibers in several foreign countries: lanital in Italy, Casolana in Holland, Polan in Poland, Tiolan in Germany, cargan in Belgium, Courtaulds casein in England, and a fiber in Japan. Another Dutch plant was ready to produce Lactofil by a different process from that of Ferretti, which was the method used in the other plants and tried in this country. Production was also reported in this country in an experimental plant by a process totally different from those mentioned above.

German magazines have shown data concerning Tiolan in some detail and have included small samples of the fiber and fabrics made with it. The Italian product has been shown at the World's Fair. It is doubtful whether the other plants are now running except, as suggested, the Japanese appear to be quite active.

Recently a trade report of Snia Viscosa's annual meeting showed that company's total output capacity to be 30 million pounds per year. Their casein supply was reported as 15 million pounds per year. Considerable improvements had been made in the elasticity and dyeing properties. The supplies of casein appeared far below the reported capacity, and it would seem that this condition must be very serious since Italy's entrance into the war.

Another report early this year stated that "during 1939 Argentina was exporting casein to Italy and also casein fiber". It is doubtful that fiber was made in Argentina, but the exports were probably intended for fiber. It was further reported that Argentina sold Japan 9 million pounds of casein this spring, some of which, at least, was indicated for fiber production.

Early this year a reviewer commented on the progress of rayon in 1939 and said of casein fiber: "At this point little attention will be given to casein rayons for the reason that there is a certain amount of doubt that these will ever achieve importance and because at this stage their mechanical properties are considerably inferior to other types of rayon." While the facts may have been correct, the conclusions were unwarranted and drew a rebuke from Ferretti.

As the inventor of lanital, Ferretti made out quite a case. He stated correctly that lanital is not a kind of rayon and consequently the two fibers do not admit of comparison. He pointed out that, whereas rayon is now much stronger than wool, nobody expects rayon to replace wool. By the same argument, cotton cannot replace wool even though it is much stronger. Protein fibers have characteristics which are difficult to measure but which make them vastly different from cellulosic fibers.

Moisture absorption is a characteristic of wool and lanital, which Ferretti points out as being an important difference as compared with cellulosic fiber. He probably means moisture regain and the quality of absorbing considerable moisture without feeling damp.

The ability of wool and casein fibers to be dyed by the same dyes is pointed out as an important point. Ferretti states that, by using certain precautions, the dye rate of wool and lanital can be made somewhat alike. Ferretti points out many other desirable qualities which his product has achieved and states that the rate of improvement of his product is far greater than the corresponding rate of improvement of rayon. He is doubtless right. He further points out some of the fields in which his product has been useful, where rayon has not and probably never can be used, particularly in felt products.

Ferretti refers to his patents on soybean casein fiber and other matters of quality. Finally, he claims that Snia Viscosa has been doubling its lanital plant at Cesano Maderno, which indicates constantly increasing use of the product. Samples of lanital reaching us at intervals have not shown the results which Ferretti claims, but they do show improvement over early samples.

ALL reported tests by other observers in England and Europe show requirements for care in the use of lanital and its offspring, which American users would not take the trouble to follow. For example, one operator says: "It is desirable to treat casein fiber at as low a temperature as possible. . . The tendency is for casein fiber to shrink in hot liquors. . . Casein fiber has a greater dye affinity for acid dyestuffs than wool, particularly at low temperatures. . . Mild alkalies such as soap reduce the resistance to extension under load." All such statements indicate qualities which will doubtless be corrected in any fiber made in this country before it is offered to the public.

Throughout recent literature, comment is to the effect that casein fiber shows interesting felting quality with wool and that sometimes the felting quality of wool-casein fiber mixtures is greater than that with wool alone. This favorable property has been repeatedly observed by us.

Certain patents indicate that the problem of spinning casein is more difficult or, at least, different from spinning cellulose filaments. Casein is regenerated or coagulated at a much slower rate than cellulose, and the machine rates and method of operation have to be materially changed to accommodate this slow coagulating rate. This point indicates the fact that casein fiber is not really workable until it has been treated with formaldehyde, and is a compound of some sort although it may be a readily hydrolyzable form. Whittier and Gould claim to have formed an aluminum compound. Ferretti, in fact, by his method of treating casein has probably chaotically broken his product down until it is partially hydrolyzed before being spun.

American users of a protein-base fiber will doubtless demand a strength capable of withstanding reasonable carding, combing, and spinning operation without help from other fibers. They will require dyeing properties similar to wool, under the same conditions of dyeing, because casein fiber and wool will be frequently mixed. Felting properties should be good in mixtures with feltable materials. The product must have a permanency which will avoid any breakdown by bacteria, mold, etc. It must withstand all common cleansing agents under normal conditions of use. In general, a satisfactory fiber must go into a textile mill, be blended with other fibers, and withstand all the operations common to a textile plant without requiring any change in operating conditions.

When, and if, a casein-base fiber is produced and offered to our domestic trade, which meets the above requirements, it will doubtless find a successful use in many classes of textile goods. In addition, such a fiber will have many properties unique to itself and, without supplanting or interfering with the use of any present textile fibers, will add materially to the versatility of the textile industry.

Soybean Protein Fibers

Experimental Production

R. A. BOYER, Ford Motor Company, Dearborn, Mich.

Production of fiber from soybean protein is described. Difficulties encountered in obtaining uniform protein necessitate strict control of the variety of the soybeans and thorough chemical analysis and fertilization of the soil on which they are grown. When good protein is used, spinning solutions containing 20 per cent protein can be obtained. Soybean fiber as made at present has about 80 per cent the strength of wool, has more elongation both wet and dry, and does not wet so easily as wool or casein fiber. It does not promote mold growth so readily as casein fiber. The fiber blends well with wool and cotton and has been processed satisfactorily on both cotton and worsted textile equipment. Plans are being made for a pilot plant capable of producing 1000 pounds per day of soybean fiber.

SYNTHETIC fiber production has been one of the most active and fertile fields for chemical research during the past twenty years. The tremendous growth of the rayon industry has stimulated the interest in work along this line, not only of textile chemists but of those employed in unrelated fields. Until recent years the greater part of the work was devoted to production and improvement of cellulose fibers such as viscose, cuprammonium, and acetate. In 1936, however, Ferretti in Italy published his work on a new type of protein fiber produced from milk casein. This fiber called "lanital" achieved a reputation commercially as a wool substitute because of its chemical and physical similarity to wool.

The success of lanital inspired fiber research on a great many other proteins, among them, fish protein, regenerated silk, peanut, corn zein, and soybean. The Ford research chemists had several years background of soybean research in 1937 and undertook the development of a fiber from soybean protein at that time. The soybean in many ways is an outstanding source of protein for fiber work. Economically it is sound. The supply of soybeans is large and increasing yearly. The large use of soybean meal at present is for cattle food, and this tends to keep the price stable and low. The bean is easily grown and finds favor with the farmers. Soybean oil, which is fast becoming one of our most important vegetable oils, is recovered in the first step of the fiber production.

Production of Fiber from Soybeans

EXTRACTION OF OIL. The continuous solvent extraction method is used to extract the oil. The crushed beans are washed countercurrently with hexane which removes the oil. The resulting oil-free meal is passed through a steam-jacketed pipe for removal of the solvent. Although the Ford extraction equipment is different, the whole operation is standard in the soybean industry with the exception that meal prepared for fiber work is treated at much lower temperatures than meal prepared for cattle food.

EXTRACTION OF PROTEIN FROM OIL-FREE MEAL. This is a critical and important part of the fiber preparation. Although protein extraction is a relatively simple operation, extreme care must be exercised in order to produce uniform batches. There are many ways of extracting protein, some of which are closely guarded secrets. The indications are that the simpler methods will be the most satisfactory. One method is to treat carefully sized oil-free meal with a weakly alkaline solvent, such as 0.1 per cent sodium sulfite solution, for a half hour. The resulting solution is clarified either by filtering or centrifuging. The protein in the solution is precipitated with an acid, and the resulting curd is washed and dried.

Because of the discoloration of protein by iron, each one of these steps must be carried out in stainless steel or glass lined equipment (Figure 1). The pH must be checked and controlled constantly. For instance, no two batches of soybean meal will have the same pH when treated with the same amount of sodium hydroxide under similar conditions. Accordingly the alkali is adjusted to bring each batch to the same pH. Clarifying an alkaline solution of protein satisfactorily is a difficult chemical engineering problem. At present stainless steel centrifuges with automatic unloading devices are being used (Figure 1). However much more work remains to be done on this point. Precipitation must be carried out at exactly the right temperature and pH in order to get a curd that can be satisfactorily handled during the subsequent washing and drying.

In spite of all these precautions we have found variations in the proteins. We have traced these back to differences in the variety of the bean from which the protein was extracted.

There are indications also that the composition of the soil on which the beans were grown has a marked effect on the protein. In order to have a uniform supply of beans for the fiber experiments, pure strains of soybeans are being grown on fields that have been thoroughly analyzed and fertilized. The crop from these fields will be stored in special metal containers in order to keep to a minimum any changes that may occur during storage. We hope by these methods to eliminate as many variables at the source as possible.

Preparation of Solution for Spinning. The third step in producing a fiber consists in dissolving the protein to produce a viscous stringy solution. It is desirable to obtain a solution having a high solids content. Because of the tendency of proteins in high concentrations to form a gel, it is difficult to prepare solutions having more than 12 per cent solids. However, by proper control during the extraction of the protein we have succeeded in producing solutions containing 20 per cent protein. These solutions have excellent spinning characteristics. They must, however, be aged at the right temperature for the correct time before the proper viscosity and "stringiness" are reached. The solution at this point should contain no undissolved particles or air bubbles, as the spinning continuity would be affected.

Spinning and Hardening. The fourth step consists in forcing the solution through the spinnerettes into the acid precipitating bath and collecting the filaments on a reel or bobbin. Although many variations in precipitating baths are possible, they usually consist of sulfuric acid, formaldehyde, and a salt such as sodium chloride or aluminum sulfate to facilitate dehydration of the filaments. Stretching is an important part of the precipitation. The filaments are pulled through the acid bath and over two glass pulleys called "Godet wheels" (Figure 2). The second wheel revolves faster than the first and thus exerts a stretching effect between them on the filaments. For staple fiber work multihole spinnerettes are used; our usual practice calls for 500-hole spinnerettes. A spinning machine having the flexibility required for experimental work is quite complicated. In order to obtain all the features wanted, we had to design and build our own machine.

Recently we have been working with a continuous machine that will enable us to precipitate, harden, and carry out the aftertreatment of the filaments continuously. The uniformity of treatment obtained by the continuous machine is a great advantage in producing fibers because of their minute size and sensitivity. Control of stretching is important, as can be shown

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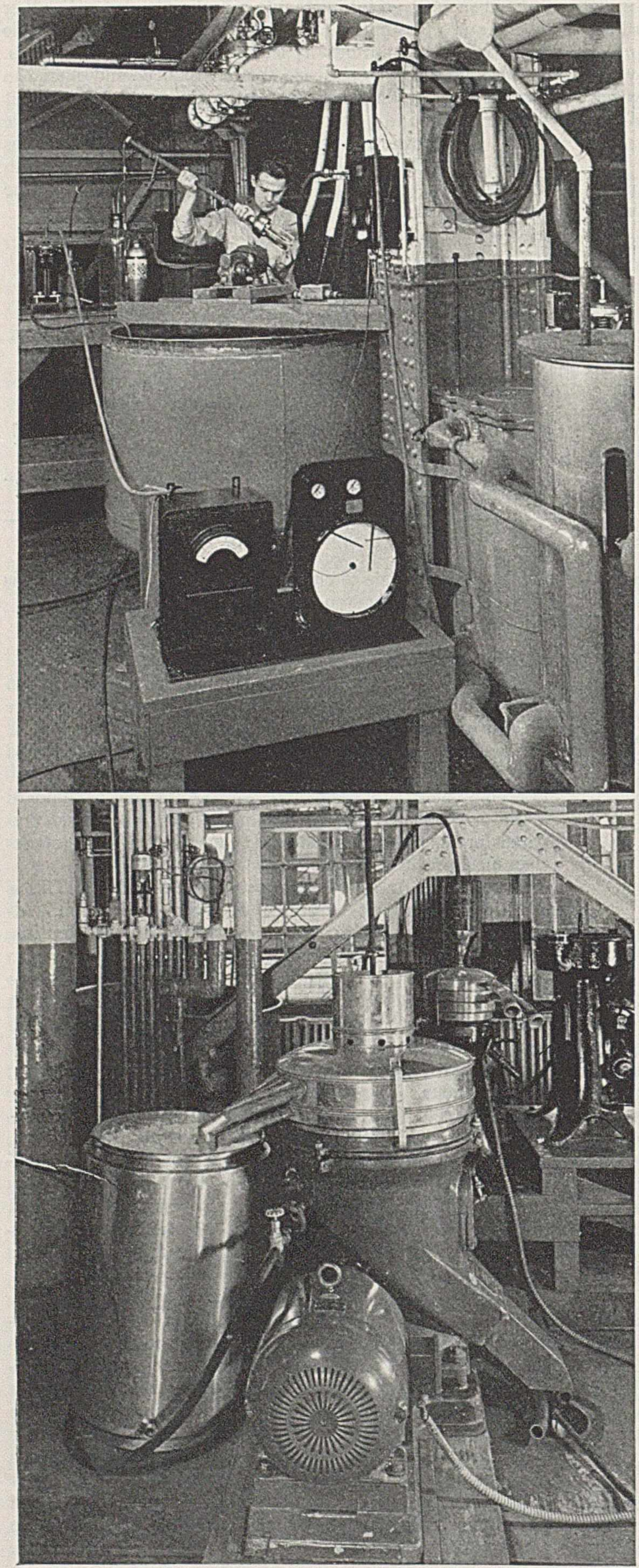

Figure 1. (*Above*) Stainless Steel Tanks and Automatic pH Controller Used in the Extraction of Soybean Protein; (*below*) Clarifying Soybean Protein Solutions with Self-Cleaning Centrifuges

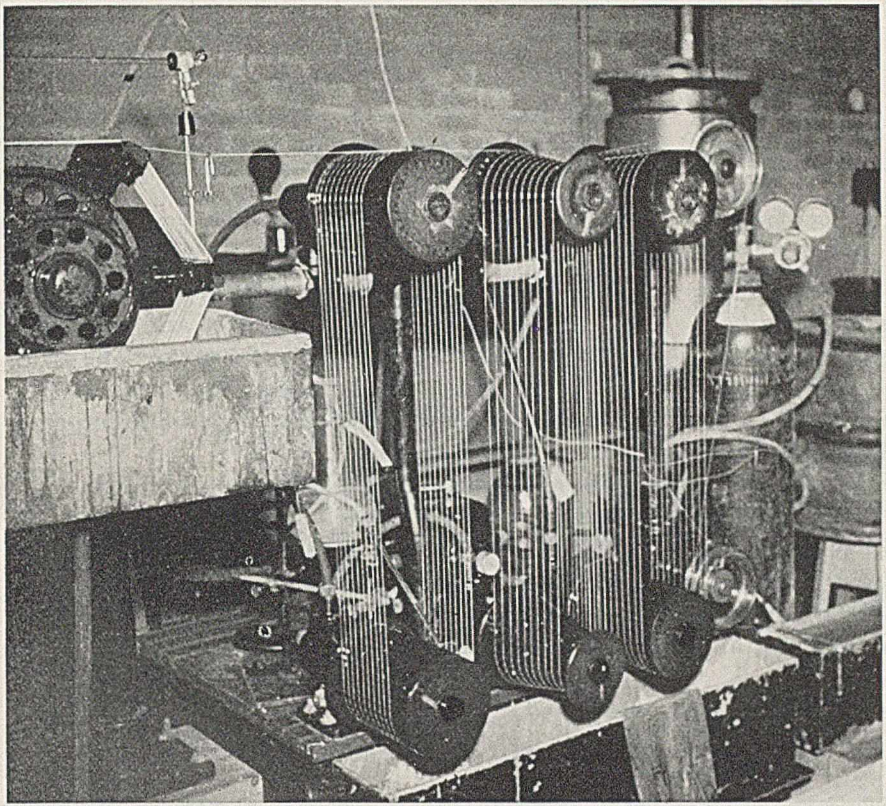

Figure 2. Experimental Spinning Machine, Showing Filaments Being Stretched between Two Godet Wheels

by producing fibers made from the same solution with and without stretching. Those made without stretching will be brittle and weak; those that are stretched during the treatment will have good elasticity and high yield points. X-ray diffraction studies of fibers show the value of stretching. Orientation occurs when the fiber is stretched under proper conditions, whereas indefinite x-ray patterns are obtained from unstretched fibers.

Aftertreatment and Drying. Aftertreatment of the fiber consists of a relatively long immersion of the fiber in a formaldehyde bath to set the fiber completely, cutting it to the desired staple length, and drying it under controlled humidity and temperature conditions (Figure 3). If the fiber has been properly treated, it will be in a loose fluffy condition resembling scoured wool.

Properties

The finished fiber is white to light tan in color with medium luster; it has a warm soft feel, a natural crimp, and a high degree of resilience.

The tensile strength of soybean fiber is about 80 per cent as compared to wool; its dry elongation of 40 per cent and wet elongation of 60 per cent are much higher. The tensile strength at break is approximately the same dry and wet; however, the yield point is lower on the wet fiber.

The specific gravity of soybean fiber is 1.31 measured in water. The fiber is nearly circular and has little pigmentation. Water does not wet soybean fiber so readily as it does casein fiber and wool. Preliminary experiments indicate that soybean fiber is very resistant to the action of mold as compared to casein fiber which is more readily attacked.

Fiber sizes range from 1.5 to 5 deniers in staple lengths of 1.5 to 6 inches. It can be produced in natural color or can be spun dyed, with or without a fixed, highly permanent crimp.

Recent refinements in processing have produced a soybean fiber highly resistant to carbonizing and to boiling in dilute acid and alkali.

The fiber has been handled on conventional cotton and worsted equipment. It shows great promise as a new, distinctly different fiber eminently suited in wool blends for use in suitings and upholstery fabrics. The availability of the fiber in fine deniers, with a fine crimp and great resilience, indicates its usefulness with cotton and spun rayon in the development of many new materials. Still another development under investigation is the use of soybean fiber with wool in felt manufacture.

While a tremendous amount of work remains to be done on soybean fiber, we feel that the results already obtained warrant proceeding with the program as fast as possible. Plans are now going forward for the installation of a complete pilot plant capable of producing 1000 pounds per day of finished fiber in the form of "top" suitable for blending with fibers used in automotive upholstery. In developing this fiber we think that a definite contribution will have been made not only to the textile industry and its customers, but also to the suppliers of the textile industry—the farmers.

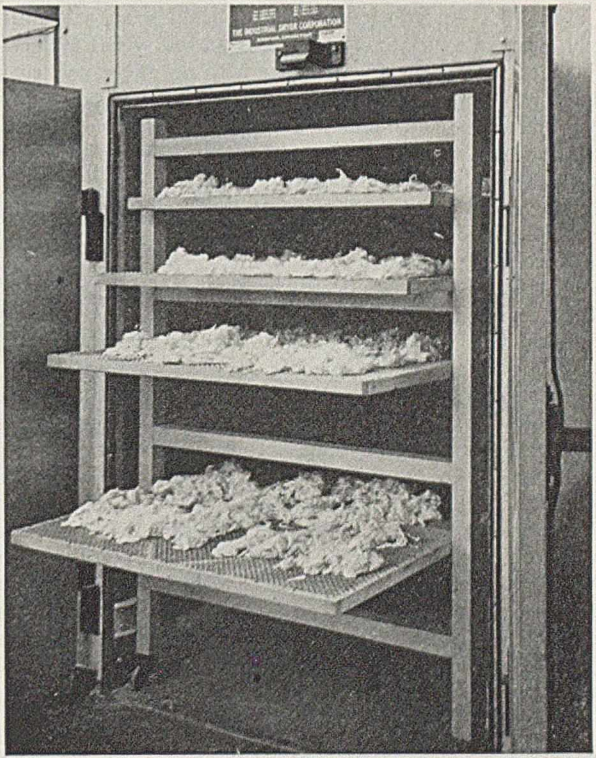

Figure 3. Drying Soybean Fiber in Humidity-Controlled Oven

Electrocoated Pile Fabrics

N. E. OGLESBY AND L. E. HOOGSTOEL, Behr-Manning Corporation, Troy, N. Y.

The electrostatic process as applied to the manufacture of pile fabrics is described. The success of the process in sandpaper manufacture indicated its possible usefulness in textiles. Two types of textile products are being manufactured commercially by the electrostatic process: women's dress goods decorated with a pile design, and an all-over covered pile product for such service as car interiors and upholstery. Many of the problems relating to the manufacture of pile fabrics by the electrostatic process are discussed.

The success of the process as applied to textiles is dependent upon accurate control of fiber length, type of adhesive, and humidity conditions of manufacture. The type of current used is also important. The relative merits of alternating and direct current are pointed out.

The outstanding feature of a pile fabric manufactured by the electrostatic process is the density of pile attainable, which reflects in the wearing properties of the product so made. As high as 275,000 fibers per square inch are obtained. Other fields of application for the electrostatic process are discussed.

THE development of electrocoated pile fabrics was an outgrowth of the development of electrocoated sandpaper. The development of electrocoated sandpaper, pioneered by the Behr-Manning Corporation, was described by D. H. Killeffer[1]. While the process as developed for electrocoating sandpaper is quite simple in its final form, extensive experimental programs were carried out over a period of years—that is, from about 1926, before the present relatively simple method was developed. The final arrangement is illustrated in Figure 1. An adhesively coated backing is fed continuously between a pair of electrodes, *A* and *B*, with the backing adjacent to the upper electrode and with the adhesively coated side facing downward. Abrasive grains are fed between the electrodes by a continuously moving belt which travels adjacent to the lower electrode, *A*, with the grain on the belt facing the adhesively coated backing. One electrode is grounded while the other is connected to a source of high potential. The potential is usually of the order of 10,000 to 25,000 volts per cm. of electrode spacing. The abrasive grains are charged with the sign of the bottom electrode, stand erect with their long axes parallel to the lines of force between the two electrodes, and, when sufficiently charged, are propelled to the adhesively coated backing sheet and are embedded in the adhesive with their long axes perpendicular to the backing sheet. Furthermore, since the grains are charged with the same sign, they repel one another and are for this reason uniformly distributed on the backing sheet. When abrasive grains are so located under the influence of an electrostatic field, it has been found that a much more efficient abrading tool is produced. This is because the sharp points are in a position to engage the work more effectively and because the grains, being uniformly spaced and standing upright, do not tend to become packed or loaded with the abraded material to the extent that a random or unoriented abrasive coating becomes loaded in use and therefore relatively ineffective as an abrading tool.

At a fairly early date in the work on sandpaper it was recognized that the electrocoating methods developed should have other applications, and a few sporadic experiments were run in which an effort was made to orient textile fibers to form simulated pile fabrics. The fact that many of the operations incident to the manufacture of a woven pile fabric would be eliminated by the use of the electrostatic method, impelled us to give serious consideration to such an application. These early experiments indicated that any real commercial success in forming pile fabrics would have to be preceded by the solution of a number of problems. For instance, a substantially constant potential on the coating electrodes was quite effective in the coating of sandpaper and was used for this purpose. When, however, textile fibers were fed to the same field in the same way that abrasive grains were fed, the fibers treed or matted in loose form between the electrodes and thereafter failed to respond to the field as required for coating. That is, even with a constant potential on the electrodes, as the grain and adhesive-coated backing passed through the electrodes, the grains repeatedly rose to the backing, returned to the belt, and were again propelled to the adhesive-coated backing until the desired coating had been built up. There was an absolute absence of the treeing and

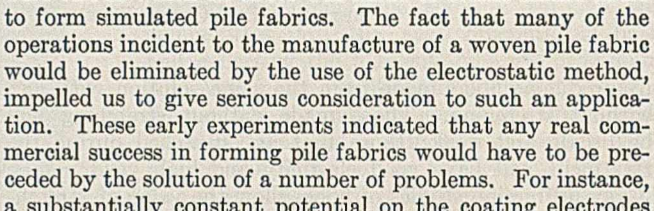

FIGURE 1. ELECTRODE ARRANGEMENT FOR ELECTROCOATING SANDPAPER

A. Negative electrode.
B. Positive electrode.
C, D. Lines of electrical force.
E. Conveyor belt carrying loose grain.
F. Paper with glue side down.
G. Abrasive grain embedded vertically in glued surface.

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[1] IND. ENG. CHEM., 29, 849 (1937).

inactivity of abrasive particles that were found in attempting to coat textile fabrics.

Methods of Coating Textile Fabrics

In general, one of two methods is used—a pulsating or interrupted direct potential, or an alternating potential. Of the two, the latter is preferred. Under the influence of an alternating potential the sign of the charge on the electrodes and on the particles is repeatedly reversed so that the particles bounce backward and forward between the electrodes without treeing and becoming inactive as is the case where an unvarying unidirectional potential is impressed upon the electrodes.

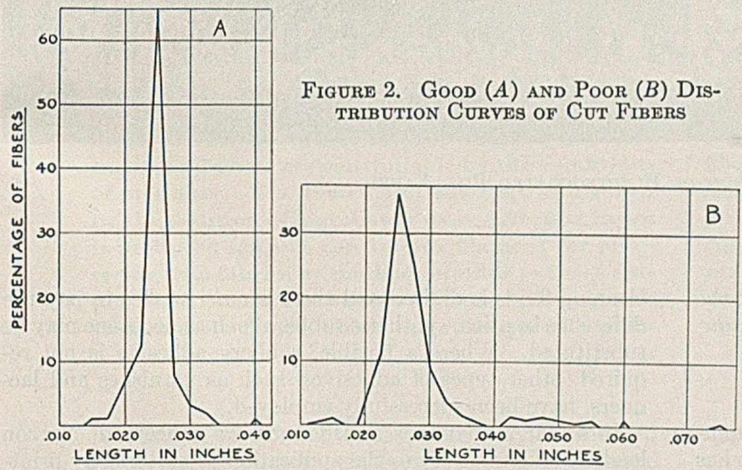


FIGURE 2. GOOD (*A*) AND POOR (*B*) DISTRIBUTION CURVES OF CUT FIBERS

There is another important difference between abrasive grains and textile fibers. Abrasive grains are dense, nonabsorbent, and relatively unaffected by moisture. Textile fibers, on the other hand, may absorb large quantities of water and vary decidedly in their electrical characteristics, depending upon their water content. Successful coating of pile fabrics by the electrostatic method, therefore, requires that there be reasonable control of the water content of the textile fibers. Furthermore, as in all textile work, it is desirable that there be some control of humidity.

In order to obtain good coatings of highest density and uniformity of appearance, the textile fibers should be cut to uniform lengths. This is a sizable development in itself. Furthermore, aside from the effect on density of coating, the cutting of the fibers to uniform length is more economical than subsequently shearing nonuniform coated fibers to obtain a level pile surface effect.

As indicated, the uniformity of cut must be controlled in order to facilitate the manufacture of pile fabrics by the electrostatic method. This control is attained by repeated testing during the cutting operation which consists in making distribution curves of the fibers as cut. A typical satisfactory distribution curve and an unsatisfactory one are shown in Figure 2. Material made with fibers represented by the distribution curve *A* would require no shearing, whereas material made with fibers represented by curve *B* might require shearing in order to get a level pile.

The first commercial use of the electrocoating process in the formation of pile fibers was in the manufacture of dress goods sold under the name "Fibredown". The Behr-Manning Corporation did not wish to go into the dress goods business and therefore licensed another company to manufacture and sell goods under the patents and applications covering the processes developed by the Behr-Manning Corporation. Figure 3 shows typical Fibredown patterns.

In running goods of the Fibredown type the adhesive is applied with a stencil or other means in the form of the pattern desired, the fibers are electrostatically propelled into the adhesive, and the adhesive is cured in conventional festoons. A number of fibers may be used—for instance, cotton or rayon. As previously pointed out, they are cut to uniform length before the coating operation, and may be either dyed or undyed. So far, Fibredown has been sold with white fibers only, but an assortment of colors will be offered at an early date.

The adhesive development was an important part of the problem. Dress goods of the type under consideration must be able to stand either reasonable laundering or dry cleaning, and repeated ironing. That the adhesive should stand reasonable laundering is quite a rigid specification, but that it must stand normal ironing without appreciable loss of loft or color make the task doubly difficult. Since white patterns are very popular, initial color and color retention of both the fiber and the adhesive are of primary importance. A number of desirable adhesives are automatically eliminated because they are thermoplastic and cannot be subjected to the normal ironing operation. Since a number of patents covering the whole development are still pending, we are not at liberty to disclose a number of the details of the process. In general, however, certain synthetic resins have been found to be the most desirable bases for adhesive compositions.

During the early stages of the experiments many trial dresses were worn by women in our organization; these were carefully checked from time to time, and it was found that the material as developed would meet all the specifications we had set out to meet. As a matter of fact, these particular garments received more rigid tests than most would have

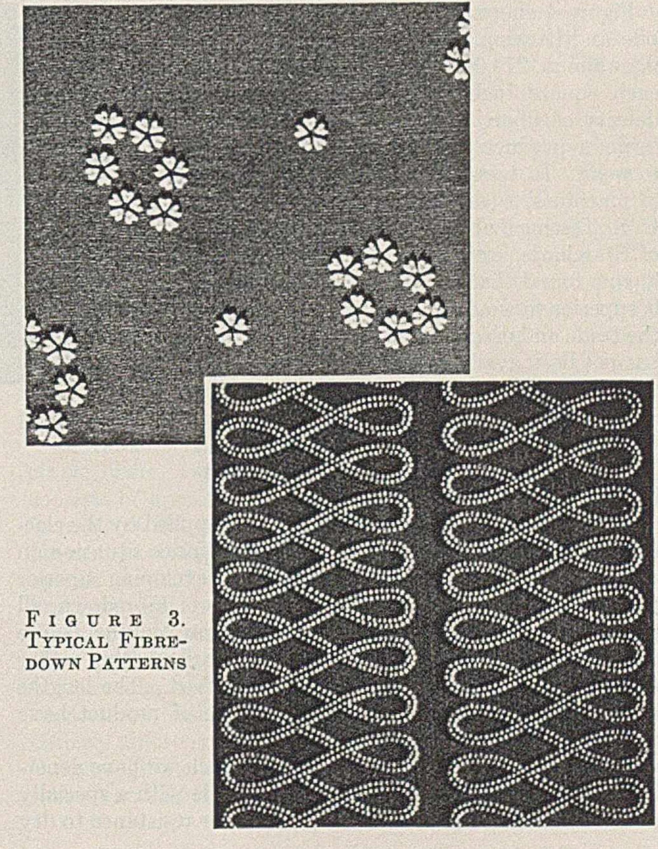


FIGURE 3. TYPICAL FIBREDOWN PATTERNS

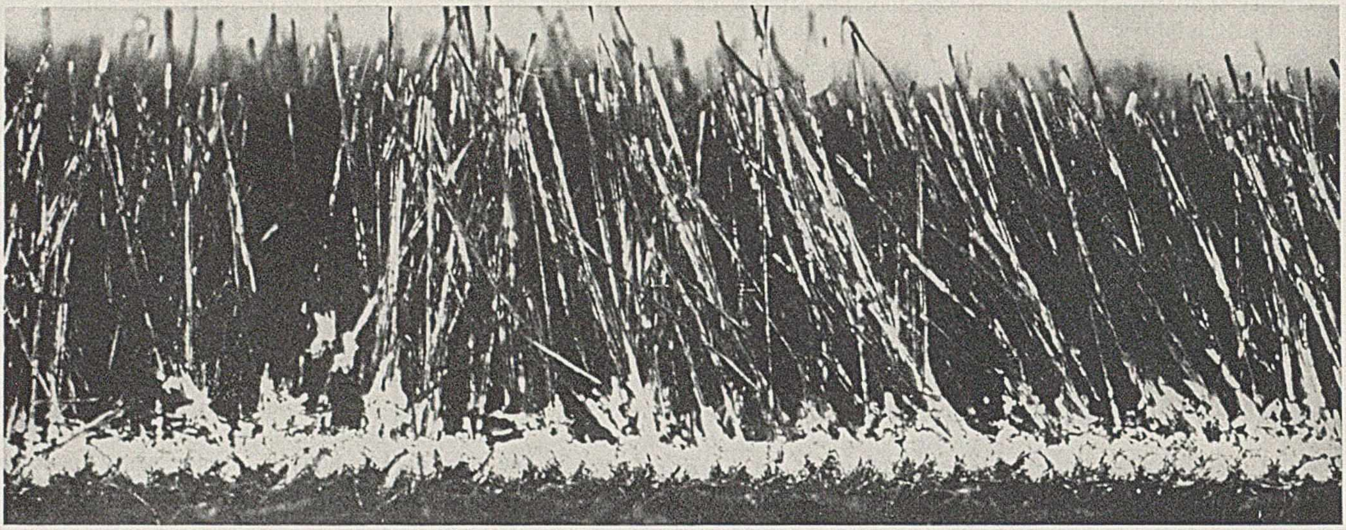


Figure 4. Cross Section of Electrocoated Pile Fabric

received, since a studied effort was made to subject them to the worst laundering practices.

Pile Fabrics

The Behr-Manning Corporation has developed and manufactured on a small scale, a product called "Norzon". It has a reinforcing backing of cotton cloth to which is applied a dense allover pile of electrically oriented fibers held to the reinforcing backing by an adhesive layer interposed between the backing and the pile. This product is intended particularly for such uses as lining the side walls of automobiles and for other upholstery uses.

Figure 4 shows a section of the oriented pile and backing. To form the dense coating, about 275,000 fibers are applied to each square inch of backing. This high density of fibers anchored to the backing forms a product with exceptional resistance to wear. In tests carried out on a number of machines, such as the Wyzenbeek, the U. S. Testing Laboratory, the U. S. Bureau of Standards, and the Shawmut machines, it was found that the electrocoated product is superior to woven pile fabrics picked up in the trade and used as controls. The product has not been available long enough to determine its useful life in practical installations. Figure 5 shows the appearance of the electrocoated pile fabric and of a woven pile fabric after 10,000 strokes on the U. S. Testing Laboratory machine.

Practically all good textile fibers can be applied by the electrocoating process. Because of the present price situation on wool, much of our time has been spent on developing superior products with rayon fibers. As in the case of Fibredown, all fibers should preferably be cut to uniform lengths before coating. The length of the fibers may be varied within rather wide limits, depending upon the result desired. The lengths most frequently used in making this type of product have varied from 0.025 to 0.060 inch.

The product illustrated in Figure 5 (which we have generally had in mind in this description) is made with a specially compounded latex adhesive. Where greater resistance to dry cleaning fluids is desired and the customer wishes to pay the difference in price, synthetic rubbers such as neoprene may be substituted. Where a flexible, rubbery adhesive is not required, other types of adhesives, such as varnishes and lacquers, have been successfully employed.

In so far as patterns and designs are concerned, Norzon lends itself effectively to the application of patterns by printing methods. This is not the only means of obtaining patterns on Norzon, but it is particularly adaptable to taking printed designs. The dense vertical pile prints without smearing.

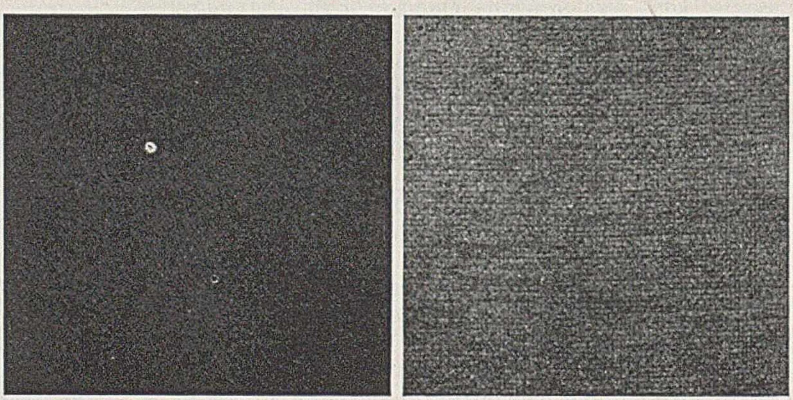


Figure 5. Appearance of Electrocoated Pile Fabric (*left*) and of Woven Pile Fabric after 10,000 Strokes

Norzon has been made in widths up to 36 inches, and it is hoped that widths up to 58 inches can be made on larger scale equipment now ready for operation.

Another project is that of making carpets by the electrocoated method. The most important difference between electrocoated carpets and Norzon as prepared for automobile side walls will be in the fibers themselves, both as to coarseness and length. In making small-scale runs of carpet material up to this time, we have used a specially treated burlap base and fibers from about 0.150 to 0.250 inch long. Encouraging results have been obtained, and it is hoped to complete this development on a larger scale at an early date.

Cellulose Acetate Rayons

Types, Properties, and Uses

HAROLD DEWITT SMITH, The A. M. Tenney Associates, Inc., New York, N. Y.

Acetate rayon filaments and fibers are produced by extruding an acetone solution of cellulose acetate into warm air under carefully controlled conditions of temperature, velocity, and relative humidity of the air, and draft or stretch of the fibers during coagulation. The diameter or denier and, to a large extent, the physical properties of the filaments and fibers are controllable by the conditions of spinning. The luster and color are controlled by the addition of pigment or dyes. Acetate rayon is produced both as continuous filament for processing into fabrics by methods similar to those employed with silk and as short fibers, called acetate rayon staple fibers, which are subsequently processed on textile spinning machinery to produce yarns of the cotton or wool type. The strength of acetate rayons compares favorably with that of wool. They are inherently white, have a soft supple nature and a good inherent resistance to creasing and to perspiration, and dye with special dyestuffs, which permits cross-dyeing in mixtures with other fibers. Their thermoplasticity requires care in ironing but permits the attainment of valuable permanent effects in finishing and in styling of garments. Acetate rayons account for approximately 30 per cent of the total rayon production, and are used in a wide variety of household and apparel fabrics for men, women, and children.

CELLULOSE acetate for the rayon industry is produced by the same methods employed for making cellulose acetates for other purposes. The general principle involves reacting purified cotton linters with acetic anhydride (dissolved in glacial acetic acid) in the presence of a catalyzer with subsequent hydrolysis of the highly acetylated product to reduce the acetyl content to the desired value. The range of acetyl content which confers the desirable acetone solubility is approximately 36 to 41 per cent acetyl content. The calculated acetyl content of cellulose diacetate is 35 per cent. Fractionation procedures are used to study the degree of uniformity of acetylation, and these studies indicate that a more homogeneous product is obtained by complete esterification followed by controlled hydrolysis than by trying to arrest the acetylation at the desired point.

The acetyl content affects the viscosity of the spinning solution: the higher acetyl values produce lower viscosities, but the viscosity for a given acetyl content is subject to a considerable control by other factors in the manufacturing process. The acetyl content affects the properties of the filaments and yarns; a higher acetyl produces a harder, more wiry filament, and a lower acetyl produces a softer, limper one. The acetyl content also affects the melting point which increases somewhat with increasing acetyl. Each manufacturer has worked out the composition best suited to his purpose, and each attains amazing uniformity in this respect by careful blending and control at every stage.

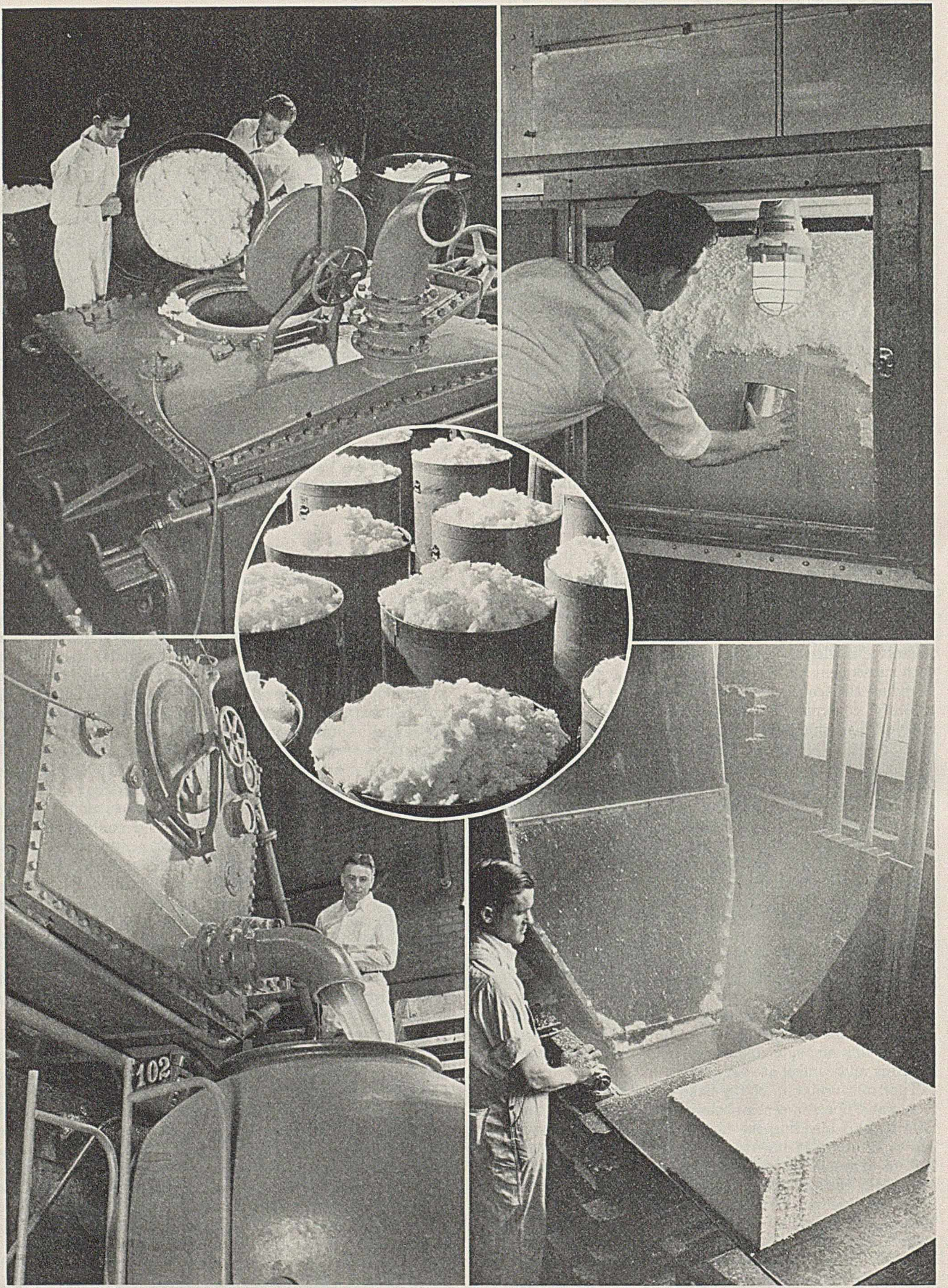
The transformation of the flake cellulose acetate into filaments and fibers is accomplished by dissolving it in acetone, filtering and blending the highly viscous spinning solution, and then forcing it downward through fine holes into a rising current of warm air which evaporates the acetone and thus coagulates the cellulose acetate in the form of continuous filaments which pass out of the bottom of the spinning chamber and are wound up on a bobbin or spool. Chemically the acetate yarn is a finished product as it winds onto the spinning bobbin. To put it into useful form for the textile weaver or knitter, it is twisted, lubricated, and wound on the desired type of shipping packages such as cones, spools, cops, or skeins.

The physical properties of the acetate filaments are controllable within rather wide limits by the spinning conditions. For example, the size of the individual filament is controlled by the rate at which the spinning solution is extruded in relation to the higher rate at which the coagulated filaments are withdrawn from the cabinet. The selection of extrusion speed and of draft as well as of temperature, humidity, and rate of flow of the air in the cabinet also permits the control, within limits, of strength and elongation of the filaments, and to some extent, the shape of the cross section.

The major natural textile fibers on which man has been dependent for thousands of years are few in number and of two fundamentally different types—namely, continuous filaments and relatively short fibers often called "staple". Silk is the only representative of the continuous filament type; cotton, linen, and wool are all examples of the staple or short fiber type. To make yarns out of the continuous filaments requires only that the desired number of filaments be laid side by side and given sufficient twist to hold them together or to impart the required character. The resulting yarns and fabrics are characterized by the sleekness, smoothness, and lustrous beauty with which we are all familiar.

To make a textile yarn from any of the short natural-staple fibers, a rather intricate technique is required. This consists of opening the tangled mass of fibers by carding to form a soft filmy strand called "sliver", partly paralleling the fibers and evening the strand by a series of drawing or drafting operations to form a uniform but soft weak strand called "roving", and finally spinning which comprises simultaneous drafting and twisting of the roving to form a yarn of the desired size, strength, and firmness. Such yarns are bulkier and fuzzier than silk because of the protruding fiber ends and crisscrossed fibers; the short fibers produce effects in fabric entirely different from that of continuous filament silk.

Although the principles of spinning are the same for all short natural-staple fibers, the differences in length, di-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ameter, and physical properties of the various fibers have resulted in the evolution of distinctive machinery particularly suited for each. Thus, cotton spinning machinery is designed to handle fibers of 0.75–2 inch staple length; woolen machinery lengths of 2 to 4 inches; worsted, mohair, and waste silk machinery in lengths from 3 to 7 inches.

Like other rayons, acetate rayon is produced in these two fundamental types—namely, continuous-filament acetate rayon and acetate rayon staple fiber. Both come from the spinning cabinet as continuous endless strands composed of a number of separate filaments. In the case of continuous-filament yarns, the spinnerette in each spinning cabinet has a number of holes equal to the number of filaments desired in the finished yarn, and these filaments from one spinnerette are wound and twisted as a group to form the yarn. Continuous-filament acetate rayon is used in the same manner as silk, and is favored for its smooth sleekness and its silklike character in the fabric.

Acetate rayon staple is made by spinning a larger number of filaments in each cabinet, combining a number of strands as they emerge from the spinning cabinets, and then chopping or cutting this thick strand or "tow" of fibers (either before or after the application of lubricant or "finish") into short fibers of the desired uniform length, which may range from 1 to 7 inches, depending on the type of textile machinery upon which they are to be processed into spun yarns. Acetate rayon staple, like other rayon staples, may be processed on cotton, woolen, worsted, or spun silk machinery, and is provided in lengths and diameters suitable for each system.

In the United States acetate rayon is manufactured by five companies under trade names as follows:

	Brand Name	
Company	Continuous-filament yarn	Staple fiber
American Viscose Corp.	Seraceta	Seraceta-Fibro
Celanese Corp. of America	Celanese	Celanese
E. I. du Pont de Nemours & Co., Inc.	Acele	Acele
Tennessee Eastman Corp.	Eastman Acetate	Teca
Tubize Chatillon Corp.	Tubize	. . .

General Properties

The principal properties of general importance which characterize the acetate rayons and ensure them an important place in the family of natural and synthetic fibers may be summarized as follows:

Suppleness and "Hand". Acetate filaments have a softness to the touch and a suppleness which, to use the most obvious comparison, can best be described as silklike. This results in excellent draping qualities and a pleasant feel against the skin, and provides one of the reasons for the large use of continuous-filament acetate rayon in taffetas, satins, and the warps of crepes. The suitability of acetate rayon for these types of dress fabrics is responsible for the rapid growth of the acetate rayon industry in the early thirties. Since that time they have become staples in the market.

Natural Crease Resistance. The nature of cellulose acetate results in a degree of elasticity or resilience in the acetate filaments sufficient to give acetate fabrics a marked resistance to wrinkling and creasing without the assistance of crease-resistant finishes of any sort.

Low Moisture Absorption. Acetate rayon is moderately hygroscopic, exhibiting the same general form of moisture isotherm as the other rayons and the natural fibers, but the amount of moisture absorbed at any given relative humidity is less than half that of wool or viscose, about half that of silk, and slightly less than that of cotton. This relative insensitivity to moisture has a number of favorable aspects, especially because of the fact that the absorbed moisture causes much less swelling of the fiber substance than in the case of the other fibers mentioned. Stains caused by tea, coffee, fruit juices, and other aqueous liquids are more readily removed from acetate fabrics because the lower swelling and moisture absorption prevents the stain from penetrating deeply into the fiber substance. The reduction of strength of the acetate rayons in the wet state is about one third as compared to almost one half for other rayons. The tendency for acetate rayon fabrics to shrink and to stretch or sag is reduced by reason of the lower moisture absorption and swelling. Wet acetate rayon fabrics dry quickly because of the lower affinity between fiber and moisture.

Color. Cellulose acetate is so nearly clear and colorless that acetate rayons need no bleaching process to produce their inherent whiteness which is stable to washing and light.

There are several properties which are disadvantageous in some respects, but which are also responsible for some of the distinctive uses of acetate rayons:

Saponification. One of these is the ease with which cellulose acetate is saponified in hot alkalies. Scouring and dyeing procedures which avoid this are used. Although all acetate rayon manufacturers have had to refuse to assume responsibility for fabric defects in cases where the acetate rayon has been chemically altered by saponification because of the difficulty of controlling this process on piece goods, many finishers of acetate rayons have undertaken to subject the goods to a partial saponification in order to permit the acetate rayons to be dyed and printed with the dischargeable dyes ordinarily used for viscose and cotton. The need for this procedure, which occasionally causes streakiness due to uneven saponification and which destroys many desirable characteristics of acetate rayon if carried too far, is about to disappear as dischargeable acetate dyes are being rapidly perfected.

Solubility. Another property which has been turned to good use is the solubility of cellulose acetate in acetone and some other organic solvents and solvent mixtures. This caused consternation and trouble when acetate fabrics first reached dry cleaners, but the solvents used were rapidly revised and for many years acetate garments have been favored by cleaners because of the ease with which they clean. Ladies, however, must still take care not to spill nail polish remover on an acetate dress. This solubility of acetate has been turned to valuable account in the production of stiffened fabrics such as collars, cuffs, shirt bosoms, etc. By incorporating a layer of acetate fabric between cotton or other fabrics or by weaving some acetate yarns into the cotton interlining and then moistening the composite fabric with acetone, a multi-ply fabric is obtained which is stiff yet flexible and porous to moisture.

Thermoplasticity of cellulose acetate at first caused practical difficulty in the handling of acetate rayon, as it necessitates care in ironing in order to avoid glazing the fabric surface or, in the case of excessive heat, melting and de-

Illustrated on page 1556

The snowy cotton linters in the center are taken from the cottonseed after the spinnable cotton has been ginned; these short fuzzy fibers are bleached and scoured to a fluffy mass of pure cellulose. The cotton linters are dumped into the specially built acetylating mixer at the upper left, together with a solution of acetic anhydride and acetic acid; powerful machinery stirs the mixture during reaction. Cellulose acetate, a crystal clear solution with the consistency of honey, is being poured from the acetylator, at the lower left, into a huge storage jar; from this substance Tenite plastic, safety film, and Eastman acetate yarn are made. From the storage jars the cellulose acetate solution plunges into cold water, precipitates into cellulose-acetate flakes; these are washed free of acid and pass into a dryer (upper right) where water whirls off. Cellulose acetate reappears in manageable cakes (lower right) which may eventually become photographic film, transparent wrapping material, plastic Tenite, or acetate yarns and Teca staple fiber.

stroying it altogether. Actually, however, when acetate garments are handled with the same care as those of silk or any fine fabric (using a warm rather than a hot iron), no difficulty is encountered. Both the garment trade and the consumer have long since learned to handle rayons with such care. The thermoplasticity of acetate rayon is particularly valuable in the production of moiré patterns or embossed designs with heated engraved rollers, because such molded patterns on acetate rayon fabrics are permanent to washing and cleaning, whereas on the natural fibers or other types of rayon the patterns are removed rather readily when the garment is washed or cleaned.

Dyeing. Probably the most interesting of the "useful disadvantages" of acetate rayon is its indifference to most of the dyes used to color other fibers. This lack of affinity for dyes, which hampered the early success of acetate rayon some fifteen to twenty years ago, turned out to be a real blessing in disguise. It stimulated the development of dyes which dye acetate but are, in general, indifferent to other fibers and thereby opened up not only the dyeing of solid shades on acetate alone or in mixed fiber fabrics by the use of mixed dye baths, but also a wide variety of effects by cross dyeing in a single bath piece goods containing mixed fibers or yarns. These had previously been made largely by the more expensive method of dyeing the fiber or yarn before weaving the fabric.

The most commonly used acetate dyestuffs belong to two general chemical groups—namely, the azo groups which are used mostly for yellows, oranges, and reds, and the aminoanthraquinones which are generally greens, blues, and violets. Both types as used are insoluble in water and are made up in the form of a finely divided dispersion. They are dispersed in a soap bath from which they are readily absorbed by cellulose acetate. The fastness to light and washing is rather good, better in fact than many so-called commercial dyes commonly used on viscose rayon and cotton, but not as good as vat dyes on those two fibers. Some gradual improvement in fastness properties has been attained by dyemakers, and several interesting new developments are either in use or imminent.

One of these is the dyeing of acetate in fiber or skein form with selected acid dyes in a bath containing alcohol and water instead of water alone. While these dyes have little or no affinity for acetate rayon under the usual methods by which they are applied to wool, the alcohol swells the fibers and permits a rapid penetration of the dye in the cold. The acetate is dried without rinsing to shrink the fibers to their original conditions and then soaped to remove surface dye. The resulting colors are bright and very fast to boil-off, bleaching, and cross dyeing of the other types of fiber present and, in general, are very fast to light.

Another recent development is the use of vat dyes on acetate. This is apparently accomplished by selecting those vats which can be solubilized at lower alkalinities and by the use of protective agents in the bath. All-acetate shirting fabrics dyed in light shades are already available commercially, and it appears that the attainment of heavy shades, at least in fiber and yarn dyeing and probably in piece dyeing, may soon be worked out.

Taffeta Dress of Eastman Acetate Rayon

The most troublesome dyeing problem during the past year or two has been the atmospheric or gas fading of acetate rayon containing blue as a component of the dye formula. The fading manifests itself by a noticeable change from blue, gray, or tan to pink. The cause is believed to be a reaction between the aminoanthraquinone type of dye and small amounts of oxides of nitrogen in the atmosphere. These are apparently generated by oxidation of atmospheric nitrogen at incandescent surfaces, such as glowing metal and particularly flames. Goods or garments which are stored in or near workshops or stores using gas-heated irons or boilers are likely to be affected. A satisfactory temporary solution of the problem has been worked out by the use of finishing agents applied to the goods after dyeing which act as inhibitors by preferential reaction with the gases. The period required to produce a visible change in shade is thus trebled, and in most cases this is sufficient to avoid trouble on this score. The careful selection of the best available dyes and the proper use of a good inhibitor would undoubtedly reduce the trouble with this type of fading to insignificance, but the trade conditions and prices in the rayon dyeing industry unfortunately have not promoted the exercise of such reasonable care. The ultimate solution of this problem is, of course, a blue dye or dyes which will not change color under these conditions. One such dye has been available for some time, but its working properties have made it rather difficult to use. Another is now available which combines high resistance to gas fading with improved working properties. This color, together with others which are undoubtedly under development, bids fair to eliminate the trouble with gas fading which, while very small in proportion to the total output of fabrics containing acetate rayon, is nevertheless a cause for just irritation on the part of the retail store and the consumer.

Types of Acetate Rayon

Both the continuous-filament and the staple-fiber acetate rayons are commercially available in a number of sizes and types. The rayon industry adopted as the unit of size for single fibers, filaments, and continuous-filament yarns the unit which had been evolved by the silk industry—namely, the denier.

The denier size of a fiber, filament, or yarn is equal to the weight in grams of 9000 meters. A natural silk fiber is approximately 1.3 deniers. Wool fibers range according to quality and type from approximately 1.2 to 25–30 deniers. Acetate filaments for continuous yarns are made in a number of sizes from 1.5 to 4 deniers per filament. Acetate staple rayon fibers are made in a much wider range of sizes ranging from 1.5 to 20 deniers per filament, and thus cover rather well the range of sizes of the major natural-staple fibers.

Continuous-filament acetate rayon yarns are composed of groups of filaments with total denier ranging from 45, which corresponds to a three- or four-thread silk yarn, to 600 deniers. The spun acetate rayon yarns which are made by textile mills of rayon staple are prepared in a wide range of sizes and types.

Acetate rayon is produced in bright luster made from spinning solution containing only cellulose acetate and solvent, and in dull luster obtained by adding a small amount of special grades of titanium oxide to the clear spinning solution. The result is a very white, dull, or matte fiber from which many interesting textures and surfaces are woven or knitted.

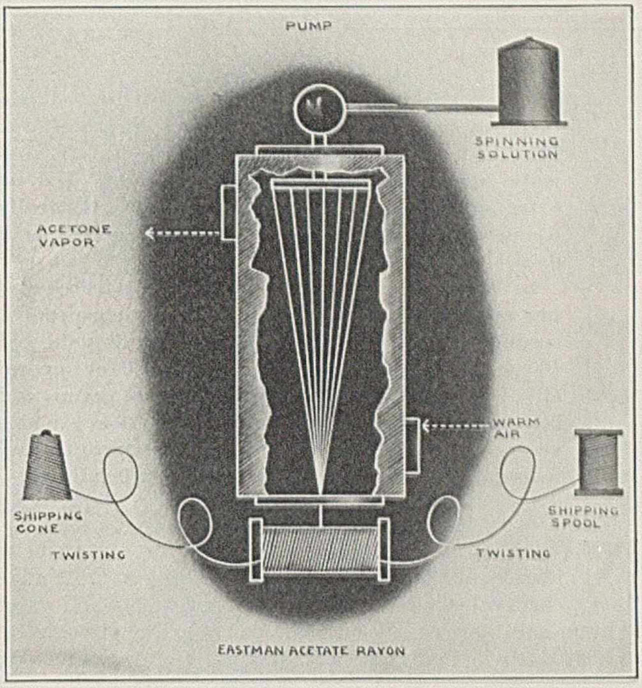
It is also possible to spin colored filaments by incorporating suitable colored dyes or pigments in the spinning solution, but the changes in the colors demanded by fashion from season to season and the complications of inventory problems have made this development of little commercial importance. The exception is solution-dyed black acetate rayon which is available commercially as continuous yarn and as staple fiber in a lustrous black which is extremely fast to all requirements, including light, washing, boiling, bleaching, crocking, and perspiration.

Acetate rayon also appears in some special forms. Among these is a plasticized yarn or fiber which is composed of cellulose acetate and sufficient plasticizer to permit the fibers or fabric containing them to be softened by heat and then reset by lowering the temperature to produce various special stiffening effects.

Another interesting type, which has made its appearance abroad, is a voluminous fiber of considerably lower density than that of ordinary acetate whose density is 1.3. This is made by entraining a great number of tiny bubbles of air or gas within the fibers as they coagulate. The result is a dull luster and a fluffy hand. Still another interesting type which was developed in England is an especially strong yarn made by stretching and partially saponifying filaments while in a softened condition. By this method, strengths greater than twice that of natural silk are attainable, and such yarns should be of particular interest for parachutes, aircraft, and other purposes where very high strengths per unit weight are desired.

Recent Progress

The acetate rayon industry is not quite twenty years old. The last ten years have witnessed an amazing expansion, first in the field of continuous-filament yarns and more recently in the field of staple fibers. The consumption has increased at a faster yearly rate than that of other types of rayon until today acetate rayon accounts for 30 per cent of the total domestic rayon consumption. This growth is due partly to the frequent appearance of radically new developments. For instance, the appearance of the dull yarns about nine years ago immediately broadened the market in women's wear to include many dull textures such as crepes, sharkskins, and tricot knit fabrics. They also opened the market to men's apparel where the bright luster yarns had not been suitable. Another step was the production of fine filament yarns in sizes which opened a field of women's lingerie fabrics that had been formerly restricted to silk. A third step was the development of a crimped acetate rayon staple which resulted in a new range of blended viscose and acetate fabrics for both men and women in sportswear and streetwear. These fabrics resemble somewhat the light woolens and worsteds in appearance, but are distinctive in character by reason of the natural crease-resistance and the stability to shrinkage and stretching conferred by the presence of the acetate staple.



Before the Cellulose Acetate Can Be Spun, It Must Be Dissolved in Acetone to Make a Clear Solution as Thick as Molasses. This Is Pumped through a Spinnerette Which Looks Like a Miniature Shower Nozzle at the Top of a Tall Shaft. Forced through the Spinnerette's Invisibly Fine Holes, the Cellulose Acetate Falls in Fine Streams Which Solidify into Filaments as They Pass through the Warm Air of the Shaft and Then Emerge as a Strand of Yarn

The other cause of the growth of the acetate rayon industry, which is at least as important as these specific new developments, has been the steady improvement in quality and uniformity which has resulted from the accumulated experience of manufacturing. There has been a gradual increase in strength, a decrease in manufacturing imperfections, such as broken filaments, poor winding, etc., and a remarkable advance in yarn finishes or lubrication, which is necessary to protect the filaments from damage by friction and from the generation of troublesome static electricity. These improvements, combined with the excellent development of processing machinery for the warping, sizing, copping, weaving, and knitting of rayon, have provided the consumer with ever higher quality in acetate rayon fabrics at a constantly decreasing cost.

The uses of the acetate rayons are too numerous to list in detail. Used both alone and in combination with other fibers they include a wide range of women's wear fabrics for daytime, for evening, and for sports; men's summer suitings, slacks, sport clothes, neckties, and socks; bathing suits and underwear for both sexes; children's clothes; household fabrics, such as draperies and upholstery; automobile upholstery; collar linings; and many other types.

Because of the great versatility and the distinctive properties of the acetate rayons, they are destined to play an increasingly important part in the textile world of tomorrow.

Nylon as a Textile Fiber

G. P. HOFF, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

Nylon is the generic name for all synthetic fiber-forming polymeric amides having a proteinlike chemical structure, derivable from coal, air, and water or other substances and characterized by extreme toughness and strength. Structurally nylon may be related to the natural proteins such as silk and wool.

In a test where yarn samples were stretched 4 per cent, held for 100 seconds, and measured 60 seconds after the load was released, nylon showed 100 per cent recovery in comparison to 50 for natural silk, 50 for acetate rayon, 40 for Cordura rayon, and 30 for ordinary viscose rayon. These fibers are also compared in respect to wet and dry strength and water absorption at 60 per cent relative humidity.

Nylon is shown to be crystalline. The melt-extruded filaments as originally produced are capable of easy orientation through stretching with relatively little force required to accomplish a fourfold increase in length. The new length and proportionately reduced diameter are essentially permanent. The oriented yarn is strong, elastic, and tough. It is notable for its ability to take a permanent set through simple treatments with boiling water or steam.

Nylon yarn and fabrics are practically nonflammable. Nylon is physiologically inert and has found use in the form of surgical sutures. In addition, it is resistant to enzymes, mildew, molds, and moths.

NYLON is used as the generic name for all synthetic fiber-forming polymeric amides having a proteinlike chemical structure, derivable from coal, air, and water or other substances and characterized by extreme toughness and strength. "Synthetic . . . proteinlike . . . polymeric amides" are the key words in this statement. Nylon may be formed into fibers, bristles, sheets, and other shapes. It follows that nylon does not refer simply to the fibers or yarn spun from a polyamide, but rather to the polyamide itself from which fibers, bristles, sheets, etc., may be formed. In this discussion only nylon in the form of yarn will be considered.

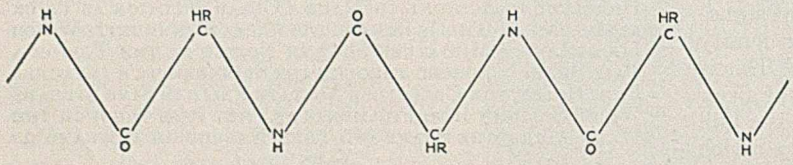


Figure 1. Structure of Natural Fiber Proteins

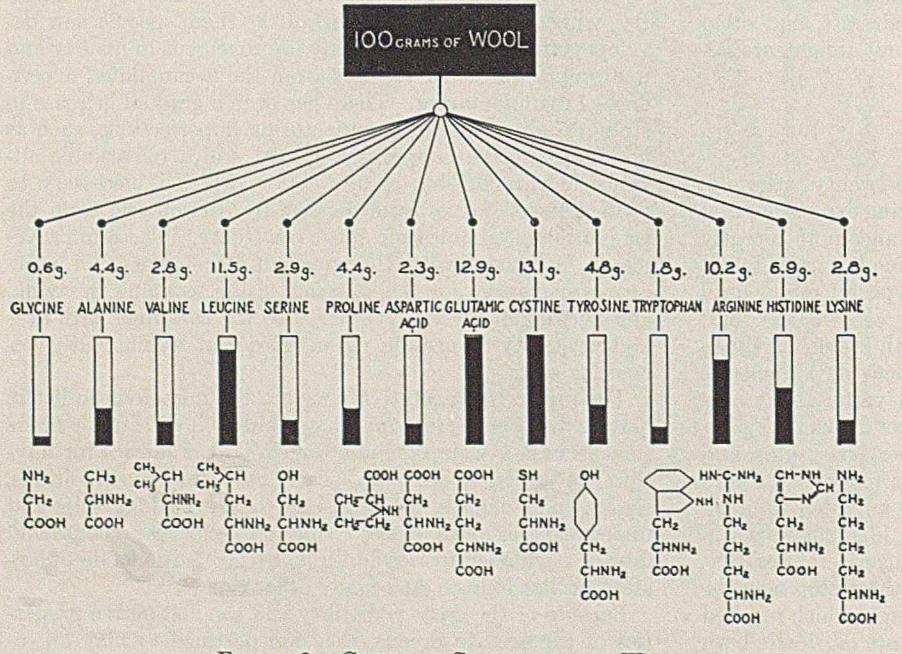


Figure 2. Chemical Composition of Wool

Relation of Structure to Natural Proteins

The recurring groups in a typical synthetic polyamide are typified by a structural formula such as

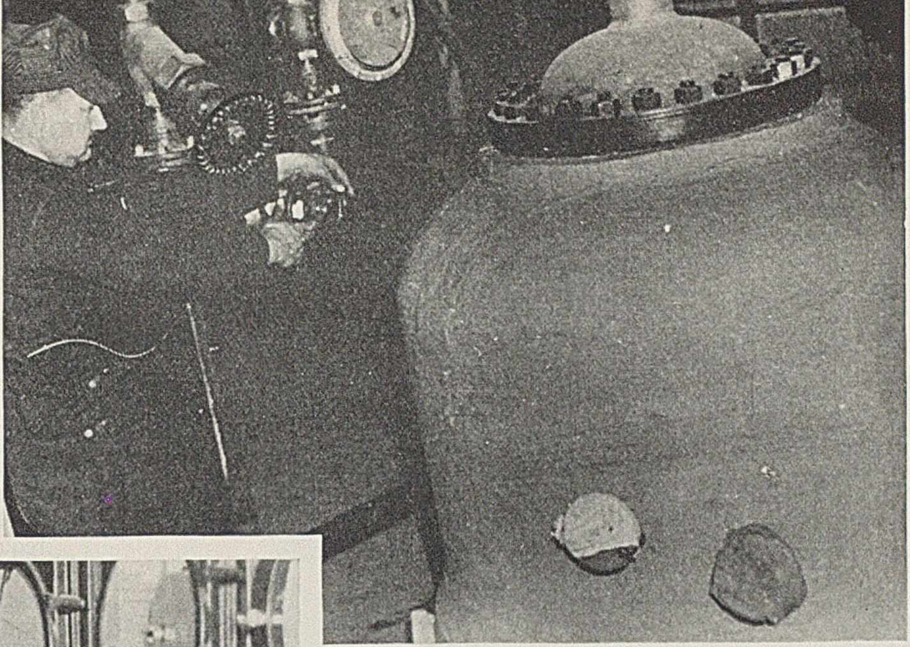
—OC—R—NH—CO—R—NH—CO—R—NH—

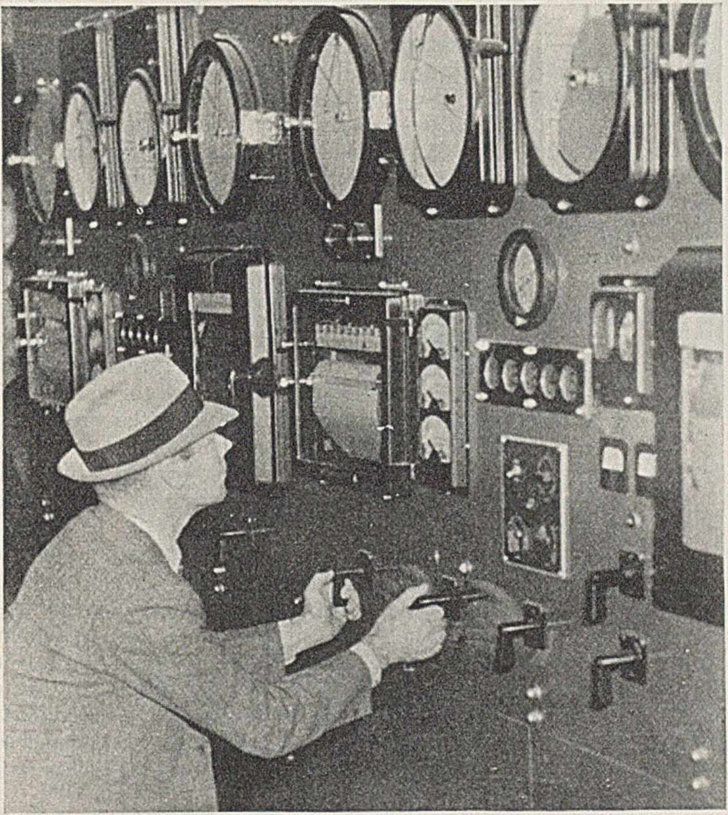
where R represents several CH_2 groups. These compositions are essentially long, straight-chain molecules or linear polymers. Structurally nylon may be related, to some extent, to the natural proteins such as silk and wool which both possess a common linear structure as Figure 1 (*1*) shows. In the case of silk R is principally methyl and for wool R is exceedingly complicated, as indicated in Figure 2 (*2*). All of these differ from cellulose, as represented by cotton and wood pulp, in that they contain carbon-nitrogen linkages and do not possess the free hydroxyl groups characteristic of the latter, as Figure 3 (*3*) shows.

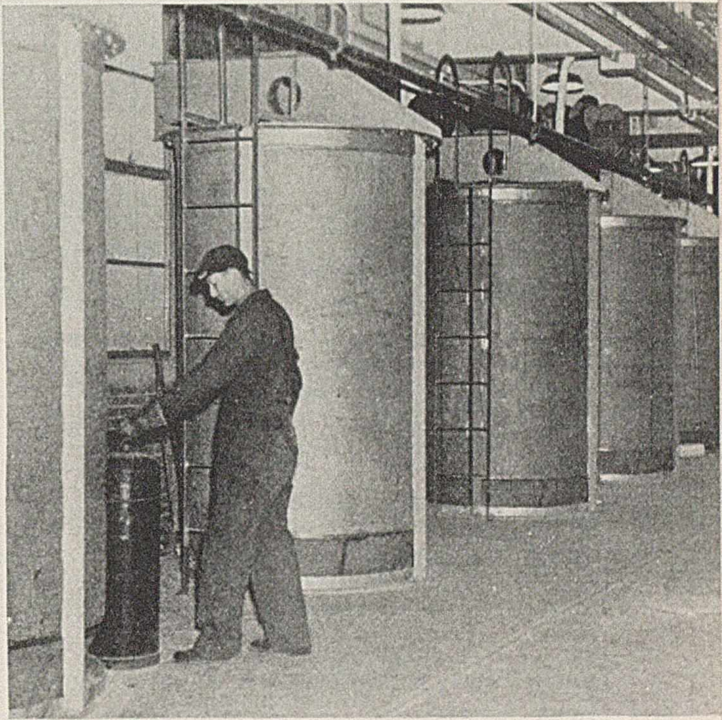
From the foregoing it is evident that structurally nylon is much more closely related to the natural proteins than to cellulose. This is equally true of its properties.

(*Right*) First Step in the Manufacture of Nylon Yarn Begins in This Giant Vessel, Set in the Floor of the Plant at Seaford, Del.

(*Below*) One of the Ingenious Instrument Panels Watching Over the Manufacture of Nylon Yarn; Precision Is Maintained by Control Lights, Chimes, and Varicolored Lines Traced on Charts Which Record the Operations





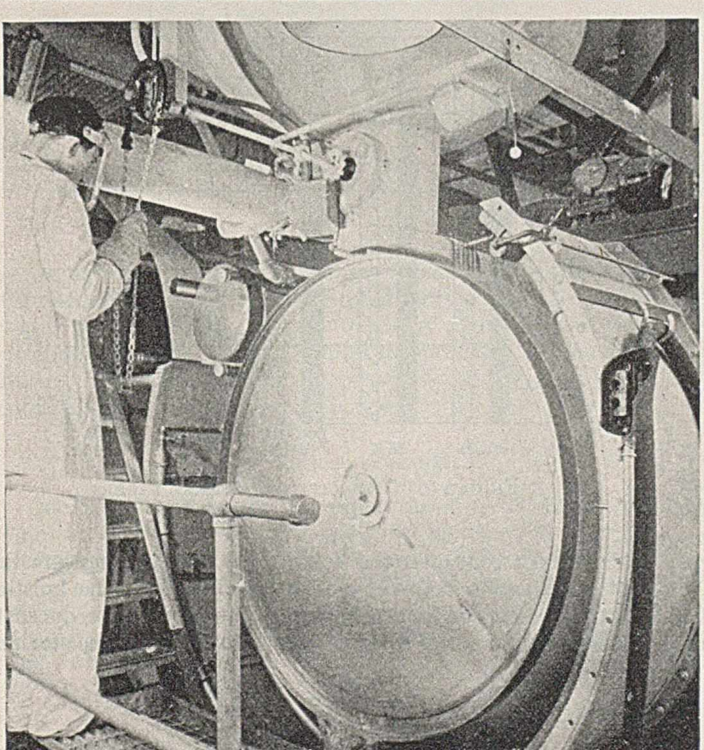


(*Above*) This Battery of Metal Canisters Contains Nylon Chips, About to Be Transformed into Yarn; Called "Blenders", They Mix the Material to Ensure a Uniform Product

(*Left*) Nylon Polymer Is Extruded in Ribbon Form on This Huge Casting Wheel

The polymer is first seen as a molten mass, but quickly solidifies and resembles ivory; in later operations it is chopped, melted, and extruded again as filaments.

(*Right*) Nylon Flake Pours from the Hoppers



Physical Characteristics

The elastic recovery of nylon is remarkable. Figure 4 gives comparisons between the fibers silk, two types of regenerated-cellulose rayon, acetate rayon, and nylon. In this test the samples were stretched 4 per cent, held for 100 seconds, and measured 60 seconds after the load was released.

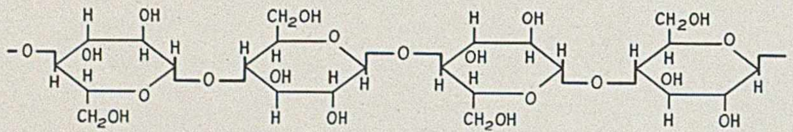


Figure 3. Structure of Cellulose

Figure 5 gives a comparison of average strengths, wet and dry, for the same group of fibers. It will be understood that appreciable variations may exist, depending on the samples chosen.

Figure 6 shows water absorption at a relative humidity of 60 per cent.

Manufacturing Process

The comparisons given have been made with drawn or oriented nylon yarn. Prior to the preparation of the yarn it is necessary to carry out condensation reactions in which low-molecular-weight polyamide units are built up to large molecules. With an adequate degree of polymerization a tough, hornlike, nylon polymer is obtained. The molten mass is extruded as a ribbon and is ground to granular form. It has a crystalline structure and melts sharply. It is completely stable and may be stored for any length of time until required for the spinning of the yarn. The flake is melted and then extruded from a spinnerette, and the resolidified filaments are collected on a suitable package. Although at this stage the material is crystalline and not amorphous, the molecules have essentially random distribution. Visualize these long-chain molecules within the filaments lying in all directions, twisted and coiled and wrinkled. The x-ray pattern characteristic of this yarn is shown in Figure 7. In this form the fibers have relatively little practical use, and it is necessary to bring about orientation through stretching of the filaments. Relatively little force is required to accomplish a fourfold increase in length. This new length and proportionately reduced diameter are the permanent attributes of the stretched or drawn yarn. In other words, although the yarn will undergo slight changes in dimension with variations in its moisture content and will shrink a few per cent the first time it is put in hot water, nevertheless it is stable in its drawn form and will not return to the undrawn, disoriented state. Orientation is shown in Figure 7 as a result of this drawing of the filaments. The drawn yarn is now strong, elastic, and tough, and shows the characteristics described above.

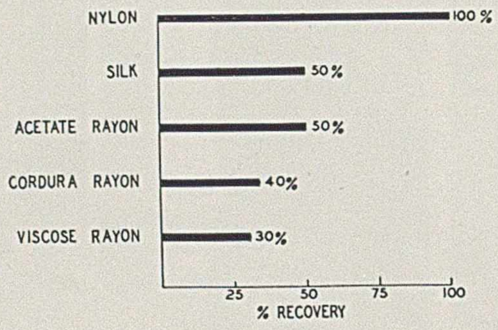


Figure 4. Comparison of Elastic Recoveries with an Imposed Load

Nylon in Full-Fashioned Hosiery

The principal use for nylon so far has been in full-fashioned hosiery. In addition to the requirements imposed on the yarn by the wearer of the hose who expects beauty, comfort, and long service, there are additional requirements imposed by the knitting, processing, and dyeing steps in hosiery manufacture.

Full-fashioned stockings are shaped to fit the leg. Such stockings are knitted flat, then seamed down the back around the heel, bottom, and to the toe. The leg is narrowed by dropping stitches as the knitting progresses down the leg.

Knitting is customarily done on two machines. First the leg, including the hem or welt, and the heel are knit on the legger. The needle bar of a full-fashioned hosiery machine has from thirty to forty-four needles per inch, each of which must be in perfect alignment. The yarn supply is at the back of the machine, the thread being delivered through various guides and mechanisms to the needle bar. One of the requirements of a satisfactory stocking is uniformity of stitch. Experience has shown that for best results the yarn should be knit wet; so in its travel to the needles the yarn passes over wicks or under guides immersed in water. Since full-fashioned hosiery machines were designed primarily to process natural silk, it was necessary to adapt nylon to this same equipment.

Commonly, only the legs are knit on the machine just described, the feet being knitted into the leg on a separate machine of the same type. To transfer the knitted stocking leg from the legger to the footer, an operation known as topping is necessary. Each loop of yarn is removed by hand from the knitting needles of the legger and transferred to those of the footer. The knitting needles are attached to needle bars which are removed from the machines with fabric attached. For ordinary size stockings the needle bar is 14 inches long. The footer continues the knitting without leaving any line of demarcation between the leg and foot. As the knitting continues on the foot, reinforcing threads are introduced to increase the wear of sole and toe. At this point the stocking

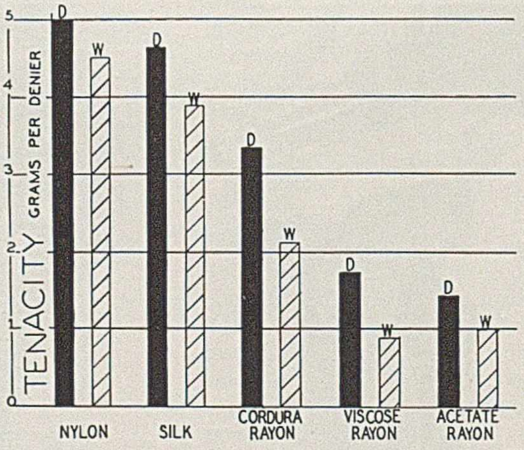


Figure 5. Tenacity of Several Fibers

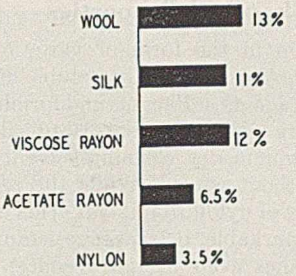


FIGURE 6. WATER ABSORPTION AT 60 PER CENT RELATIVE HUMIDITY

Data on silk, viscose rayon, and wool from Wilson and Fuwa (4).

has the appearance shown in Figure 8 (center). Next the seams must be sewn to form the feet and to close the stocking at the back of the leg. The stockings are then ready for dyeing and for shaping by putting on a wood or metal form called a "board".

During these operations there are many handlings of the fabric, and it is easy to snag and pull out individual filaments unless suitable protection is given them. This is a problem with natural silk although it has a protective coating called "sericin" which binds the filaments together. The sericin softens during the wetting-out of the yarn and hardens again on evaporation of the moisture to give a firm fabric with all the loops held in place. It was necessary to find a material called a "size" which would do for nylon what sericin does for natural silk—adhere to the nylon, soften when wet with water without becoming tacky or sticky, redry to give firm positioning of the loops in the fabric, protect the filaments during the various handling operations, and be easily removed after it had served its purpose.

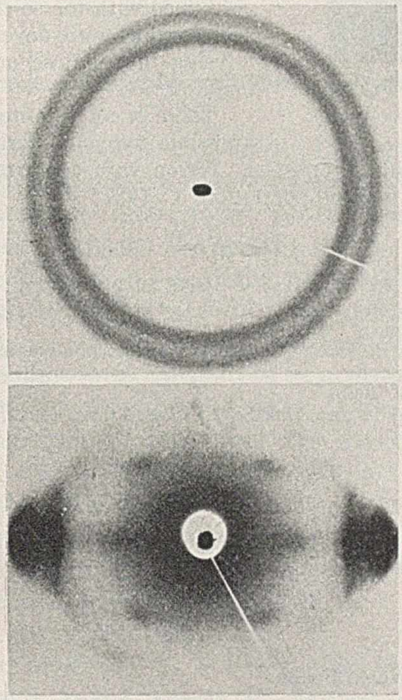


FIGURE 7. X-RAY PATTERN OF UNORIENTED (*above*) AND ORIENTED NYLON YARN

Setting Characteristics

One of the most interesting properties of nylon hose is its ability to take a permanent shape or set by means of a simple treatment with boiling water or steam. Figure 8 (right) shows a nylon stocking dyed in a manner normally used for silk or other fibers, and shaped on a standard boarding form. Note the wrinkles in the stocking. Figure 8 (left) shows a stocking which has been placed on the boarding form and subjected to steam at 5 pounds gage pressure (228° F.) for 5 minutes before being dyed. Each stocking has taken a permanent set; one obviously is desirable and the other is not. By giving the first stocking a treatment at a higher temperature for a longer time, the wrinkles can be removed. Generalizing, nylon under conditions of heat and moisture tends to take a permanent set which can be modified only by more drastic conditions—that is, higher temperatures and longer times.

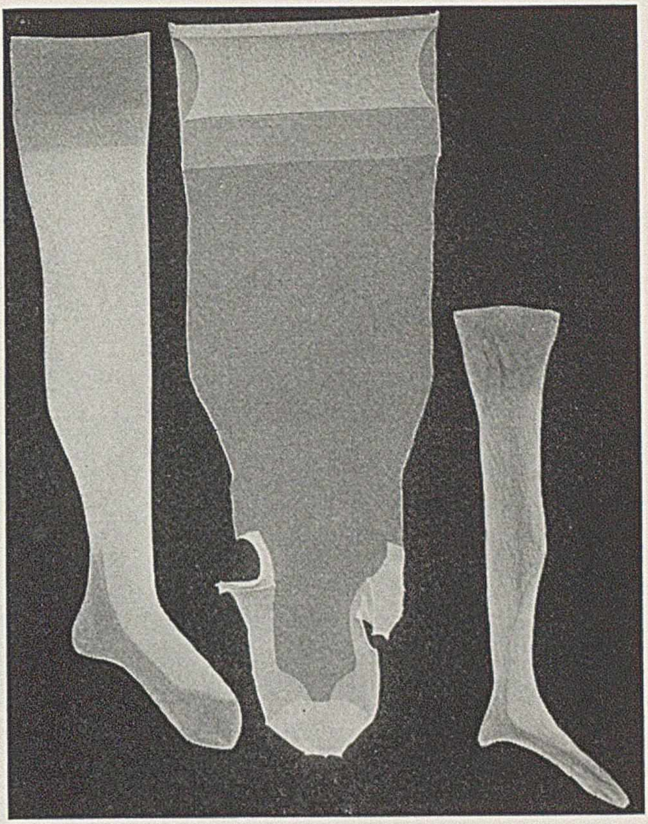


FIGURE 8. APPEARANCE OF GRAY STOCKING PRIOR TO LOOPING AND SEAMING (*center*); (*right*) NYLON STOCKING DYED LIKE SILK OR OTHER FIBERS AND SHAPED ON FORM; (*left*) NYLON STOCKING AFTER BEING PLACED ON FORM AND SUBJECTED TO 5 POUNDS GAGE PRESSURE BEFORE DYEING

This phenomenon is really an exaggeration of a similar phenomenon which takes place in the pressing of cotton, wool, or silk garments. To put a crease in a pair of trousers or to remove the wrinkles from a dress, it is customary to iron through a wet cloth or to use a press supplying the pressure

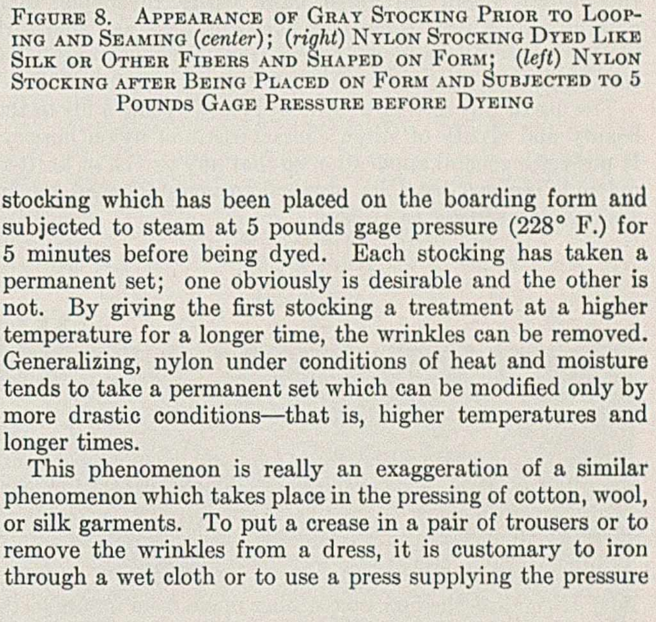
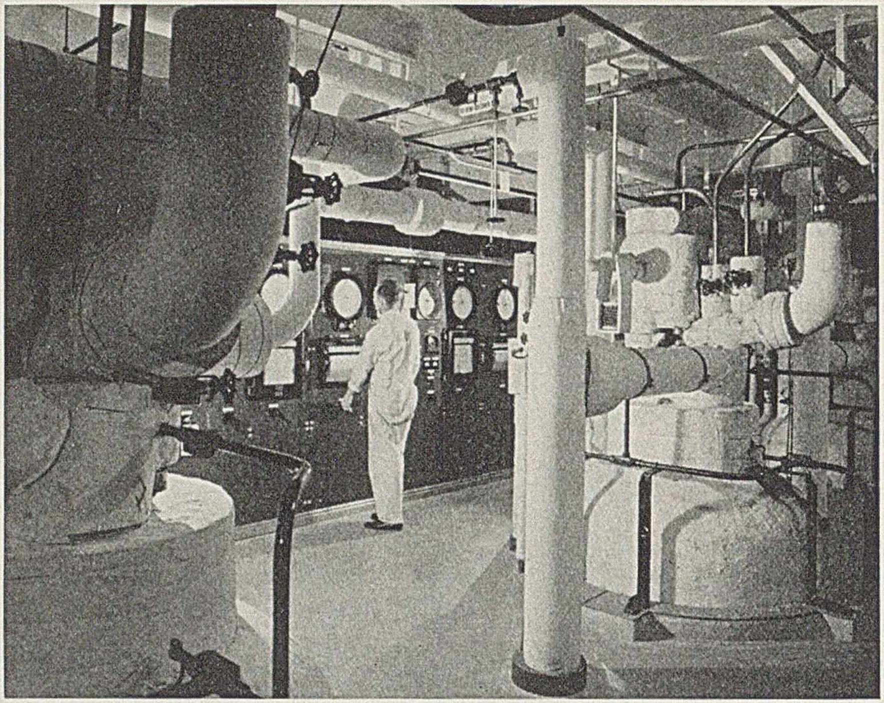


FIGURE 9. ALKALI RESISTANCE OF NYLON



Autoclaves in the du Pont Nylon Plant, Where Polymerization Takes Place

and the moisture in the form of steam. These operations on the natural fibers are much more easily reversible than with nylon. A brief shower or even the heat and moisture of the body will remove creases from the best of suiting materials.

The use of this setting treatment before dyeing adds to the beauty and clarity of stitch characteristic of nylon hosiery. It possesses general application so that any woven or knitted nylon fabric can have its physical form established by an appropriate setting treatment.

Chemical Properties

Nylon in the form of yarn, or otherwise, is difficultly soluble in most reagents. Phenols and formic acid are active solvents, but all the common dry cleaning solvents are without effect. While the resistance of nylon to mineral acids is not remarkable, it is quite resistant to alkalies even in fairly concentrated solutions and at elevated temperatures (Figure 9).

Nylon yarn and fabrics are practically nonflammable. Nylon has been exhaustively tested for physiological activity. It is completely inert and has found use in the form of surgical sutures. It is resistant to enzymes, mildew, molds, and moths.

While nylon shows affinity for a great many classes of dyestuffs, the best results to date have been obtained with the so-called acetate colors which were developed for the dyeing of cellulose acetate yarns and fabrics.

There is an infinite number of possible nylons, differing widely in their physical properties. Nylon yarn as currently offered has a high melting point, 253° C. (487° F.).

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Vinyon

FREDERIC BONNET

American Viscose Corporation, Marcus Hook, Penna.

VINYON is the new textile fiber made from an unplasticized vinyl resin which is a copolymer of vinyl chloride and vinyl acetate. S. D. Douglas[1] pointed out that these resins are prepared by polymerization rather than by a condensation reaction, as is the case with the phenolic, urea, and alkyd types. Moreover, the resulting molecular structure of these vinyl polymers is linear or straight chain, in which the monomers have reacted with one another at the double bond to give high-molecular-weight molecules.

Such a straight-chain structure seems to be most important if the resin is to find use as a textile fiber; and the longer the straight chain (i. e., the larger the molecules of the polymer), the stronger and more resilient will be the resulting fibers and textile yarns. This is also exemplified by the polyamide nylon which is a long straight-chain compound and, like "Vinyon", must be stretched to give a serviceable yarn.

Although "Vinyon" is made from vinyl chloride and vinyl acetate, it must not be assumed that it is a mere mixture of the two. Mixtures of the chloride and acetate polymers even when most thoroughly and carefully blended give only weak and indifferent results of little or no industrial interest. When, however, the monomers are mixed so that they may be copolymerized—i. e., polymerized together—a whole series of resins result whose properties depend not only upon the initial mixture of the monomers but also upon the degree of polymerization which has been allowed to take place. It is the degree of polymerization which determines the molecular weight or the length of the straight-chain molecules.

This copolymerization is interesting in that the vinyl acetate seems to plasticize the vinyl chloride internally, and

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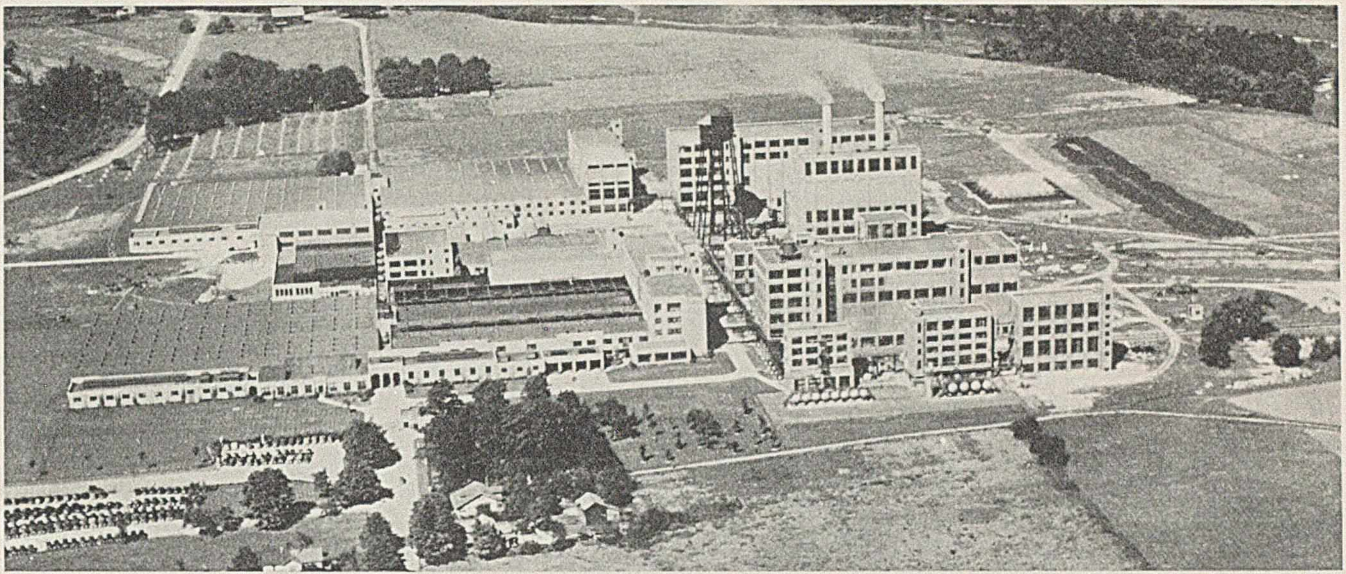
[1] Ind. Eng. Chem., 32, 315 (1940).



Acetate Rayon Plant of American Viscose Corporation at Meadville, Penna., Where Vinyon Is Now in Commercial Production

Vinyon is a copolymerized vinyl resin made of vinyl chloride and vinyl acetate. The vinyl acetate internally plasticizes the chloride, making the resin stable. The polymerization takes place at the double bond and gives a straight-chain linkage which is important for a resin textile.

The copolymer is dissolved in acetone and spun in air as is cellulose acetate. The spun yarn is not strong but, after stretching several hundred per cent, may attain a strength of 80,000 pounds per square inch. The yarn is very resistant to strong acids and alkalies at ordinary temperatures. It is practically water repellent and is as strong wet as it is dry.

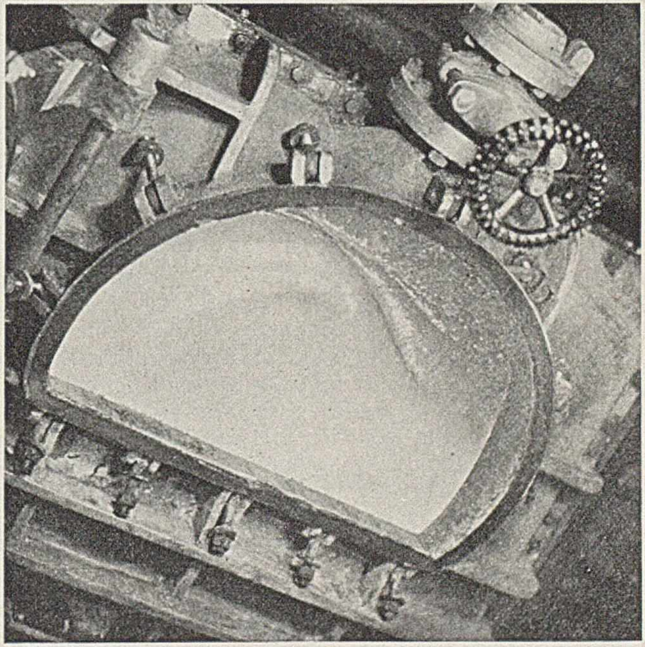
It can be dyed. It is thermoplastic, and shrinkage takes place if heated above 65° C. Largest use at present is in industrial filter cloth, but many other uses are suggested by its remarkable properties.

no other plasticizer is necessary. The ordinary type of external plasticizers are high-boiling liquids, waxes, gums, etc., and with many resins such plasticizers are still necessary; but resins so plasticized are always subject to a change in composition owing to a loss of plasticizer by evaporation, oxidation, or solvent extraction. In the case of these vinyl resins, where the polymers are actually combined, such changes cannot take place, and the resins are stable, which is most important for a textile fiber. The resin used for "Vinyon" contains 88–90 per cent vinyl chloride and 12–10 per cent vinyl acetate with a molecular weight around 20,000.

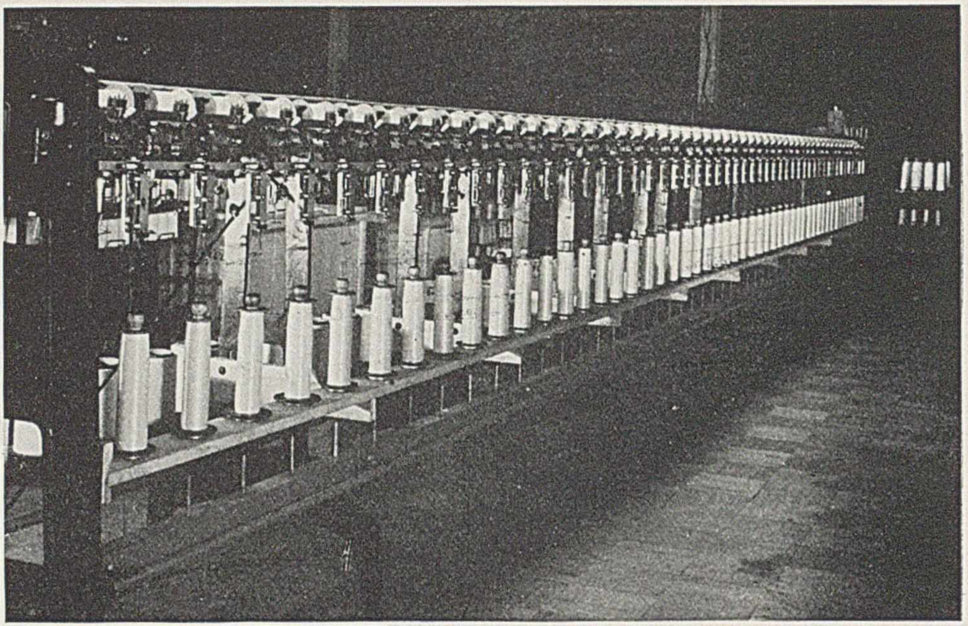
Spinning

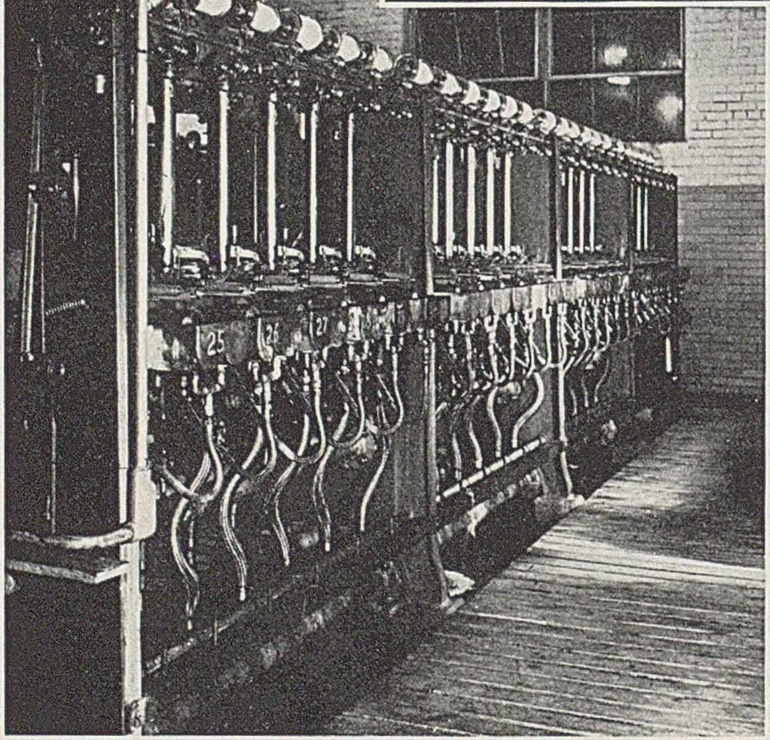
The copolymer resin, as a white fluffy powder, is dissolved in acetone to get a rather heavy, viscous spinning dope containing about 25 per cent by weight of the resin in solution. This is filtered, deaerated, and spun downward in air through multiholed stainless-steel jets, just as is done in acetate spinning, the solvent acetone being removed by a current of warm air and recovered.

After being conditioned on the take-up bobbin, the yarn is stretched either directly or after being plied with one or more ends. This stretching operation is of great importance in producing a serviceable yarn of good strength, extensibility, elasticity, and resiliency. For high strength the yarn is stretched several hundred per cent; for lower strengths but



Overhead View of Mixer Used in Vinyon Manufacture





(*Right*) EQUIPMENT FOR SPOOLING VINYON

(*Below*) MACHINE FOR STRETCHING VINYON

greater softness and more extensibility the stretching is correspondingly less.

After stretching, the yarn is set by heating, while under tension, to about 90–100° C. This treatment makes the yarn stable as to shrinkage up to at least 65° C., but when heated above this temperature, shrinkage of the yarn occurs with a corresponding reduction in tenacity and increase in elongation. This shrinkage is quite definite for the temperature to which it may be subjected; e. g., at 75° C. there is a shrinkage of about 12 per cent, at 80° C. there is further shrinkage with a tendency for the filaments to adhere to one another, while at 135–140° C. definite tackiness develops.

The yarn as spun has comparatively large filaments which, in the stretching process, become smaller. In fact they can be reduced to gossamer fineness without the yarn becoming brittle or in any way lower in quality. For example, a yarn with 10 filaments but only 8 denier in size has filaments much finer than silk, yet such a yarn is strong enough to be knit on a regular circular stocking machine.

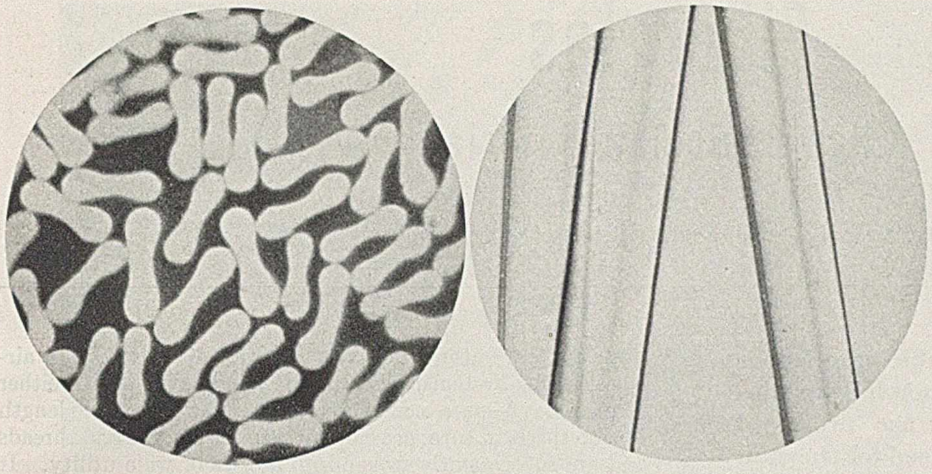
Properties

"Vinyon" yarn is definitely thermoplastic so that if heated above 65° C. it will shrink. Mineral acids and alkalies do not attack it at room temperature, even in high concentrations. Thus 70 per cent nitric acid, aqua regia, hydrochloric and hydrofluoric acids at maximum concentration do not affect it, nor do 30 per cent sodium hydroxide, 28 per cent ammonium hydroxide, salt solutions, or even copper ammonia solution, which is so effective in dissolving cellulose. It is also unaffected by alcohols, glycols, or aliphatic hydrocarbons (gasoline, mineral oils, etc.). On the other hand, it is dissolved by ketones, and softened or partly dissolved by esters, certain halogenated hydrocarbons, ethers, certain amines, and aromatic hydrocarbons.

"Vinyon" is unaffected by water; in fact, it may be considered water repellent although its surface may be wetted by using some of the commercial wetting agents. Neither bacteria, molds, nor other fungi grow on its surface so it is not subject to so-called mildew of any kind; therefore it should find use in damp climates.

The yarn is not flammable nor will it support combustion. When heated in a flame it melts and then chars, but it will not burn.

The tenacity can be controlled within a range of 1 to 4 grams per denier, the higher strength having the lower extensibility and vice versa. One to four grams per denier is roughly equivalent to 20,000 to 80,000 pounds per square inch. Because it is unaffected by water, this new yarn shows the same tenacity and elongation, both dry and wet. For comparison the following table shows the tenacity and elongation of various fibers:



Cross (*left*) and Longitudinal Views of Vinyon (× 300)

Yarn	Dry (Relative Humidity, 65%)		Wet	
	Tenacity *G./denier*	Elongation *Per cent*	Tenacity *G./denier*	Elongation *Per cent*
Silk (degummed)	4.22	16	3.4	26.3
Viscose	2.00	18	1.0	25
Acetate	1.40	27	0.85	36
"Vinyon"				
High-stretch	..	..	4.00	18
Medium-stretch	..	..	2.30	25
Unstretched	..	..	1.00	120

The ordinary yarn is bright but, as with acetate or viscose, it may be dulled by incorporating pigments in the spinning dope. Its specific gravity is about the same as acetate or wool—namely, 1.34 to 1.36. It does not conduct electricity and, as water does not affect it, is an excellent insulator which easily develops and retains a static charge. Its flexing strength and its stability to the action of sunlight are excellent. It has true elasticity.

Aside from coloring the "Vinyon" by adding pigments to the spinning dope, dyeing of the fibers or fabric seemed at first to offer great difficulties because of the low dyeing temperature required and because it was so inert to water. However, investigation soon showed that "Vinyon" could be dyed with water-insoluble acetate rayon dyestuffs in the presence of small amounts of certain solid organic chemicals—for example, *o*-hydroxydiphenyl—termed "assistants". The ordinary amount of dyestuff can be used (e. g., 2 per cent) which in the presence of the assistant is satisfactorily exhausted. The choice of assistant is, however, quite important because it influences the fastness property of the dyestuff.

Uses

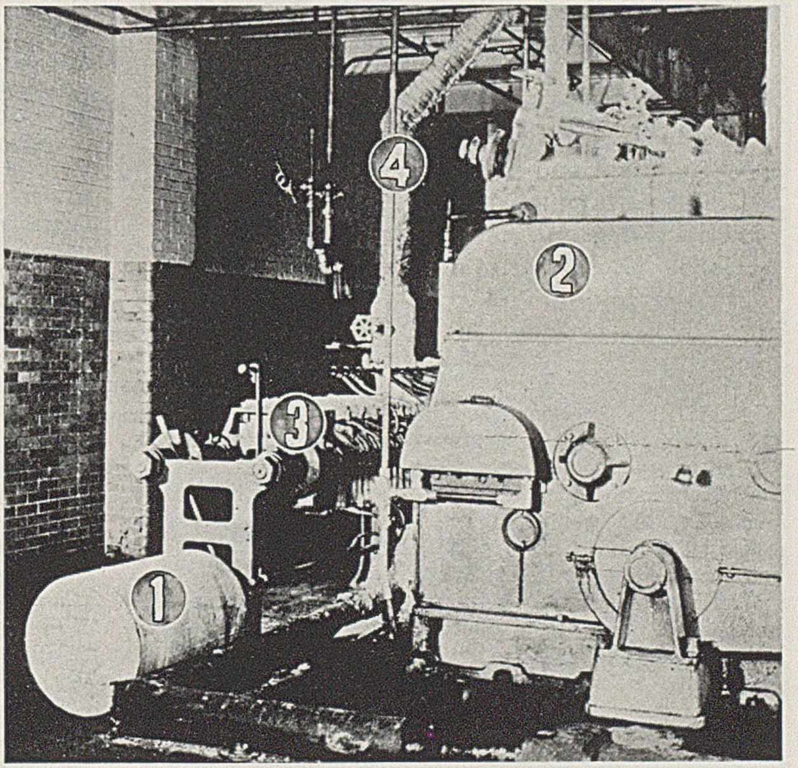
Small amounts of "Vinyon" staple have been successfully used in making cotton, wool, and glass felts; the thermoplastic resin functions as a binder which not only gives added strength but shortens the time of manufacture.

The largest use of "Vinyon" at present is in the manufacture of industrial filter cloth because of its unusual properties, particularly its resistance to chemicals either acid or alkali, and its high strength both wet and dry.

The weaving of the cloth offers no special difficulty; a gelatin size with an ordinary softener is suitable for warping, but weaving should be done at high humidity to avoid the production of static as much as possible.

Some successful trials have recently been made with "Vinyon" fish nets and lines along the Florida coast. Not only did the "Vinyon" nets catch twice as many fish as did the ordinary tar-impregnated cotton nets, but in a 6-month test they gave no sign of deterioration, whereas all the other types tested at the same time showed partial or complete disintegration.

Other suggested uses, some of which are rapidly developing, are for shower curtains, bathing suits, waterproof acid- and alkali-resistant clothing, full-fashioned hosiery, fireproof awnings, curtains, sailcloth, umbrella fabrics, tent and tarpaulin materials, shoe linings, braids, and various knit fabrics, etc. However, in commercially developing these various uses, a policy of careful test and experimentation is being followed so that the new textile shall be used only for such purposes and under such conditions as are warranted by its special properties.



Steps in the Manufacture of Vinyon

(1) Vinylite resin as it arrives at the plant; (2) mixer; (3) filter press; (4) insulated piping, indicating the importance of close temperature control in Vinyon fiber production.

Fiberglas

A New Basic Raw Material

GAMES SLAYTER, Owens-Corning Fiberglas Corporation, Newark, Ohio

Glass fibers possess desirable properties not found in any other commercially available material. These fibers are produced as a wool-like fiber, largely used for thermal insulation, and as a textile fiber, either continuous or in staple lengths, employed to form yarns, threads, and woven fabrics.

Glass fibers are inorganic, incombustible, nonabsorptive. They possess extraordinary tensile strength, electrical properties, and heat resistance. They are chemically stable and resist attacks of many chemicals. They do not rot, decay, or feed fungus growths or vermin. Colors in the glass itself are sun-fast and durable; dyes may be used for surface coloring of the fibers.

Wool forms are used for insulation of houses, ships, trains, aircraft, ranges, refrigerators, and similar equipment, and for industrial insulation at temperatures from below 0° to over 1000° F. Textile forms are used for electrical insulation, electric storage battery retainer mats, chemical and fume filtration services, and a wide variety of industrial applications. Decorative fabrics have found many practical applications. Glass fabrics are not recommended for wearing apparel.

LEADERS of science and industry have shown great interest during the past few years in the development of a new all-glass fiber which has come to aid the other basic fibers in doing the work of the world. This interest is understandable when we remember that glass fibers possess properties and characteristics not found in similar combination in any other commercially available material.

We all know the attributes of glass which make it one of the most perfect of all man-made materials—its plasticity when molten, its hardness and strength, its cleanliness and its great durability. All of these desirable attributes of glass in solid form are retained when glass is transmuted into fibrous form. But in addition, the original properties are extended by many new properties not found in other organic or inorganic materials of comparable utility.

There are two basic forms of Fiberglas—a wool form and a textile fiber form. Wool-like fibers are used primarily for thermal insulation purposes; coarser fibers of this same basic type are also extensively used for air filtration in air-conditioning systems. The textile fibers are made in either of two ways—as a continuous filament or as staple length fibers; these, in turn, are employed to form yarns and threads and are subsequently woven into fabrics of wide utility. It is this second form that will be discussed here.

Production

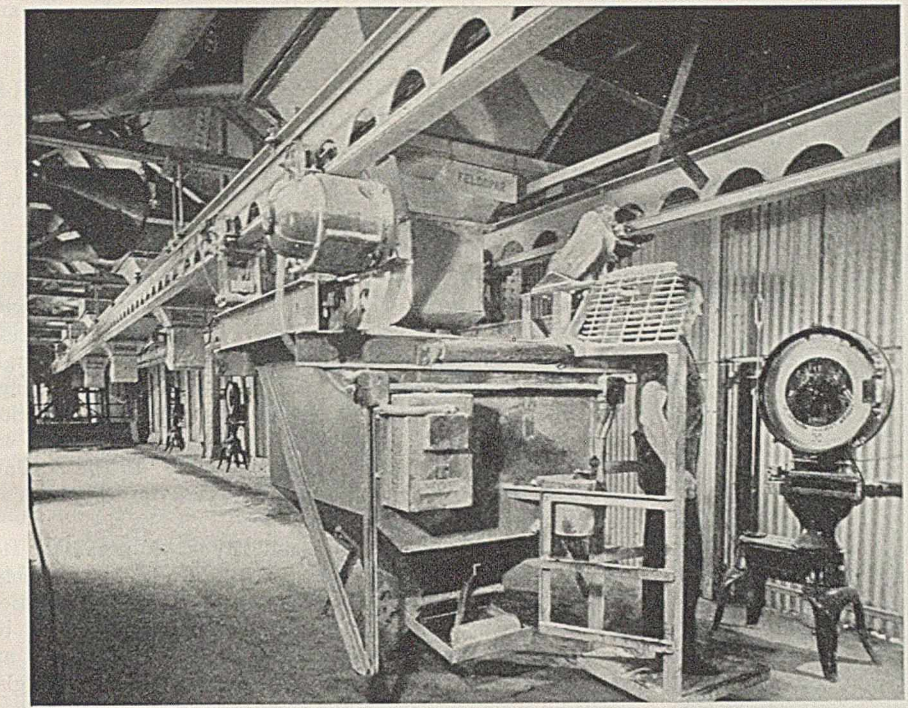
The production of Fiberglas in all its forms begins with the manufacture of virgin glass from carefully selected silica sand, limestone, and other pure mineral ingredients according to precision formulas. The raw materials are checked with great accuracy, the batches are compounded under the protective control of automatic recording scales, and the ingredients are melted under close temperature control. Various types of glasses are produced in this manner, each designed to provide the desired characteristics of the products ultimately formed.

The glasses used in the production of textile fibers are further refined by remelting in electrical furnaces just prior to drying into fibers. There are two Fiberglas textile processes. One produces staple fiber and the other makes continuous filament. The staple process is named after the common textile term measuring a limited length. Glass staple fibers average 8 to 15 inches in length, which is much greater than the length of the best long-staple cotton. The fiber diameter most commonly made averages 0.00027 inch, but recent developments have shown the desirability of making fibers of other diameters, and we are now beginning the production of staple fibers of somewhat larger size. To translate these figures into more commonly understood terms, our standard fibers have a diameter about one fifteenth that of a human hair. The individual fibers are smooth and substantially cylindrical.

In the staple process the glass cullet is melted electrically and the molten glass pours from orifices beneath the furnace. High-pressure jets of steam or air tear the stream of glass and draw the particles into long smooth fibers. These are gathered on a traveling belt in the form of a web or ribbon of interlaced fibers, from which they are gathered, without twist, as a sliver. In the gathering process the fibers are slightly drafted so that the majority lie parallel to the length of the strands.

This is the raw material of staple fiber rovings and yarns. Glass textile terminology is the same as that of other textiles. A roving is a sliver with a low twist and is formed simply by twisting the sliver on a standard twister or flyer twister. A yarn is a sliver or roving given a higher twist. Fine yarns of Fiberglas staple fiber are made by drafting sliver in a manner similar to the worsted spinning process. Coarse yarns are made without drafting.

A small amount of mineral oil lubricant is used on staple fibers. This lubricant improves the processing characteristics and minimizes friction between the individual fibers, which tends to cause scratching and breakage. This lubri-



Equipment for Accurate Proportioning of Raw Materials According to Precise Formulas for Making Fiberglas

Beneath each storage bin is a weigh hopper connected to a recording scale. The proper amount is weighed out into the hopper, and then the batch of combined materials is gathered by a collecting car running on rails beneath the bins.

cant may readily be removed by washing with soap in hot water or by carbon tetrachloride or ether.

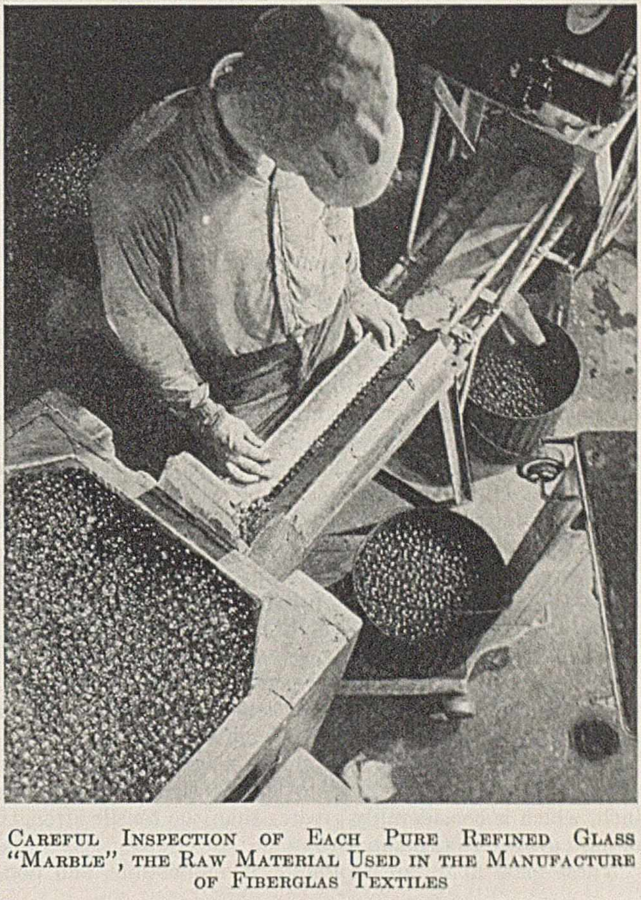
The process of making Fiberglas as a continuous filament is different from the staple fiber process. The continuous filament form is unique in that the glass is drawn continuously to indefinite lengths, the latter being limited only by the problems of packaging. The average diameter of the individual filaments is 0.00022 inch, although here again we can make finer or coarser filaments to vary the characteristics of the final products.

A large number of filaments (generally 102 or more) are drawn simultaneously gathered together in a strand, and caught on a winder that draws them at a speed in excess of a mile a minute. These combined strands are still so fine that they can scarcely be seen as they are gathered by the winder; yet the speed at which they are produced is incontrovertible evidence of their great tensile strength.

A small amount of lubricant and coating is used on the continuous strand. This material serves to facilitate manufacturing operations and to keep the individual glass fibers apart. Glass fibers may be thought of as very small glass rods which few substances will scratch, but which will scratch one another. Once scratched, the fibers are easily broken. The coating used is generally composed of starch and vegetable oil. It may readily be removed by washing with soap in hot water. Being organic, it is also removable by heating the finished textile at 600° to 700° F. in a well-ventilated oven for one hour.

Fiberglas yarns are processed on standard textile machinery after slight modification and adjustment found desirable in plant operations. Practically every type of weave which may be made with other textile materials can be made with glass fibers. The continuous filament strands are twisted together in any desired construction to form yarns or threads. The staple fibers are treated much like worsted yarns. They are drawn into slivers and yarns of various counts, some moderately fine to coarse, according to their subsequent use.

The textile fibers made of Fiberglas are subjected to numerous quality control tests. In one test the fiber is magnified hundreds of times so that an operator can check for diameter uniformity. In another test a quality control checker examines the twist in Fiberglas yarns. Still another test determines the tensile strength of the yarn. Representative samples are taken from production at regular intervals to ensure uniformity in tensile strength. Standard textile



Careful Inspection of Each Pure Refined Glass "Marble", the Raw Material Used in the Manufacture of Fiberglas Textiles

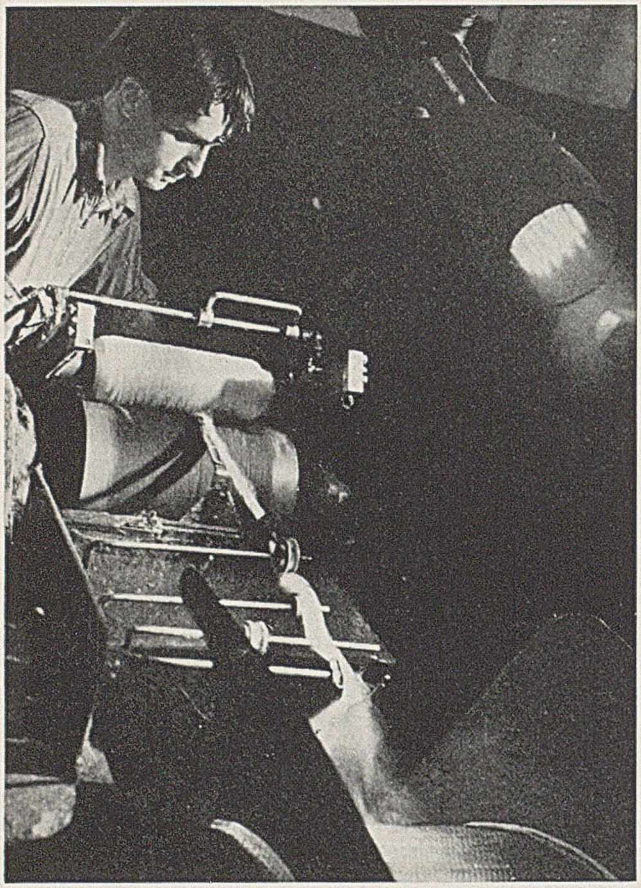


Photo by Robert Yarnall Richie

STEAM-DRAWING PROCESS FOR GLASS STAPLE FIBERS
The molten glass pours from orifices through a high-pressure steam jet; the fibers are driven downward onto a rapidly revolving drum from which they are immediately gathered into a roving and are wound on a spindle or spool.

testing machinery is employed in these tests, which are made constantly in order to ensure uniform quality at all times.

Properties

The utility of Fiberglas lies in its unique combination of physical, electrical, and chemical properties. Let us think for the moment of the properties of glass in its more common forms—in windows, in bottles, in the glassware essential to every chemical laboratory, and in cooking ware now becoming essential to most housewives. Think of it also as electrical insulators on telephone and power lines, as a structural material, and as a sanitary product indispensable to the modern hospital. In all of these applications we find glass to be clean, hard, strong, durable, and usually brittle.

When glass is reduced to the form of fine fibers it retains all of these properties, even brittleness, but the latter disappears as a practical consideration. In place of brittleness there is flexibility and resiliency. But in addition, there is also extraordinary tensile strength. We have produced fibers in the laboratory which have a measured tensile strength in excess of 2,000,000 pounds per square inch. Fibers of the size used in continuous filament have a tensile strength in excess of 400,000 to 500,000 pounds per square inch, which is considerably greater than the tensile strength of hard drawn, steel piano wire.

These glass fibers are inorganic, incombustible, and nonabsorptive. Being inorganic, they do not provide sustenance for vermin, fungus growths, or other forms of decay.

Glass is an incombustible material; the fibers will melt but they cannot burn. Their temperature resistance is high when formed in the mass or woven as a fabric. Fiberglas yarns, tapes, and fabrics used in the electrical industry can safely withstand temperatures in the neighborhood of 1000° F. At 800° F. electrical tapes of Fiberglas have a greater strength than is presented by cotton tapes of similar size and thickness at ordinary room temperatures.

The electrical properties of glass have long been known to the scientific world. These properties are retained by glass in fibrous form, augmented by the use of glass compositions that are free from metallic oxides. The resulting Fiberglas electrical insulation products combine high dielectric strength and electrical insulation resistance with extremely low moisture absorption. These insulating materials combine well with electrical varnishes and impregnants. In consequence, Fiberglas electrical insulation materials have already achieved a high place in that industry.

Glass is also known as a chemically stable product. It is not harmed by any acid except hydrofluoric. Nevertheless the advanced chemist knows that different glass compositions have different degrees of solubility and show minute, but measurable, reactions with many different substances and solutions. This characteristic is of no importance to glass in solid form, but when the surface area of the glass is expanded many thousands of times, as it is in the formation of glass fibers, one must become cautious in discussing complete immunity from attack.

Broadly speaking, glass fibers are chemically resistant. One of their new and important uses is in the formation of

FIBERGLAS-INSULATED DIVING SUIT FOR SALVAGE VESSELS ATTENDING UNITED STATES NAVY SUBMARINE SQUADRONS
In these electrically heated insulated suits, divers can stay at great depths twice as long as in the present equipment.

battery retainer mats for use in storage batteries. These mats, which greatly extend the life of the battery by keeping the active material in place on the battery plates, render good service because the glass is resistant to the acids of the battery solutions and at the same time possesses the desired electrical insulation characteristics.

Fiberglas fabrics have found other uses in the chemical field, notably for anode bags in electroplating processes and as filter cloths in a number of applications involving liquids or gases at temperatures that are destructive to other filtering materials or under conditions which would be corrosive to other materials but not to the gases employed.

The thermal properties of Fiberglas wool have resulted in its widespread use wherever heat is conserved, controlled, or excluded. The unusually desirable electrical properties of Fiberglas have resulted in its use wherever electricity is employed for power or light. The filtering characteristics result in the use of Fiberglas in the great majority of modern air-conditioning systems. If only these factors were considered, it can readily be understood why Fiberglas has become important to every industry, to every branch of commerce, and almost to every form of human activity.

Present and Future Uses

Although the wool forms of Fiberglas are not strictly within the scope of this paper, they constitute an important use of this fiber and deserve brief mention. Fiberglas thermal insulation materials are used extensively for the insulation of houses, ships, and vehicles of all types, including trains and aircraft. It is employed in ranges, refrigerators, water heaters, and similar domestic and industrial equipment. It is used for industrial insulation at temperatures ranging from below 0° to over 1000° F. These and other uses have followed the introduction of Fiberglas because the material combines light weight, high thermal efficiency, great durability, and low cost.

The principal use for the textile forms of Fiberglas is found in the electrical industry. The fine yarns are utilized for insulating magnet wires; coarser yarns, for heavier wires and cables. Woven into tapes, braided sleevings, cloths and tying cords, Fiberglas is now extensively used in the insulation of electric motors, generators, transformers, and other types of operating and distribution equipment.

Next in importance in the textile field are parallel developments in decorative and service fabrics. Industrial uses range from the fabrics enclosing all-glass turbine blankets to wicks for kerosene or oil lamps and stoves.

The decorative applications of Fiberglas fabrics have attracted world-wide attention. Today we are making gleaming damasks, shimmering brocades, lustrous satins, rustling taffetas, and sheer nets entirely of glass. They are woven in the smartest of designs on standard Jacquard looms, all 50 inches wide and made of pure glass thread. These new products include overdrapes, glass curtains, shower curtains, bedspreads, tablecloths, lamp shades, and awnings. In addition there are neckties, hats, and other articles. Fiberglas draperies and other textile products are being used today in homes, offices, hotels, restaurants, public buildings, clubs, Pullman cars, ocean liners, and transcontinental and transoceanic airplanes.

Aside from their novelty, these new fabrics have many advantages over better known fabrics, chief among which are their colorfast properties and durability. Fiberglas fabrics are not affected by climatic conditions and therefore will not sag or shrink. They are fireproof and heat resistant to a high point. Even a cigaret may burn out its length on this fabric and not destroy it; the resulting stain is easily removable with soap and water.

Fabrics of Fiberglas are practically soil-proof and are definitely mildew- and vermin-proof. Dust or dirt remains on the surface much the same as flecks of dust on a mirror, and can be wiped off with a damp cloth. Fiberglas fabrics at the present time come in seventeen different designs with others being added constantly.

There are several colors to choose from. Drapery materials come in pure white, ecru, medium dark gray, a light and a medium dark periwinkle blue. And we are working on the development of other colors.

In spite of the many advantages that are apparent in Fiberglas as a textile material, it does not have universal applicability. It is not suitable in its present forms for dress fabrics of any type. You may have seen pictures of charming young ladies dressed in wedding gowns and other forms of glass cloth. These are all imaginative previews of future potentials. But today we do not sell or recommend any form of Fiberglas for use as a clothing material except as the products may be combined in shoes, hats, dress accessories, or even neckties.

Fiberglas is not the competitor of many modern textile fibers. It is only occasionally the competitor of the more commonplace fibers which the world has known for many generations. Fiberglas is finding usefulness in places where other fibers, lacking some of the qualities combined with others in our product, do not render fully satisfactory service.

There are many such applications where the characteristics of glass in fibrous form open new doors for textile products. Looking into the future, we see potential applications in the aircraft industry which require light weight combined with great strength, complete fire resistance, and durability. It may prove advantageous to use Fiberglas for sandbags in military defense or protection against floods, because Fiberglas will not rot in such service, and bags can be made up long in advance of need and stored ready for the emergency. We are already far into the development of awning fabrics of Fiberglas, which will not be burned by cigarets thrown down from above and which will be permissible even in the most strictly controlled fire zones of our largest cities.

Fiberglas is the product of research and its future growth depends upon continued research. Although the industry is scarcely nine years old, it is today producing Fiberglas at the rate of many carloads daily.

Correction—*P-V-T* Relations of Propylene

E. E. Roper has pointed out that the apparent discrepancy (*4*) in the determinations of the vapor densities of propylene at 25° C. and 1 atmosphere (*2*, *4*) and at 0° C. and 1 atmosphere (*1*) is nonexistent. If the compressibility factor, $Z = PV/RT$, at 0° C. and 1 atmosphere is computed, there are obtained from Roper's data (*3*), 0.9809; from Batuecas', 0.9803; and from Vaughan and Graves' (by interpolation on a Z *vs.* P plot), 0.980. The perfect agreement is noteworthy. We have found that although Batuecas' density, 1.9149 grams per liter at 0° C. and 1 atmosphere, is correctly given in our paper (*4*), an error of omission of a digit was made in the calculation to 25°, giving rise to the question. It may now be said that all of the data (*1–4*) are well coordinated.

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WILLIAM E. VAUGHAN AND NOEL R. GRAVES

Corrosion Control with Threshold Treatment

Inhibition of the Corrosion of Iron and Steel with Hexametaphosphate

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Threshold treatment with hexametaphosphate in concentrations of 0.5 to 5 p. p. m. has previously found extensive application for the stabilization of waters which tend to precipitate calcium carbonate. In addition to the property of stabilizing moderate supersaturation with respect to calcium carbonate, the treatment has a marked inhibitive action upon the corrosion of iron and steel. Laboratory tests with black iron pipe have qualitatively demonstrated the inhibition of corrosion by threshold treatment. For the quantitative evaluation of the inhibitive action of the treatment, the decrease in oxygen concentration which resulted upon passage of the water through a column of steel wool has been used as a measure of corrosion. The results obtained are in good agreement with the visual evidence from the tests with black iron pipe. Data show the effect of hexametaphosphate concentration, rate of water flow, presence of previously formed rust, and pH upon the rate of corrosion at normal tap water temperatures. It is postulated that the effect of threshold treatment upon corrosion is due to the adsorption of hexametaphosphate, or a complex thereof, upon the metal or metal oxide surface.

CORROSION and calcium carbonate scale have long been two of the chief sources of trouble for the water chemist supervising the operation of a distribution or cooling system. The elimination of calcium carbonate scale by threshold treatment was described in previous papers (*10, 15, 16*). Threshold treatment is a process by which moderate supersaturation with respect to calcium carbonate is stabilized, in effect, by the presence of 0.5 to 5 p. p. m. of a molecularly dehydrated phosphate, such as sodium hexametaphosphate (*10, 18*). It has found extensive application for the prevention of afterprecipitation following lime-soda softeners (*12, 15, 16*) and for the elimination of scale in heat exchange equipment (*15, 16*). However, calcium carbonate scale has frequently been employed as a means of checking corrosion (*2, 3*), and numerous investigations have been conducted with the object of obtaining uniformly thin, continuous, carbonate coatings for the isolation of the metal surface (*3, 6, 11, 14*). Thus, it might appear that elimination of scale by threshold treatment would be simply an invitation to "red water", tuberculation, and other corrosion troubles; such is not the case, as the hexametaphosphate employed exerts a definite inhibitive action upon the corrosion of ferrous metals.

Qualitative Pipe Corrosion Tests

Preliminary tests to determine the effect of threshold treatment with hexametaphosphate upon corrosion were conducted on 2-foot (61-cm.) sections of $^1/_4$-inch black iron pipe (9.2-mm. bore). Pittsburgh tap water with and without treatment was passed through these sections, and the attack which resulted during a 2-week period was determined by visual inspection. From these tests it was at once apparent that a marked reduction in corrosion was brought about by the threshold treatment. Even in the presence of too little hexametaphosphate for the exertion of its maximum inhibitive action there was no evidence of the localized attack which so often characterizes the use of insufficient amounts of corrosion inhibitors; the rust formed was more tightly adherent, darker in color, and apparently much more dense than that resulting with the untreated water. The inhibitive action of threshold treatment was evident throughout the range of pH tested (6 to 9.5), although the rust which did form at the higher pH values was of the tubercular type characteristic of this range. Iridescent interference colors on the pipes which had been protected by threshold treatment indicated the formation of an otherwise invisible film upon the pipe surface due to the action of the hexametaphosphate.

Experimental Method

Comparison of corrosion by visual examination is satisfactory in showing the type of attack—whether it is general over the entire surface, or localized in the form of tubercles and pits—but it is not suited for the detection of other than wide variations in the rate of corrosion. Moreover, once rust has formed, it is difficult to judge the further course of corrosion unless the test is prolonged over an extended period. Oxygen absorption has been considered the most generally satisfactory method for the quantitative measurement of the corrosion rate, but unless an extensive system of pipe is used, this quantity is too small for accurate evaluation. Since it is desirable to run a number of these tests simultaneously

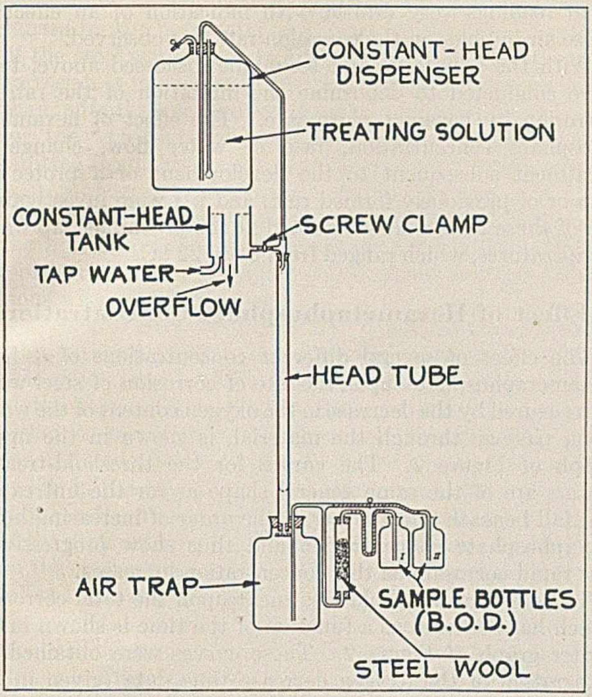

Figure 1. Continuous-Flow Apparatus for Measurement of the Corrosion Rate of Steel Wool

so that identical tap-water conditions may prevail during determination of the effect of a single variable, the use of such pipe systems appears too cumbersome for a laboratory method. In order to employ oxygen absorption as a laboratory method for the convenient evaluation of the effect of various treatments upon the corrosion rate, it is desirable to employ a form of iron or steel which offers a fairly extensive surface without occupying excessive volume and which ensures intimate contact of the water with the metal surface. Such a form is offered by steel wool. The method adopted comprises the determination of the decrease in dissolved oxygen when tap water, to which the desired treatment has been added, is passed through a column of steel wool; the drop in oxygen content is taken as a measure of the corrosion. The increase in the head required for the maintenance of a definite rate of water flow through the steel wool is also determined and serves as a measure of the plugging of the material with corrosion products.

Apparatus. One of the test units employed in measuring the corrosion of steel wool is shown in Figure 1. A uniform flow of tap water from the throttled effluent of a constant-head tank enters the top of the head tube through a tee where it receives the desired chemical treatment from the constant-head dispenser. It then flows down the head tube, through the air trap, and upward through the column of steel wool, and finally overflows from the first sample bottle. By opening the pinch clamp on the tube which leads to the second sample bottle, portions of the water prior to passage through the steel wool may be obtained.

Each dispenser is adjusted to a rate of 3–4 ml. per minute by means of a capillary section in the siphon.

Throttling of the effluent of the constant-head tank is accomplished by means of a screw clamp on a section of rubber tubing. Line rates are checked daily; if the rate is off by no more than 5 per cent, it is readjusted; if greater variation occurs, the determination is discarded.

The rubber stopper at the bottom of the head tube is so drilled as to deliver the water to the air trap in a horizontal direction and thus prevent shorting of the trap. The air trap both removes entrained air bubbles and allows time for any added alkali to react completely with the dissolved carbon dioxide.

No. 3 steel wool is employed in these tests. The wool is washed with acetone immediately prior to use, to remove any oil or grease present. Twenty grams of this material are packed in a 1.25-inch (3.2-cm.) diameter glass tube to occupy a length of 6 inches (15.2 cm.). Portions from the same batch of wool are always used in a given series of tests.

Analytical Procedures. Oxygen determinations are made by the method of Winkler (*1*). Iron is determined colorimetrically with *o*-phenanthroline, using hydroxylamine as the reducing agent (*7*, *19*). The colorimetric technique of Beaver (*4*) is employed for pH measurements. While corrosion tests are in progress, daily analyses of tap water are conducted; total hardness is determined by the soap method, calcium and magnesium by the modified Clark soap test (*5*), sulfate, chloride, total alkalinity, and total solids by the A. P. H. A. standard methods (*1*). During the course of a given corrosion series, little variation in the tap water analyses or temperatures has been observed. Hence, only the average values during each test are given in Table I. Hexametaphosphate, in the quantities used, was found to have no effect upon the pH, hence, except in cases where acid or alkali is added, pH is determined only in the daily tap water analyses.

Experiments conducted at the same time and with the same treatment have yielded quite constant results; oxygen determinations at the start agreed to within 0.2 p. p. m., in the later stages to within about 0.15 p. p. m. Tap water samples were taken from the individual test units just before the start of a run, then only after the first 5 hours of the run in order to avoid temporary disturbance of the flow rate during the initial period in which the oxygen drop was changing relatively rapidly. Variations in successive tap water samples of the order of 0.15 p. p. m. were sometimes observed, but the average was not found to vary during the day, when the load on the mains was substantially constant. After the first 5 hours, tap water samples were taken after each set of samples of the effluents from the steel wool. No variations were observed during the tests which could be attributed to differences in the steel wool. Considerable variation did occur between tests conducted at different times, but these differences appeared to follow gradual trends and may be attributed to changes in corrosive behavior of the tap water. In no case did variation occur in the general effect of a given treatment upon the corrosion rate.

Calculation of the surface area of 20 grams of No. 3 steel wool (the quantity employed in the corrosion tests) from microscopic measurements of the average cross-sectional dimensions of the steel strands gives a value of 1700 sq. cm. This is equivalent to the internal exposed area of 19.6 feet (6 meters) of $^1/_4$-inch pipe. Parallel tests were conducted to compare the rates of corrosion with approximately equal surface areas of black iron pipe and steel wool; tap water, at a rate of 0.5 liter per minute, was passed through 20 feet (6.1 meters) of $^1/_4$-inch pipe and 20 grams of No. 3 steel wool, respectively. The maximum drop in oxygen concentration of the water traversing the pipe was 0.4 p. p. m., while that for the water passing through the column of steel wool was 2.8 p. p. m. Thus, the corrosion rate for a given area of

Table I. Average Tap Water Conditions during Corrosion Tests

Tests shown in Figure No.	2, 3	4	5*A*	5*B*	6	7	8	9	10
Tap water analyses									
Temp., ° C.	22	6	18	18	6	6	11	9	6
pH	5.2	6.0	6.2	6.3	6.1	6.0	6.1	6.4	6.0
Oxygen, p. p. m.	7.9	12.8	8.4	8.3	13.1	12.8	11.0	11.0	12.7
Chloride, p. p. m.	36	12	48	43	16	12	6	22	10
Sulfate, p. p. m.	216	55	108	97	50	54	27	82	43
Calcium, p. p. m.	49	19	38	33	18	18	12	24	16
Magnesium, p. p. m.	4	2	7	6	3	3	0.3	6	2
Total hardness, p. p. m. $CaCO_3$	141	56	123	108	56	56	32	84	48
Total alkalinity, p. p. m. $CaCO_3$	3	9	20	18	13	7	5	9	5
Total solids, p. p. m.	404	105	308	279	133	119	80	195	114
Rate of water flow, l./min.	1.0	0.5	...	...	0.5	0.5	0.5	1.0	0.5

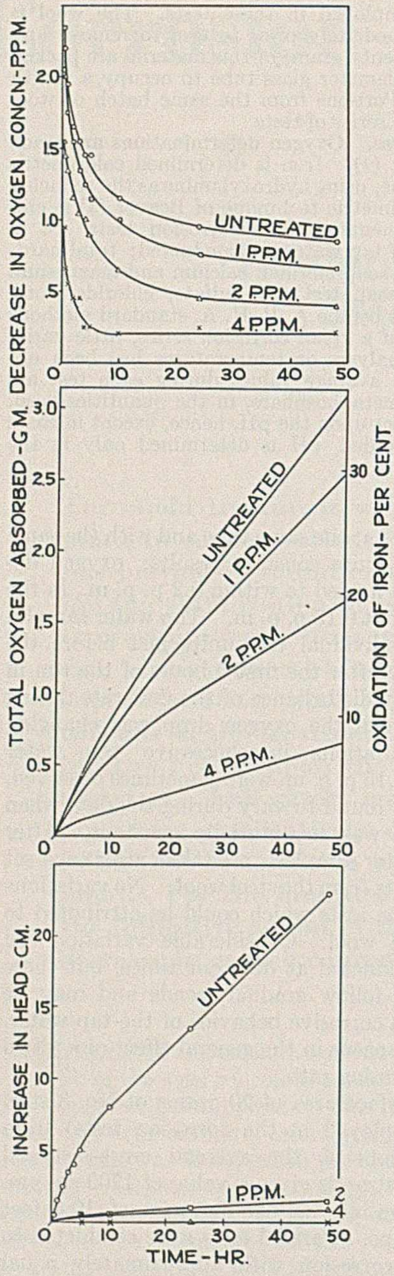

FIGURE 2. INFLUENCE OF SODIUM HEXAMETAPHOSPHATE CONCENTRATION ON THE DECREASE IN OXYGEN CONCENTRATION (*above*), TOTAL OXYGEN ABSORPTION (*center*), AND PLUGGING OF STEEL WOOL WITH CORROSION PRODUCTS (*below*) WHEN PITTSBURGH TAP WATER IS PASSED THROUGH STEEL WOOL

steel wool is considerably higher than for a similar expanse of black iron pipe. In traversing the column of steel wool, all of the water is brought into close proximity to the steel wool while in the pipe, the major portion of the water is usually relatively remote from the metal surface. The acceleration of the corrosion tests with steel wool appears to be the result of the intimate contact between the water and the steel surface.

The use of steel wool for short-time tests of the effect of certain treatments upon the corrosion rate has proved satisfactory. The chief limitation of the method is the small available mass of iron. This precludes its use in prolonged tests, for even an extremely low corrosion rate results in an appreciable rate of consumption of the steel wool. The method does not appear suited to the determination of the effect of corrosion control methods which rely upon covering the metal surface with a layer of scale, both because a prolonged period of time is generally required to obtain a dense protective scale, and also because by the time it attained sufficient thickness to be of value, the wool would be plugged.

A slight local acceleration of corrosion was observed at the points of contact of the strands of steel wool and glass container, but the actual area of steel thus affected was extremely small compared with the total present.

The change in head, as a measure of the plugging of the wool with corrosion products, gave satisfactory results except in periods when the water was supersaturated with dissolved air, as was the case during the winter months. During these periods air bubbles released in the wool made the head readings very erratic. No indication of an effect of these air bubbles on the corrosion rate was observed.

With the apparatus and technique discussed above, tests were conducted to determine the inhibition of the rate of corrosion by hexametaphosphate. The effect of hexametaphosphate concentration, rate of water flow, change in treatment subsequent to the development of a protective film or of previously formed rust, and pH were investigated. All of these tests were conducted at the prevailing tap water temperatures, which ranged from 6° to 22° C.

Effect of Hexametaphosphate Concentration

The effect of several different concentrations of sodium hexametaphosphate[1] upon the rate of corrosion of steel wool, as measured by the decrease in the oxygen content of the water upon passage through the material, is shown in the upper graph of Figure 2. The curves for the threshold-treated waters are of the same general shape as for the untreated, but fall beneath one another in the order of increasing hexametaphosphate concentration and thus show progressively less rapid corrosion as this concentration increases.

The effect of threshold treatment upon the total corrosion which has occurred as a function of the time is shown in the center graph of Figure 2. These curves were obtained by integration of the oxygen decrease–time data (given in the upper graph of Figure 2) between zero and various time intervals, and multiplication of these values by the flow rate of the water. The scale for percentage iron rusted, included in the center graph, was calculated on the basis of all of the absorbed oxygen converting iron to ferric oxide and thus gives only a rather rough approximation of this quantity.

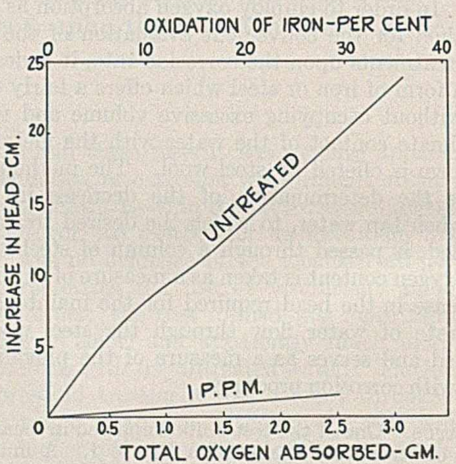

FIGURE 3. INFLUENCE OF SODIUM HEXAMETAPHOSPHATE ON THE PLUGGING OF STEEL WOOL WITH CORROSION PRODUCTS WHEN PITTSBURGH TAP WATER IS PASSED THROUGH STEEL WOOL, AS A FUNCTION OF TOTAL OXYGEN ABSORPTION

The plugging of the steel wool by corrosion products, as manifested by the increased head required for the maintenance of a constant flow rate, and the effect thereon of hexametaphosphate are shown in the lower graph of Figure 2; these data were obtained from the same series as the oxygen decrease values shown in the upper graph. It is evident that threshold treatment has a pronounced action in reducing the plugging of the wool. This reduction of the increase in

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[1] In all of the experimental work reported in this paper, the sodium hexametaphosphate used was a technical product supplied by Calgon, Inc., Pittsburgh, Penna.

head is not solely the result of the decrease in total corrosion caused by the hexametaphosphate treatment. The plugging of the steel wool which results from a given total amount of corrosion is much less in the presence of hexametaphosphate than in its absence, as may be seen from Figure 3. The curves for the two higher hexametaphosphate concentrations are omitted from this graph; that for 2 p. p. m. superposes the 1 p. p. m. curve, while no head change occurred at 4 p. p. m. From these results it would appear that the rust formed in the presence of hexametaphosphate is more dense than that which results in its absence; this confirms the visual observations with black iron pipe.

That the rust formed in the threshold-treated water is more adherent was apparent during these tests. Considerable precaution was required when changing sample bottles in the tests with untreated water in order to prevent the dislodgement of rust from the wool; this difficulty was not encountered when the water contained hexametaphosphate.

The initial increase in the corrosion rate for the untreated water in the upper graph of Figure 2 is apparently the result of the destruction of the protective oxide film initially present on the steel surface. The rather rapid drop in the rate which follows this initial rise is probably caused by the protective action of the gelatinous rust formed upon the surface of the wool. The curve then levels off somewhat but slowly continues to drop, apparently as a result of the plugging of local areas within the wool as well as to an actual decrease in the metal surface. The plugging of local areas, when using the untreated water, is indicated by the appearance of black patches in the steel wool, the result of reduction, by the remaining iron, of previously formed hydrated ferric oxide in areas blocked off from the flowing water. In the case of the 4-p. p. m. curve in Figure 2 (upper graph) there is no initial increase in the corrosion rate due to the rapidity with which the inhibiting action of the hexametaphosphate makes itself evident. The initial drop in this curve appears to be due to the formation of an invisible protective film upon the metal surface; it is definitely not due to a rust layer. The 4-p. p. m. curve then flattens out at a constant low value, which may indicate an equilibrium corrosion rate for the protected surface. In the case of the curves for 1 and 2 p. p. m., a combination of the factors operative with the untreated and 4-p. p. m. curves is probably present, except that there is no evidence of plugging of local areas within the wool.

Very small concentrations of hexametaphosphate exert a stabilizing action upon dissolved iron, which reduces the tendency for its precipitation. In view of this action, it might be thought that threshold treatment for corrosion control would result in an excessive increase in the dissolved iron content of the water, but Figure 4 shows the effect of hexametaphosphate upon the iron pickup to be very similar to its action upon the oxygen drop; it causes a marked decrease in each of these quantities. The 4-p. p. m. curve for the iron pickup continues to show a decrease after the corresponding oxygen drop has attained an apparent equilibrium value, which indicates that the full protective action of the hexametaphosphate is not attained so rapidly as the latter values would indicate. This is quite possible, since these oxygen-drop values are so low as practically to coincide with the experimental error of the procedure. The iron pickup values for the untreated water appear quite erratic during the early stages of the test. This was not due to mechanical entrainment of dislodged rust in the effluent, as filtered samples showed the same variation, but might be ascribed to occasional exposure of regions of high dissolved iron content previously beneath the rust layer.

Examination of the steel wool at the conclusion of the tests discussed above offered some interesting comparisons. The samples which had been exposed to the action of the untreated water showed marked disintegration; the fibers exhibited a swollen and agglomerated appearance and practically fell apart upon removal from the tubes, while only a small amount of the material which remained resembled steel wool. The samples which had been treated with 4 p. p. m. of sodium hexametaphosphate showed no physical disintegration upon removal from the tubes. Those which had been exposed to the action of the lower hexametaphosphate concentrations showed considerable rusting, but the rusted portions did not exhibit the swollen and agglomerated appearance of the samples which had been used with the untreated water; this is in line with the relative rates of increase in head in Figure 2 (center graphs). Upon removal of the steel wool which had been used with the lower concentrations of hexametaphosphate, the portions near the inlet end of the tube were found to be in much better condition than those at the exit end. This suggests that the rate of inhibition of corrosion may be a function of the rate of supply of hexametaphosphate to the steel surface rather than solely of its concentration in the water.

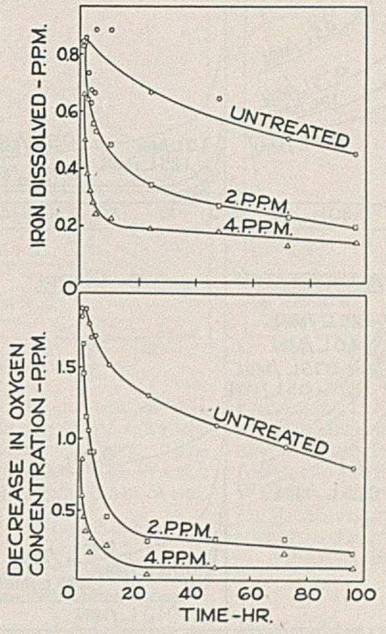

Figure 4. Influence of Sodium Hexametaphosphate on the Increase in Dissolved Iron and Decrease in Dissolved Oxygen When Pittsburgh Tap Water Is Passed through Steel Wool

Influence of Flow Velocity

The influence of the velocity of flow upon the oxygen drop which results from the passage of tap water through steel wool and the effect thereon of 4 p. p. m. of sodium hexametaphosphate are shown in the upper graphs of Figure 5. The decreasing drop in oxygen concentration with increasing velocity of flow with both the untreated and treated water is to be expected, since the time of contact between the metal surface and a given quantity of water decreases as the rate of flow is increased. On the other hand, the speed with which 4 p. p. m. of hexametaphosphate decreases the rate of drop in oxygen concentration increases as the water velocity becomes greater, which indicates that the rate of development of corrosion-inhibitive properties is a function of the rate of supply of hexametaphosphate to the surface, rather than solely of its concentration in the water.

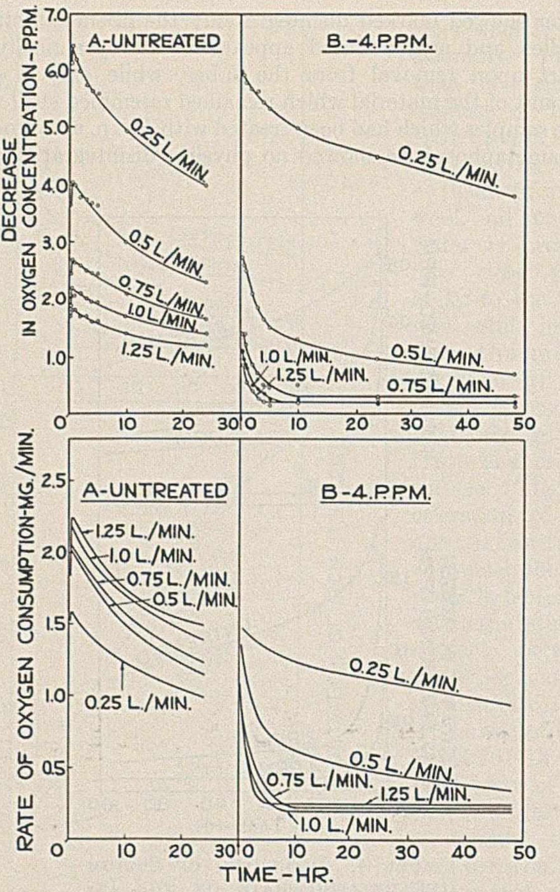

Figure 5. Influence of Rate of Flow on the Decrease in Oxygen Concentration (*above*) and on the Rate of Oxygen Consumption (*below*) When Pittsburgh Tap Water Is Passed through Steel Wool (*A*), and the Effect Thereon of 4 P. P. M. of Sodium Hexametaphosphate (*B*)

The effect of the velocity of flow upon the rate of oxygen absorption—hence the rate of corrosion—is shown in the lower graphs of Figure 5. These rates are calculated from the data given in the upper graphs. Comparison of the curves for the untreated water shows that the rate of oxygen absorption decreases as the flow rate becomes lower. This is in agreement with the results of other investigators (*20*). In the case of the threshold-treated water, this relation is reversed for the lower flow rates, the rate of oxygen absorption decreasing with increasing velocity. The cause for this reversal lies in the fact that the curves for 0.25 and 0.5 liter per minute include only the period in which the protective film is being built up, and the rate of its formation is a function of rate of supply of hexametaphosphate, hence of velocity of flow. At the higher flow rates the same reversal is present in the initial portions of the curves which represent the period of protective film formation, but the rate of corrosion after this film has formed is the same within the limits of experimental error for rates of 0.75, 1.0, and 1.25 liters per minute. Within the velocity range covered in which complete formation of the protective film is attained, the effect of the velocity of flow upon the corrosion rate of the protected surface is too low to be detected.

Change in Treatment Subsequent to Development of Protective Film

In the earlier discussion of the effect of hexametaphosphate concentration upon corrosion, it was noted that for the lower concentrations (1 and 2 p. p. m.) the gradual decrease in the oxygen drop during the latter stages of the experiment appeared to be due partly to the continued development of a protective film and partly to the decrease in the area of the steel surface. To avoid the difficulty of the disappearance of the metal surface during the determination of the effect of very low hexametaphosphate concentrations, tests were conducted in which the protective film was developed by pretreatment with a concentration sufficient to form this film rather rapidly, and the effect of subsequent treatment at a lower concentration was determined. The results obtained from such a test are shown in Figure 6; curves which show the effect of complete discontinuance of the treatment and the effect of the low concentration without pretreatment are included for comparison. It is evident that, after the protective film has been developed with 4 p. p. m. of sodium hexametaphosphate, it can be maintained with 0.5 p. p. m. It appears probable that, even without pretreatment, continued treatment with 0.5 p. p. m. would finally result in the formation of a film as protective as that given by the 4-p. p. m. pretreatment, provided that a sufficient mass of steel was present and that the experiment was continued long enough. It is evident from the 0.5-p. p. m. curve without pretreatment that the attainment of the full protective action would occur very slowly with this low concentration. The actual amount of hexametaphosphate required for the production of the protective film would thus be considerably higher for treatment with a very low concentration than for a higher rate of treatment.

Figure 6 also shows that, after pretreatment with 4 p. p. m., the rate of oxygen absorption rises only slowly after the discontinuance of the hexametaphosphate treatment; even 120 hours after the treatment was dropped, it had not attained the range to be expected with untreated water. Thus, it appears that once the protective film is formed as a result of hexametaphosphate treatment, it exhibits a definite resistance to removal upon discontinuance of the treatment.

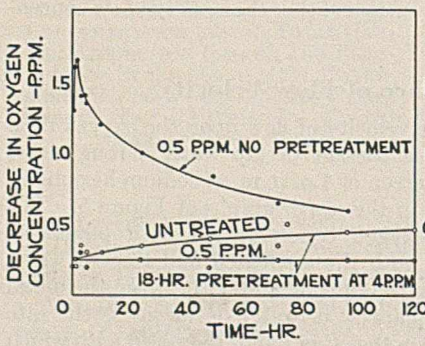

Figure 6. Effect of Change in Treatment, Subsequent to the Development of a Protective Film with Hexametaphosphate, on the Decrease in Oxygen Concentration When Pittsburgh Tap Water Is Passed through Steel Wool

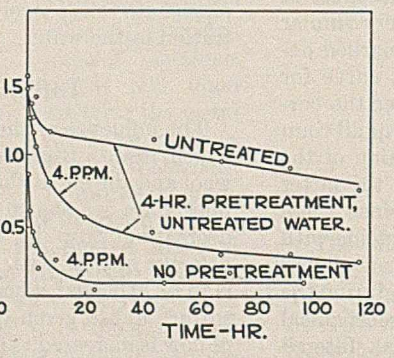

Figure 7. Effect of Sodium Hexametaphosphate on the Decrease in Oxygen Concentration When Pittsburgh Tap Water Is Passed through Previously Rusted Steel Wool

Action of Hexametaphosphate on Rusted Surfaces

The effect of hexametaphosphate upon the further corrosion of steel wool which has already acquired an obvious coating of rust as a result of pretreatment for four hours with untreated water, is shown in Figure 7. Soon after threshold treatment has been started, the oxygen-drop curve for the treated water commences to fall below the curve for the continued use of untreated water. This indicates that the inhibitive film which results from the hexametaphosphate treatment is beginning to form. However, the action of the hexametaphosphate is not exerted so rapidly upon the rusted surface as upon an initially unrusted surface. The retardation of the rate of development of the protective film which results from the presence of previously formed rust appears to be due to the adsorption of the hexametaphosphate by the rust. That such an adsorption can occur is indicated by the efficacy with which threshold concentrations of hexametaphosphate can be removed from solution by means of a hydrous ferric oxide floc.

The action of rust in retarding the formation of the protective film may, to a considerable extent, be responsible for the slowness with which the latter is formed with very low rates of supply of hexametaphosphate—for example, in the 0.5-p. p. m. curve in Figure 6. Considerable rust forms before the film develops sufficiently to retard the rate of corrosion very markedly; as a result of the presence of this rust, further development of the protective film is retarded. This effect appears to account for the observation that when the water is less corrosive, a lower rate of hexametaphosphate supply is required to produce the maximum inhibitory action in a given period of time.

Influence of pH

The effect of pH upon the rate of corrosion of steel, in the absence of hexametaphosphate, is shown in Figure 8. In these tests the pH of the tap water was 6.1; the lower values were obtained by treatment with hydrochloric acid, and the higher, with sodium hydroxide. These oxygen-drop curves for the different pH values show two features in common—namely, an initial inflection followed by a decrease. The same two features were discussed in conjunction with the curve for the untreated water in Figure 2 (upper graphs). At pH 4.2, 5.0, and 6.1 in Figure 8, the initial rise in the oxygen drop is rapid, which indicates the oxide film to be attacked quickly. At pH 8.9 the presence of a second factor, one which opposes the effect of the breakdown of the initial film is indicated; at pH values of 10.0 and 10.4 this factor appears progressively stronger. This opposition to the breakdown of the film makes itself felt by a retardation of the rate of increase in the initial portions of the curves for pH 8.9 and 10.0. At pH 10.4 the factor becomes sufficiently strong so that an apparent equilibrium between it and the tendency for the breakdown of the original film is rapidly attained. This opposing factor appears to be the result of the tendency for the precipitation of the corrosion products very close to the point of attack; such self-stifling is commonly observed in corrosive attack at high pH. The curves for pH 6.1 and 8.9 cross, as the greater rate of corrosion during the initial periods at pH 6.1 results in a more rapid surface obstruction with a consequent more rapid decrease in the oxygen drop.

The data in Figure 8 indicate the corrosion rate to decrease with increasing pH, as pointed out by previous investigators (*21*). However, simple elevation of the pH from 6.1 to 8.9 or even 10.0 does not appear to be a particularly effective means of checking corrosion; to accomplish satisfactory reduction of corrosion by this means would require pH values in excess of 10.4 at least. The data in Figure 8 were obtained with water with a low content of dissolved solids, a condition generally favorable for inhibition with alkali.

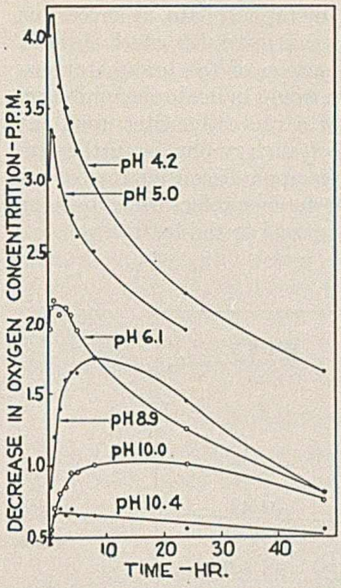

Figure 8. Influence of pH on the Decrease in Oxygen Concentration When Adjusted Pittsburgh Tap Water Is Passed through Steel Wool

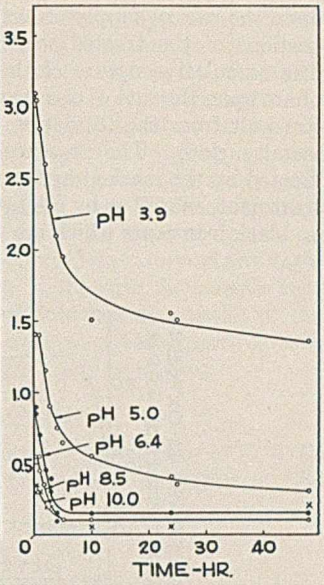

Figure 9. Influence of pH on the Decrease in Oxygen Concentration When Adjusted Pittsburgh Tap Water Containing 2 P. P. M. of Sodium Hexametaphosphate Is Passed through Steel Wool

The effect of pH upon the inhibition of corrosion by threshold treatment with 2 p. p. m. sodium hexametaphosphate is shown in Figure 9. In these tests the tap water pH was 6.4 and the other pH values were obtained by treatment with sodium hydroxide or hydrochloric acid. From pH 6.4 to 10.0 the oxygen-drop curves flatten out at the same value within the limits of error of the procedure. Moreover, the maximum protection of the surface is attained at practically the same rate from pH 6.4 to 10.0. Full development of the protective film is not attained in the tests at pH 3.9 and 5.0, although in view of the increased corrosivity of the water at the lower pH values, this retardation of the rate of protective film formation would be expected. However, from the shape of the curves at pH 3.9 and 5.0, there is no evidence that they are not approaching the same low final value of the three tests at higher pH.

In order to determine whether the curves at the lower pH values actually were approaching the same equilibrium oxygen drop observed at the higher pH values, tests were conducted in which the protective film was formed by pretreatment at a pH such that the film could be obtained fairly rapidly and the effect of subsequent lowering of the pH then determined; the results of such tests are given in Figure 10. These curves show that the equilibrium oxygen drop attained at the higher pH values can be maintained down to pH 5.2 but not at pH 4.1 or 3.5. Thus it appears that the curve for pH 5.0 in Figure 9 was probably approaching the same equilibrium oxygen drop as that obtained at the higher pH values, but that the curve for pH 3.9 was not.

From the results of tests at different pH values, it may be concluded that the corrosion rate of a steel surface protected by hexametaphosphate is essentially constant between pH 5.2 and 10.0, but that upon dropping much beneath this lower value, the rate increases.

Discussion

The data presented appear to show that the inhibition of corrosion by threshold treatment is the result of the cumulative action of hexametaphosphate which has been brought into contact with the metal surface. This is indicated by the gradual decrease in the rate of corrosion, at a speed dependent upon the rate of supply of hexametaphosphate, as successive portions of the treated water pass over the steel surface. The cumulative nature of the action of the hexametaphosphate upon the rate of corrosion would indicate the inhibition to result from the formation of a protective film upon the metal surface. The presence of such a film is further indicated by the marked hysteresis upon discontinuance of the treatment, as well as by the interference colors which develop on black iron pipes which are exposed to the treatment.

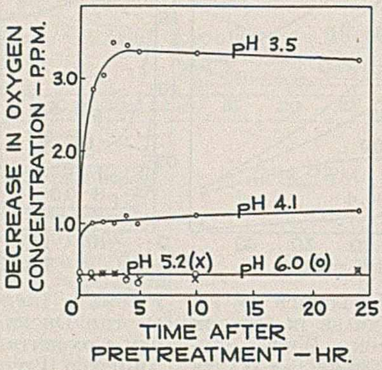

Figure 10. Effect of Change in pH, Subsequent to the Formation of a Protective Film with 4 P. P. M. of Sodium Hexametaphosphate, on the Decrease in Oxygen Concentration When Adjusted Pittsburgh Tap Water Is Passed through Steel Wool

In conjunction with the curves for 1 and 2 p. p. m. in Figure 2 (upper graph) it is noted that as a result of the low rate of supply of hexametaphosphate to the metal surface, considerable corrosion takes place before the complete formation of the protective film, but that the steel wool at the inlet end of the column shows considerably less severe attack than that at the outlet. This difference in the relative protection afforded the inlet and outlet ends of the column appears to indicate that the hexametaphosphate is partially removed from the water upon passage through the initial portions of the steel wool, with the result that insufficient remains in solution to give the same degree of protection to the remainder of the material. It would thus appear that hexametaphosphate is at least a partial component of the protective film which results upon exposure of a steel surface to the action of threshold-treated water. Evidence of the formation of such films of hexametaphosphate, or complexes thereof, as a result of threshold treatment was observed in conjunction with the application of the treatment for the prevention of calcium carbonate deposition (*10*). Even upon prolonged exposure of the metal surfaces to the action of hexametaphosphate, the film thereon has not been found to develop into a visible solid phase. Nor would this be expected, since the metal ions in question do not appear to cause the precipitation of these low concentrations of hexametaphosphate. Thus it appears probable that the inhibition of the corrosion of iron and steel by threshold treatment is due to the formation of an adsorbed film of hexametaphosphate, or some complex thereof, upon the metal or metal oxide surface.

In the discussion it has been emphasized that the inhibitive action of threshold treatment appears to be a result of the cumulative action of the hexametaphosphate which has been brought into contact with the metal surface, rather than solely of the small amount present in the water actually in contact with the surface at a given time. It might therefore be assumed that immersion of a portion of steel wool in a beaker of threshold-treated water would not result in an appreciable reduction in the corrosion rate; visual examination of steel wool so treated indicates that this assumption is correct. (The process of supplying the metaphosphate in a concentration of a few p. p. m. continuously over a period of time cannot be simulated by introducing the same total amount of metaphosphate in much higher concentrations in a beaker test. These higher concentrations, even of the order of tenths of a per cent, exert a definite solvent action uniformly over the metal surface, presumably as a result of the well-known property of sodium hexametaphosphate of forming soluble complexes with many metals.)

Threshold treatment for corrosion control has much in common with its use for the prevention of the deposition of calcium carbonate. The oxygen-drop curves which show the effect of hexametaphosphate upon corrosion exhibit considerable similarity to those which represent the drop in alkalinity when water supersaturated with calcium carbonate is passed over a solid calcium carbonate surface (*10*); the chief difference is that, while the alkalinity drop can be eliminated completely, the oxygen drop can be reduced only to a low value. In each of the processes, upon cessation of the treatment there is a marked lag in the return to the normal behavior of the water.

The mechanism which has been suggested for the prevention of calcium carbonate scale by threshold treatment (*9, 10*) is similar to that suggested above for its use in reducing corrosion. The treatment appears to alter neither the corrosive nature of the water itself nor its supersaturation with respect to calcium carbonate. In both processes the action of the hexametaphosphate appears to be due to its effect upon the respective solid surface—steel in the case of corrosion inhibition, calcium carbonate in the case of deposition prevention.

In testing the action of threshold treatment on corrosion and on deposition, the same factors which were stressed above should be kept in mind—namely, that the effect upon the solid surface is a cumulative action and that there is a marked hysteresis in the return of a surface which has been exposed to the treatment to its normal behavior. Immersion of steel wool in a beaker of threshold-treated water will no more indicate the action to be obtained upon exposure of the metal surface to a continuous flow of such a water than will the application of the usual calcium carbonate stability test (*1*) indicate the effect of continued passage of a threshold-treated supersaturated water over a calcium carbonate surface. Neither a steel nor a calcium carbonate surface which has been once used in a continuous-flow test with threshold-treated water should be re-employed in tests with a different water without prolonged treatment with the latter water to ensure that no trace of the action of the hexametaphosphate persists.

All of the data presented here were obtained with steel surfaces. A similar inhibition of the rate of corrosion as a result of threshold treatment was observed when cast-iron shot were substituted for the steel wool in the apparatus shown in Figure 1. These shot were not employed regularly in the corrosion tests because of the rapidity with which plugging with corrosion products occurred when the untreated water was used, and also because of evidence of stagnant water conditions in the interstices near the points of contact between the individual shot.

In conjunction with the discussion of the effect of threshold treatment upon the iron pickup (Figure 4) it was mentioned that threshold concentrations of hexametaphosphate exerted a stabilizing action upon dissolved iron. Thus, the treatment exerts a twofold action for the prevention of "red water"; it reduces the corrosion and the resultant pickup of iron, and it also tends to prevent the precipitation of iron which was initially present in the water.

The present investigation has been concerned chiefly with the corrosion of steel by waters which simulate, in composition and temperature, those encountered normally in cold-water distribution systems. The quantitative data have all been obtained with Pittsburgh tap water, with and without further chemical treatment. However, qualitative tests of the effect of threshold treatment upon the corrosion of steel have been conducted on a number of municipal water supplies with a portable apparatus essentially similar to that used in the present laboratory investigation (Figure 1); the effect of the treatment was evaluated by comparison of the appearance of steel wool which had been exposed to the water supply with that which had been exposed to the threshold-treated supply. A rather wide range of types of municipal supplies has been tested in this manner—soft waters typical of the Atlantic Coast, hard bicarbonate waters of the Midwest, and the effluents of both zeolite and lime-soda softeners—and in all cases the treatment with small amounts of hexametaphosphate has been found to result in a marked decrease in the rate of corrosion.

Numerous tests in the field, which specifically show the effect of threshold treatment upon corrosion, are yielding promising results (*8*, *17*, *22*). It might be mentioned that much industrial heat-exchange equipment is being maintained in a scale-free condition by the use of threshold treatment with hexametaphosphate without a resultant difficulty with corrosion. However, data are not available concerning the corrosive attack on bare metal surfaces in these systems by the untreated water, owing to the heavy scale upon these surfaces prior to the treatment.

Investigation of the effect of threshold treatment upon the inhibition of corrosion under a variety of special conditions, as well as upon the stabilization of dissolved iron, is being continued in this laboratory. The ease with which continuous-flow tests of the type described in this paper may be conducted has led other investigators to make direct tests upon various industrial and municipal water systems, rather than to rely solely upon chemical analysis as a guide to the probable behavior of their waters. As the results of these field tests multiply, the range of conditions under which corrosion may be controlled by threshold treatment should become more clearly defined.

The application of threshold treatment to a system is extremely simple; the only precaution which must be observed is that the treatment should not be applied ahead of a coagulation or a cold lime-soda softening process, since both of these are inhibited to some extent by the treatment. The hexametaphosphate is fed from solution, and any proportioning device of reasonable accuracy may be employed. The treatment is not sensitive to intermittent variations in the feed—probably due to the hysteresis effect previously discussed—and fluctuations up to several hundred per cent can be tolerated as long as the average remains fairly constant. Sodium hexametaphosphate, even in concentrations far above those employed in threshold treatment, has no harmful physiological action (*13*) nor does it impart any taste or odor which might render the water unfit for human consumption. This, combined with low cost as a result of the low concentrations employed, makes corrosion control with sodium hexametaphosphate particularly promising.

Acknowledgment

The writers wish to acknowledge the assistance of C. S. B. Freese with much of the analytical work described in this paper.

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PRESENTED before the Division of Water, Sewage, and Sanitation Chemistry at the 99th Meeting of the American Chemical Society, Cincinnati, Ohio.

Correspondence—Cyanamide, Dicyandiamide, and Melamine

SIR: With reference to the paper on the above subject, published in the September, 1940, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY (pages 1187–8), our attention has been called to an article by K. Heydrich [*Z. Kryst.*, 48, 243–305 (1911)] giving optical and crystallographic properties for melamine and dicyandiamide. Published under the title "The Relation between Density and the Index of Refraction in Solid, Crystalline, Isomeric, Organic Compounds", the article covers a broad field and compares the relation between density and index of refraction of inorganic compounds with that of organic ones. Being so general in scope it was not indexed under melamine and dicyandiamide in *Chemical Abstracts* and thus was missed when the authors made their search of the literature.

Heydrich carefully described for both melamine and dicyandiamide the refractive indices α, β, and γ (to four decimal places), $2V$, optical sign, axial ratios, the most common crystallographic forms, many face angles, etc. There is some duplication of this data in our article; and there is agreement within experimental error for β index, $2V$, and the optical sign for dicyandiamide, and for the optical sign for melamine. Other values for refractive index are not comparable directly because we gave values for extinction directions in the planes of the common crystal faces, rather than in imaginary crystallographic directions, the purpose being to include data for determinative purposes rather than classical crystallographic description.

T. G. ROCHOW

FILTER MEDIA

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FILTER technique has been limited because the substance filtered and the material doing the filtering have been incompatible. The impossibility of changing processes to meet limitations of filter media has had a resultant which has taken an opposite, natural direction—that of developing media to meet the rigors of industrial use. Though far from achieving the desired goal of an acceptable medium for every industrial purpose, progress has been made during the past few years in the production of different, workable, filtering surfaces that are solving many formerly impossible plant filtration problems. Outstanding are cloths made of glass, rubber, wire, and resins. Although new and hardly past experimental stages, chemical industry has accepted and tried all of these and this article presents, as far as possible, the known facts about service, applications, and weaknesses to be expected from them.

Glass Filter Cloth

Inherent characteristics of glass would make it almost an ideal filtering substance if corrosion were the only factor involved. These same characteristics, however, limit its free application to all problems, and special adaptations of either equipment or cloth are necessary. The three main advantages of glass cloth are corrosion resistance, high thermal resistance, and high filtering capacities. Another feature is that the composition and diameter of the fibers may be altered in any manner necessary.

Glass cloth wears quickly when subjected to flexing, such as the constant flexing into exit ports of the plate-and-frame press. In use, mechanical wear and crushing must also be avoided, and the practice has been to impregnate cloth with a solution of latex, either of natural rubber or of the rubber-like polymers, at plate contact surfaces and exit ports. This treatment prevents crushing of fibers by compression between bearing surfaces, prevents leakage along edges, reinforces edges against flexing along the bearing surfaces, prevents unraveling of cloth, and arrests failure of damaged spots on the cloth. Inspection of filter plates will indicate areas likely to experience crushing or flexing and will serve as a guide in applying rubber coatings. However, in filter units specially designed for glass cloth, wear is satisfactory because excessive crushing and vibration are avoided.

For best service on a plate-and-frame press, a backing of some material should be used, such as a perforated lead plate, rubber mat, cotton or wool cloth, or wire screen. As an example of what might be expected if this is done, the data in Table I were obtained in actual plant operation on a 30-inch Shriver plate-and-frame wash press. Plates were of hard lead with side feed, and lead sulfate was filtered from 3–5 per cent solution of sulfuric acid. The filter cycle was as follows: filtering pressure 45–60 pounds per square inch; hot wash with water 7 minutes at 35 pounds per square inch; air blow, 6 minutes at 45 pounds per square inch; followed by two cycles of hot water wash at 35 pounds per square inch for 8 minutes and air at 55 pounds per square inch for 10 minutes. These conditions are rather severe, not only because the material being filtered is severe, but because vibration and flexing due to changes in rate of liquid flow are great. As a basis for comparison the life of cotton duck is given. In these examples the failure of glass was entirely mechanical. The more rigid the backing, the greater was the service. Thus, a rubber and a canvas backing gave about a 50 per cent life increase over unbacked glass. Lead backing increased the service of the glass more than 100 per cent. The stainless steel plate decomposed under service, and no conclusions may be drawn. The lead, stainless steel, and rubber plates were all porous.

Damage from handling cannot be evaluated for the cases given, and as a general rule glass cloth must be handled carefully, especially when wet. Care should be taken in removing filter cake; and to facilitate slurry discharge, ordinary wrapping paper is often placed over glass filters. Because flexing is so damaging to glass cloth, reduced pressures are desirable for drying and washing cycles; grooved plates are preferable to pyramid or cone types; recessed plates are not so desirable as the flush types; and side feeds are better than center feed types. To reduce pressure fluctuation during filtration cycles, centrifugal pumps should be used if possible or pressure dampening devices should be included with diaphragm or plunger type pumps.

TABLE I. LIFE OF FILTER MEDIA ON PLATE-AND-FRAME PRESS

Type of Cloth	Av. Life, Cycles	Features
18-oz. twill, cotton	10	Failure due to chemical action
8-oz. sailcloth, cotton	3	
8-oz. chain stitch, cotton	5–6	
Twill glass:		
WB-0146 medium-weight broken	4	Latex-impregnated; failures are all mechanical
WB-0147 medium-weight	4	
WB-0110 heavy-weight broken	20	
WB-0110 heavy-weight broken	44	Lead plate backing
WB-0110 heavy-weight broken	28	Stainless steel backing
WB-0110 heavy-weight broken	30	8-oz. canvas backing
WB-0110 heavy-weight broken	30	Rubber backing

Abrasion by fine particles in suspension may cause some wear to glass, but this is stopped as soon as a bed or coat of filter cake has been built up. Caustic liquids might be assumed to have a greater damaging effect than acid liquids, and this is probably true as far as chemical action is concerned. However, alkaline liquids have a lubricating effect on glass, and active life is about the same for each type of service; the acid materials cause much more mechanical wear which, in comparative service, about balances the damaging effect of chemical disintegration by alkaline substances.

Polar liquids are thought to be more destructive than nonpolar types. Liquids, such as gasoline, kerosene, and lubricating oils, give a longer service life.

In gas filtration, the resistance of glass to heat is especially valuable. It makes it possible to filter above the dew point of the gas and obviates the necessity of bleeding in air to reduce the temperature to a point where usual fabrics are not harmed. Shaking to discharge accumulated dust, as is done on gas filtration installations, may cause failure of glass filter bags because of the effect of continued flexing on one area.

Pressure drop through glass fabric is relatively low, as shown in Table II.

TABLE II. AIR FLOW RESISTANCE OF GLASS FABRICS

Weave	Weight, Ounces/ Sq. Yd.	Thickness, Inch	Resistance to Air Flow, Inches of Water for 7 Cu. Ft. of Air per Sq. Ft. per Min.
2/2 twill	19.72	0.035	0.09
4 shaft satin	25.28	0.032	0.03
4 shaft satin	19.32	0.026	0.338
Taffeta	40.73	0.048	3.042
Taffeta	30.90	0.050	0.269
Taffeta	18.50	0.037	0.020
Taffeta	17.12	0.029	0.303
Double weave	42.88	0.063	1.295

Vinyon Fabrics

"Vinyon" is a trade-mark for vinyl resin yarns. Fabrics made of these yarns inherit the same resistance to corrosion that the resin possesses, and this has been advantageous in adapting these fabrics to filtration uses. Because of the newness of this fabric, uses are not clearly indicated, but it is certainly finding application in acid and strong alkali filtration, in clay industries where its resistance to mildew is important, and as anode bags in electrochemical work. There are two disadvantages which limit the application. Since Vinyon is thermoplastic, high temperatures shrink and fuse fabrics made of it; and fabrics must be engineered to the job in hand.

The first disadvantage, softening with heat, is characteristic of vinyl resins and use in solutions hotter than 150° F. (65° C.) is not recommended. There are cases where filtration has been carried on at temperatures higher than this because the plate and frame held the cloth tightly enough to prevent shrinkage. However, this is the rare case and the general rule holds.

Vinyon is successfully used in cold acid filtrations. In the filtration cycle described in the section on glass, it has lasted well over two hundred operating periods with only one notable change—the acid concentration has been increased 26 per cent to a total of 30 per cent.

So far, nineteen different fabrics have been developed in plain, twilled, and chain weaves. Though cotton duck constructions have been duplicated with Vinyon, similar fabrics cannot be considered interchangeable. Each application must be studied and a fabric specially designed for the problem. The reason for this lies in the different wet porosity values of cotton and Vinyon fabrics. Cotton will swell when wetted, Vinyon will not. Most duck filtering weaves were developed by trial and error in actual manufacturing operations; and even though cotton weaves are duplicated in Vinyon, this is no guarantee of similar filtering efficiency. Cotton has numerous cross hairs, or fuzz, which help retain particles and this, in addition to wet swelling and closing of pores, makes an analysis of filter surface and porosity a virtual impossibility—at least for predicting results with a new fiber. Vinyon fiber is smoother and is nonswelling in most liquids. It must have a porosity, when dry, about equal to the wet porosity of the cotton fiber that it is to replace. However, this is not an inflexible rule and should be accepted as a generalized statement. The lack of protruding hairs in vinyl resin cloth has a particular advantage in cake discharge since the smoothness of surface requires a minimum of scraping to dislodge accumulated slurries and cake. Blinding is less apt to occur because of the absence of fuzz, and acid cleaning is more apt to be successful than with cotton cloth. Abrasion resistance is reported good, though care must be taken in scraping to avoid holes. The continued use of Vinyon fabrics in chemical processing should result in the accumulation of extensive data which will simplify selection of fabric.

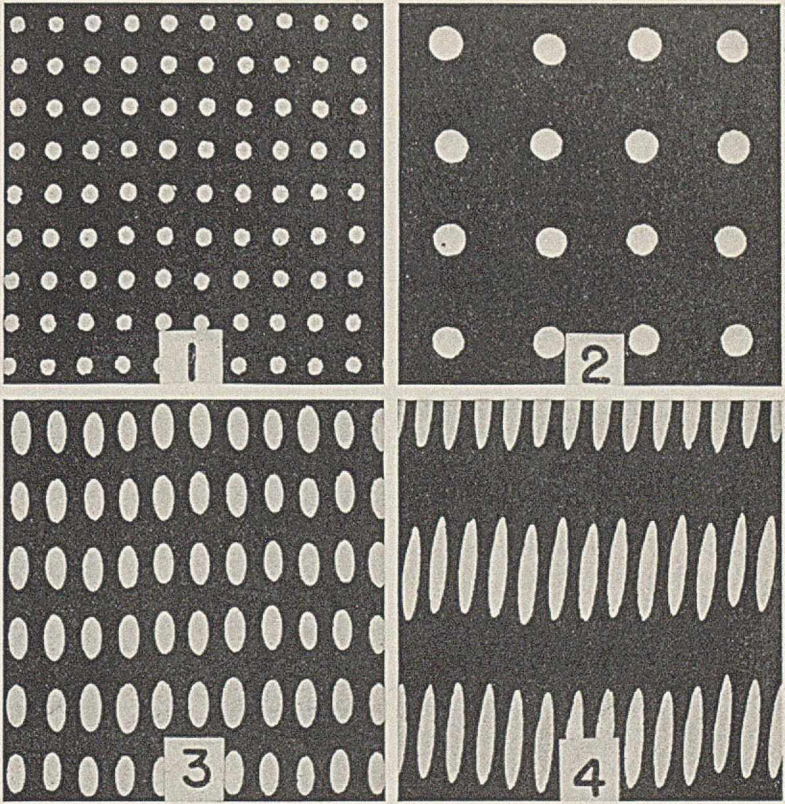
Rubber

Two distinct types of rubber filter media are commercially available in sheet form: "Multipore" (*2*), a latex product, contains filter holes of macroscopic size which run straight through the rubber sheet; and microporous hard rubber, a sheet of spongy texture, is made up of interconnecting pores of microscopic size. As a filter medium Multipore has been on the market for a longer time than has microporous hard rubber; consequently more data on its performance have been obtained.

Multipore, though resembling the usual perforated rubber sheet, has far more holes per square inch and these are smaller in diameter than has ever been obtained by punching methods. In Multipore (*3*, *4*) the holes are formed by the expansion of air through a film of liquid latex, and as a result of this and other features of the process, a porous rubber sheeting suitable for filtration purposes is now available.

There are four basic types of plain Multipore (Table III), the differences lying in the variation of hole size and the number of holes per unit area.

A desirable characteristic of filter media is a high flow rate or permeability to liquids. There is no simple relation be-



Courtesy, United States Rubber Company

FIGURE 1. PHOTOMICROGRAPHS (× 15) OF REPRESENTATIVE TYPES OF MULTIPORE

Sample No.	Holes/Sq. In.	Type of Multipore	Pore Dimensions, In.
1	6400	Plain	0.004 (diam.)
2	1100	Plain	0.010 (diam.)
3	3200	Expanded 50%	0.005 × 0.011
4	3200	Hard rubber, expanded 250%	0.005 × 0.040

TABLE III. MULTIPORE SPECIFICATIONS

No. Holes per Sq. In.	Av. Hole Diam., Inch	Calcd. % Voids	Standard Thicknesses, Inch
6400	0.004–0.005	8–10	0.030, 0.050
3200	0.005	6– 7	0.030, 0.050, 0.070, 0.090
1700	0.005–0.006	3– 4	0.030, 0.050, 0.070, 0.090
1100	0.010–0.011	8–10	0.030, 0.050, 0.070, 0.090

tween permeability and porosity, or percentage of voids, because flow rates depend not only on size of the filter channels but also on the path of the liquid. Although Multipore has a relatively low porosity, its permeability is comparable to many materials of higher void area because of the low resistance to flow offered by the size and shape of the filter channels. The permeability of the basic types of Multipore (Table III) ranges from 100 to 300 gallons of water per square foot per minute under a pressure head of 1.3 cm. of mercury (18 inches of water).

The shape and number of holes of the base type may be changed further by a stretching operation applied before the rubber sheet is vulcanized; the product is known as expanded Multipore (*1*), and is described in Table IV and Figure 1. Expanded types of Multipore have higher permeability. All styles of Multipore may be obtained in soft rubber, hard rubber, flexible hard rubber, and neoprene, with the exception that soft rubber and neoprene cannot be obtained in sheets expanded more than 100 per cent.

TABLE IV. PHYSICAL CHARACTERISTICS OF EXPANDED MULTIPORE (STRETCHED IN ONE DIRECTION)

				6400-Hole Multipore			
% expansion	0	25	50	75	100	150	250
Holes/sq. in.	6400	6000	5000	4700	4100	3200	2900
Hole dimension, in.	0.004	0.004 × 0.007	0.004 × 0.008	0.004 × 0.010	0.004 × 0.013	0.004 × 0.017	0.004 × 0.002
% porosity	8	9	12	14	17	19	22
				3200-Hole Multipore			
% expansion	0	25	50	75	100	150	250
Holes/sq. in.	3200	3000	2600	2300	2000	1700	1300
Hole dimension, in.	0.005	0.005 × 0.007	0.005 × 0.011	0.005 × 0.016	0.005 × 0.018	0.005 × 0.018	0.005 × 0.040
% porosity	6	8	10	12	15	17	22
				1100-Hole Multipore			
% expansion	0	25	50	75	100	150	250
Holes/sq. in.	1100	850	840	700	600	500	400
Hole dimension, in.	0.010	0.010 × 0.015	0.010 × 0.020	0.010 × 0.030	0.010 × 0.040	0.010 × 0.045	0.012 × 0.070
% porosity	8	10	13	15	18	20	25

Because of its mechanical and chemical characteristics and ease of installation, soft rubber is considered the most practical all-purpose material. It may be used for filtering aqueous solutions and most chemicals, with the exception of rubber solvents, strong oxidizing agents, and the halogen acids. Temperatures above 212° F. are not recommended if reasonably long life is required. In one specific case, soft-rubber Multipore is satisfactorily filtering 35 per cent phosphoric acid at 166° F.; in another, it has shown little deterioration after 8-week processing of slurries containing 25 per cent sulfuric acid at 180° F.

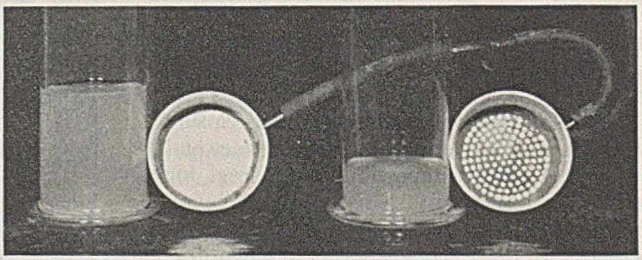
Hard and flexible hard rubber are used either where greater corrosion resistance is desired, or for the filtration of solvents, such as petroleum oils, which attack soft rubber but do not affect the hard variety. Hard rubber becomes thermoplastic above 70° C. (158° F.) but may be used up to 100° C. (212° F.) if properly supported.

In addition to its chemical resistance, a number of other advantages are claimed for Multipore. The smooth surface and the absence of surface fibers permit easy discharge of cake; and much thinner cakes may be removed from the filter surface of continuous filters and thereby increase capacity. Rubber has excellent resistance to abrasion, vibration, flexing, and plate crushing, and should give good service where these conditions prevail. Relative freedom from blinding results from the size and shape of the holes and the natural tendency of the rubber to clean itself on blowback. Slight expansion of the rubber on blowback loosens particles that may have become lodged in the pores, and they are either blown out or washed through on the next filter operation. Relative freedom from blinding has been proved in commercial mining operations in the filtration of granular ores which, when filtered through cotton duck, had high blinding characteristics.

Since the holes in Multipore go straight through the sheet, there is no cross drainage in the sheet itself (as in woven filter fabrics), and its effectiveness as a filter medium will be reduced unless it is properly mounted. If Multipore is placed on a filter which has a drainage member comprised of flat ribs or flat-topped pyramids, the effective filtering area will be reduced because the filtering holes over the flat support will be sealed off. This is illustrated in Figure 2. The difficulty may be overcome by mounting the rubber over wire screen or cider-press cloth, or by the use of a new type of Multipore which has a layer of open-mesh rubberized cloth bonded to the back. All of these methods allow adequate drainage. Corrosion resistance, however, is limited thereby to the material used for support or backing.

For large drum filters, several sheets of Multipore may be lapped and wired in place to produce the required width. If a flat surface or endless belt is required, sheets may be cemented together with no loss in strength. Unlike plain rubber sheeting, Multipore may be sewed without the usual tendency to tear. The many holes facilitate the passage of the sewing needle without structural damage. This is an advantage where shaped filter bags are required, such as those used on Sweetland or American filters.

Multipore is not suitable for filtering finely divided substances unless a precoat is used. However, it may be used

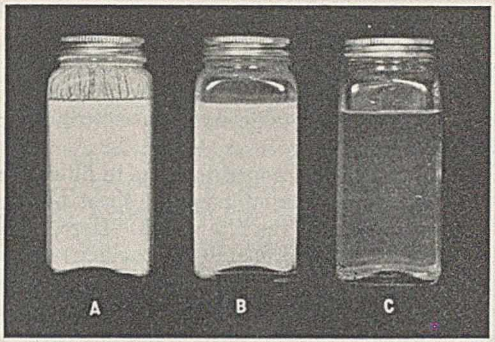


Courtesy, United States Rubber Company

FIGURE 2. COMPARISON OF FILTRATION RATES OF MULTIPORE WITH PROPER AND IMPROPER DRAINAGE

(*Left*) Adequate drainage under 6400-hole Multipore obtained with 10-mesh wire screen. Note even cake formation and volume of filtrate obtained for 5-seconds filtration at 25 inches of mercury.

(*Right*) Improper drainage, with Multipore placed directly in contact with surface of Büchner funnel. Only those holes in Multipore directly over the holes in Büchner funnel are effective. Note uneven cake formation and low volume of colored filtrate under same conditions as shown at left.



Courtesy, United States Rubber Company

FIGURE 3. CHALK SLURRY (*A*), FILTRATE FROM *A* USING A COMMERCIAL COTTON FILTER CLOTH (*B*), FILTRATE FROM *A* USING MICROPOROUS RUBBER FILTER MEDIA (*C*)

successfully for filtering granular slurries even though the particle size is considerably smaller than the pore size in the Multipore, because of the natural tendency of such substances to bridge over the pores. In general, materials as fine as 300 mesh may be filtered satisfactorily, although a slight turbidity of the filtrate during the first portion of the filtration cycle is usual. Where it is possible to do so, kraft paper can be used to cover the Multipore sheet.

The finer pore sizes will successfully retain all the commercial grades of diatomaceous earth used as a precoat material. In conjunction with a precoat, this filter medium has proved satisfactory not only for the clarification of corrosive liquids, but for numerous other noncorrosive solutions where life of the precoat support, ease of cleaning, freedom from blinding, sterilization, and other factors cause difficulty.

Commercial applications of Multipore, where a rubber filter medium has proved advantageous, include the clarification of wine and other fruit juices by the use of a precoat in plate-and-frame presses, the centrifugal filtration of fruit juices and sirups, filtration of ores and granular materials on rotary filters, filtration of corrosive liquids, and as air diffuser membranes in flotation cells in the mining industry.

Microporous Rubber

Microporous rubber is not a new material; it has been used as a battery separator for a number of years. As a filter medium, however, it is a rather recent development and, as the name implies, is a porous rubber sheet permeated by interconnecting microscopic channels running in all directions through the material.

Pore size averages 2 to 3 microns, the volume of pores ranging from 65 to 75 per cent of the total volume of the sheet. Permeability is such that 20 gallons of water per minute per square foot pass through a diaphragm 0.040 inch thick under a head of 25 inches of mercury. Resistance to corrosive chemicals approximates that of ebonite, while flexibility is comparable to that of cloth.

The material as marketed is reinforced with the type of backing (such as asbestos, cotton, or stainless steel) that will best fit the specific application. The unbacked medium has insufficient strength because of its exceptionally high porosity. Backing is vulcanized directly to the microporous sheet, and permeability, after reinforcing, ranges from 7 to 15 gallons of water per minute per square foot under a head of 25 inches of mercury, depending on the closeness of weave of the backing chosen. After reinforcing, Mullen bursting strengths may be as high as 450 pounds. The material may be sewed readily with cotton, glass, or Vinyon thread, and may therefore be readily fitted to different types of filter covers.

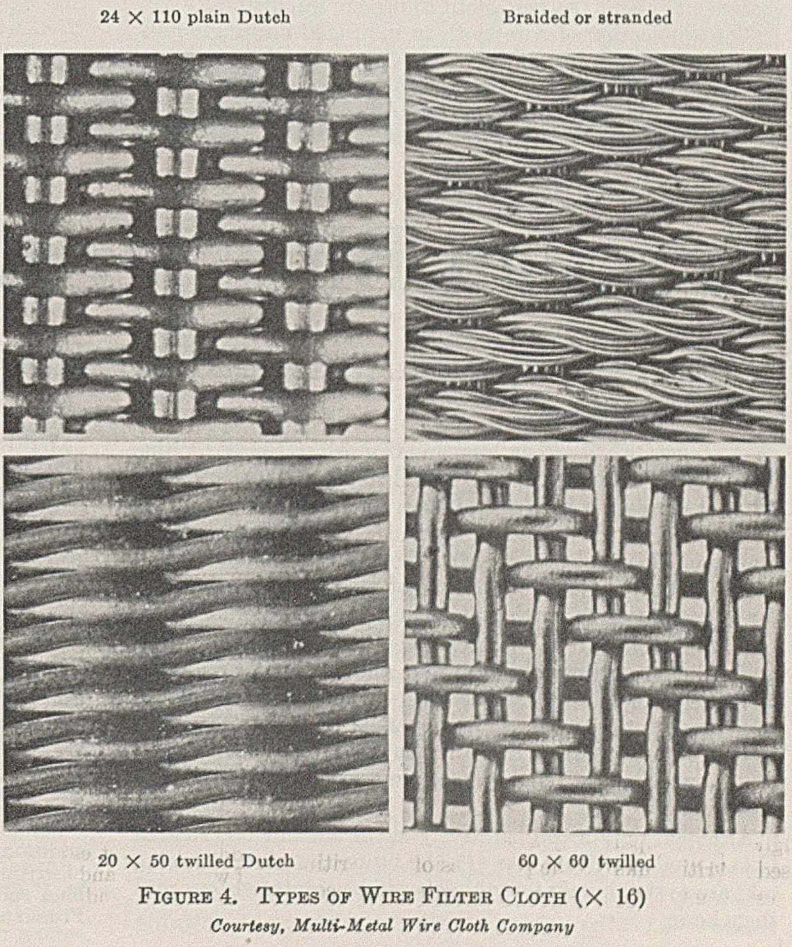
Microporous rubber has a smooth surface from which cake is easily discharged, and is readily washed and sterilized. If the sludge gives a free-filtering cake, brilliantly clear filtrates may be obtained without the use of a precoat or filter aid. Where abrasion is an important factor, microporous rubber, reinforced on both sides with fabric, is available.

Preliminary commercial tests indicate successful applications in many industries, including the food, sugar, chemical, and mining fields.

Wire Cloth

Wire cloth can hardly be classified as a new filter medium, for it was one of the earliest materials to be fabricated for use in the fight against corrosion. There are no facts which may be cited as new except that familiarity with wire cloth and filtration problems has increased the uses and simplified application in industrial work. To marshal all the data pertinent to the use of wire cloth would be impossible, and only a brief review is here attempted.

There are two distinct classes of wire filter cloth. The first is the Dutch type which has weaves designated as plain Dutch or corduroy, and twilled Dutch. The second class is the braided weave. To these cloths there must be added a certain number of open-mesh wire cloths which, though not properly defined as filter cloth, are used extensively in filter work. Twilled weave is typical of this class. The construc-


24 × 110 plain Dutch

Braided or stranded

20 × 50 twilled Dutch

60 × 60 twilled

FIGURE 4. TYPES OF WIRE FILTER CLOTH (× 16)

Courtesy, Multi-Metal Wire Cloth Company tions of these various weaves are shown in Figure 4. Metals of almost every composition are used: Monel; nickel; 18–8 stainless steel; 18–8–3 molybdenum stainless; bronze; and in fact almost every metal which may be drawn into wire and woven is used for this purpose. With such a variety of metals, corrosion and abrasion resistance, strength, and contamination effects may be altered almost at will and the maximum benefit obtained.

Corrosion resistance is not a simple problem, however, and one cannot use corrosion data obtained on metal sheets and then expect duplication of results with wire cloth. The wire has a greater exposed area of metal per equivalent flat surface, and corrosion may attack from four instead of one or two directions as is the case with continuous sheets. Generalities may be derived from such data quite properly, for it follows that over-all qualities will not alter. Quantitative predictions, however, should rest only on actual operating data obtained with screens under similar filtration conditions. Abrasion is another factor making predictions quite risky, for it continuously presents fresh damaged surfaces to the corrosive medium.

Selection of weave for the particular filtration problem or press is not standardized. For vacuum filtration of pulps or other large particles, various sizes of plain and twilled weaves are used. If sludge were being filtered, braided or twilled Dutch would find greatest use. For general plate and frame uses, twilled Dutch is probably the most popular. However, equipment is not the only factor in determining the cloth finally used. Processes, experience, and filtering methods are a deciding influence. This is illustrated by the fact that in the filtration of lime sludge, an apparently standardized manufacturing operation, the entire range of wire cloth constructions are relied on for proper filtration results. Until influencing factors are known more definitely, categorical statements about the best cloth to use are impossible.

The application of wire cloth to industrial filtering equipment carried with it many problems. Its more popular early use was on rotary filters. Demand soon brought cloth suitable for utilization on pressure and plate-and-frame presses. In the latter case leakage, raveling of wire, and plate crushing caused trouble. Gasketing of edges with rubber and cotton cloth was introduced to eliminate these faults, and to these was soon added a metal strip welded to the cloth by electric or other means. Such metallic seals also contribute to a more rigid filtering surface.

Another difficulty was proper drainage in filters where supporting members or plates of punched sheet blocked whole areas of the underside of the filter cloth. Here, as with rubber, the difficulty was eliminated by backings of open-mesh screen, which allow adequate drainage.

A recent trend, though not a new technique, is to back cotton duck with open-mesh screen. This prevents the cloth from sagging into drainage channels and blocking filtrate flow. The tendency of cloth to assume and retain the shape of the drainage grooves of the plate, so well known to plant engineers, is also eliminated through the use of such backing.

For the high pressures experienced in hydraulic presses used in the filtration of rubber, plastics, cocoa, and other highly viscous substances, multiple wire pads have been designed which have shown good service records. The pad consists of wire filter cloth supported or reinforced by heavy open-mesh screens. The unit is rigidly held together by metal bindings.

The applications of wire filter cloth have become legion. The pulp and paper industry has long been a user of wire screens in thickeners and save-alls, and readily accepted wire filter cloth for other operating equipment. The oil industry has adapted wire not only to clay towers but, like the food and chemical industries, has applied it to every filter and process in which its characteristics are of particular value.

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Prussian Blue Writing Inks

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IN A RECENT article Finn and Cornish stated (*3*): "Blue inks usually are colored with Prussian blue." This is not consistent with our observations and with the results of subsequent investigation reported here. Although this statement does not detract from the value of the main body of their contribution, elucidation of this point is necessary for identification of writing fluids and written records.

Prussian blue (ferric ferrocyanide) is insoluble in water, and ordinary writing inks are water solutions. The reference to Prussian blue in this article will be wholly to soluble Prussian blue [potassium ferric ferrocyanide ($KFe(FeC_6N_6).H_2O$, Colour Index 1288) or ferric ferrocyanide plus oxalic acid] (*1, 5*), which may be dispersed in water to give a blue "solution".

Although only a comparatively small amount of Prussian blue is used in writing inks (*1*), the properties of such writing inks are so striking that we think it will be of interest to record them here:

Writing made with Prussian blue ink cannot be bleached by most ink eradicators since the color is not destroyed by ordinary oxidizing agents.

The writing on paper is exceedingly permanent, and resistant to soaking in water and to strong light. We have seen such writing, still legible after one year's exposure outdoors facing south.

The color is destroyed by solutions having an alkaline reaction. This treatment often leaves a faint brown color of ferric hydroxide. The addition of hydrochloric or sulfuric acid restores the blue color. If the paper is rinsed in water after treatment with the alkali, the addition of acid merely dissolves the brown iron stain. In any case, however, it is difficult to bleach the writing without having some effect on the surface or texture of the paper.

Water solutions of soluble Prussian blue attack the 14-karat gold alloy used in fountain pen nibs, particularly at the air-liquid interface.

Soluble Prussian blue, dispersed in water, precipitates with the addition of most electrolytes, which includes many other types of writing inks, and products of the reaction between the Prussian blue solution and metal surfaces which are attacked by the Prussian blue.

A misstatement is corrected concerning the extent of the use of Prussian blue in writing inks, and information is given on what types of blue actually are used. The properties of Prussian blue inks and typical experimental results are outlined. New testing methods are proposed.

A few facts are presented concerning sulfates and chlorides in writing inks, for the consideration of those interested in ion-migration determinations on questioned documents.

Reactions of Writing Fluids on Paper

A few tests were made using the following writing fluids: (1) a commercial blue-black, (2) a commercial ink containing soluble Prussian blue, (3) another commercial ink containing soluble Prussian blue, (4) solution of a soluble Prussian blue (10 grams per liter), (5) solution of another soluble Prussian blue (10 grams per liter).

The customary streaks (*2*) were made on paper. Strips were cut off and immersed in the solutions of Table I, and then assembled as shown in Figure 1. The marks under ink 1, where they remain visible, are shades of bluish gray. Inks 2, 3, 4, and 5 are the characteristic blue, except for solutions *h*, *i*, and *j*, which are reddish brown.

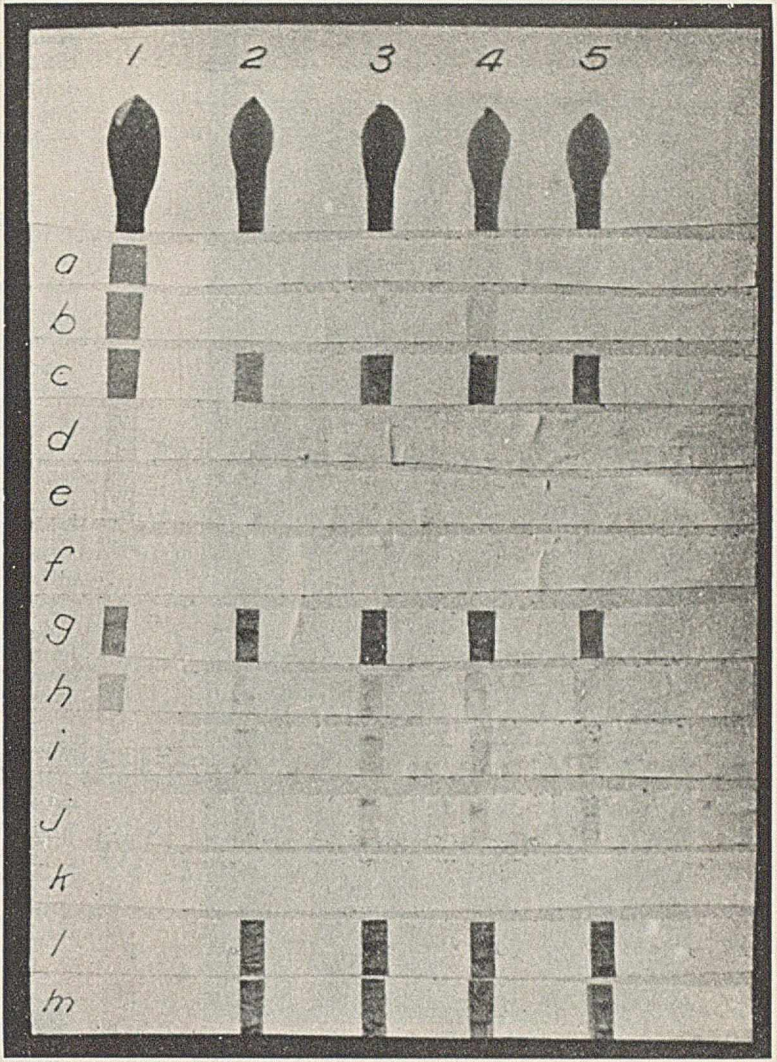

Figure 1. Reactions of Blue-Black and Prussian Blue Writing Fluids on Paper

Gold Nib Test

Fourteen-karat gold fountain pen nibs were washed, rinsed in acetone, dried in an oven at 105° C., cooled in a desiccator, weighed, and partially immersed in writing fluids 1 to 5 under the conditions given in Table II. When they were removed from the solutions, the washing, drying, and weighing were repeated, and the loss in weight was noted.

Table II. Loss in Weight (Grams) of Fountain Pen Nibs

Ink No.	1	2	3	4	5
2 days, 70° C.	0.0000	0.0017	0.0009	0.0005	0.0015
Test repeated on same nibs	0.0000	0.0039	0.0014	0.0018	0.0008
12 days room temp.	0.0000	0.0003	0.0002	0.0002	0.0004

To get strictly reproducible quantitative results, it would be necessary to expose the metal to exactly the same conditions of aeration and area of contact with the liquid, such as total immersion with agitation and aeration. However, it is obvious that the ordinary blue-black writing fluid does not attack 14-karat gold alloy used for fountain pen nibs while inks containing Prussian blue do so. Figure 2 shows the same effect on different makes of gold nibs.

Table I. Solutions Used for Immersing Paper

	Solution	Time Immersed	pH
a.	White soap, 10 grams/liter	15 hr.	. . .
b.	Same as *a*, 5 g./l.	15 hr.	. . .
c.	Same as *a*, 1 g./l.	15 hr.	. . .
d.	"GC" sodium silicate ($Na_2O.2SiO_2$), 50 g./1000 g. H_2O	15 hr.	12 (*6*)[a]
e.	"Metso" sodium silicate ($Na_2O.SiO_2$) 10 g./1000 g. H_2O	15 hr.	12.5 (*6*)[a]
f.	Same as *e*, 20 g./1000 g. H_2O	15 hr.	12.75 (*6*)[a]
g.	0.01 *N* NaOH	15 hr.	12 (*4*)
h.	0.033 *N* NaOH	15 hr.	12.5 (*4*)[b]
i.	0.06 *N* NaOH	15 hr.	12.76 (*4*)
j.	0.1 *N* NaOH	15 hr.	12.97 (*4*)
k.	Exptl. eradicator	10 min.	. . .
l.	$KMnO_4$ (25 g./l.) rinsed with H_2O, followed by $NaHSO_3$ (0 g./l.)[c]	10 min.	. . .
m.	KClO, about 1%	10 min.	. . .

[a] Interpolated from curve.
[b] Interpolated from table.
[c] Used in this laboratory and plant for removing writing fluid and dye stains from the hands.

Recording Sediment Formation

A convenient method of observing, measuring, and recording the formation of insoluble matter in writing fluids after various tests is to fill the bottom, hemispherical portion of an Antigen centrifuge tube with a soft wax or wax mixed with diatomaceous earth, or a quick-setting patching plaster, impregnated with melted wax after it is thoroughly dry. A small tool is prepared by grinding a sharp edge on the end of a steel rod, perpendicular to the axis of the rod. The rod is inserted into the tube and rotated; the wax or plaster is scraped just after it has set, so that it will be square across the tube and even with the first graduation. Then after the sample is centrifuged, it is easy to estimate the volume of insoluble matter

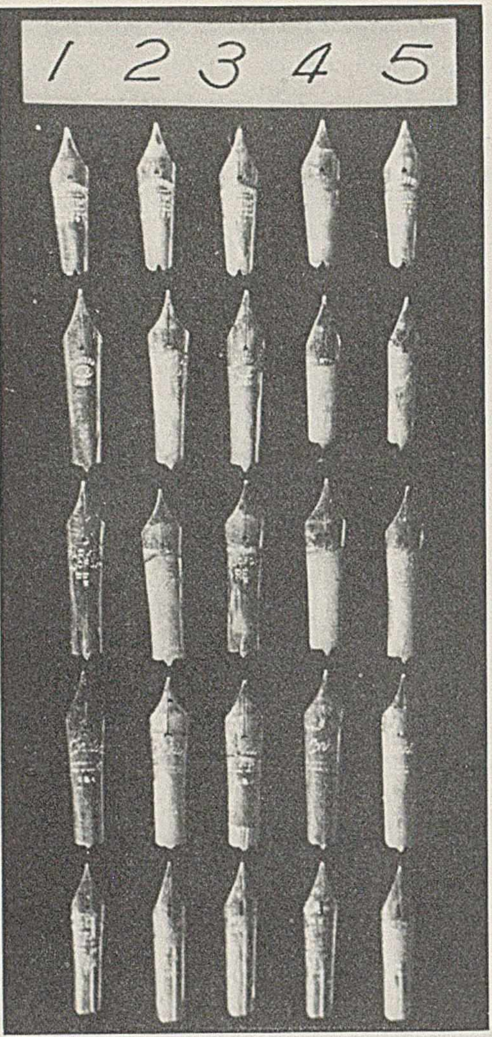

Figure 2. Action of Prussian Blue Inks on Gold Fountain Pen Nibs

to tenths of the smallest division, or to 0.01 cc. This is especially desirable when the total volume of precipitate is less than 0.1 cc., the smallest division on the tube. (For fountain pen use, the volume of precipitate is more significant than the mass.)

Water may then be added, the tube centrifuged again, and the water poured off, to remove soluble coloring matter (which might stain the filter disk, see below). The insoluble matter is washed out and collected on filter disks (finer than Whatman No. 2), cut to fit a Büchner funnel, about 40 mm. in diameter and fitted with a porous fritted glass disk instead of the customary perforated plate. This allows the insoluble matter to be distributed evenly over the surface of the disk, which, after drying, may be mounted on a piece of paper and covered with a thin, transparent plastic sheet, such as a regenerated cellulose sheet. This can then be filed for reference, since the disks give a good comparison between different solutions, especially where only a small amount of precipitate is involved. Of course, 50 cc. or more of the solutions can be centrifuged and the precipitate washed into a 10-cc. tube for measuring.

To 10 cc. of each of the above writing fluids was added 0.5 cc. of another commercial blue-black writing fluid. After about an hour the solutions were transferred to the Antigen tubes and centrifuged 15 minutes in an International clinical centrifuge. The liquid was poured off and the volume of precipitate noted (Figure 3).

In transferring the precipitate from Prussian blue inks 2, 3, 4, and 5, the addition of pure water redispersed part of the precipitate. We have never seen this effect with tests on ordinary blue-black inks. The use of a 10 per cent salt solution in place of the water eliminated this difficulty in transferring the precipitated Prussian blue.

Results of Investigation

Inquiries were sent out to determine, if possible, the relative amount of soluble Prussian blue used for writing fluids, the other types of blue dyes used, and the materials commonly used for standardizing such dyes, as a possible source of chloride and sulfate for ion-migration determination (*3*). Some of the replies were as follows (*1*):

> . . . A relatively small amount of soluble Prussian blue is used in writing inks. . .
>
> Without having any definite figures, we would say that to each pound of Prussian blue, 500 pounds of blue Schultz No. 539, 50 pounds of methylene blue, and 100 pounds of naphthol blue black are being used.
>
> The standardizing agents employed for soluble blues used in inks may be common salt, calcined Glauber salt, sugar, or glucose.
>
> Glauber salt and sodium chloride are sometimes used for diluting dyes so as to establish uniform tinctorial power. They cannot however be used with soluble Prussian blue as they would cause precipitation.
>
> The color mostly used for so-called permanent inks is soluble blue Schultz No. 539.
>
> Blues of the anthracene and anthraquinone series are used very extensively. These are organic dyestuffs and are standardized with dextrine.
>
> The classes of blue colors sold for inks are Helvetia blue . . . and the trisulfonic blues. . .
>
> With regard to the standardization of these products, we very rarely find it necessary to add any reducing agent inasmuch as we

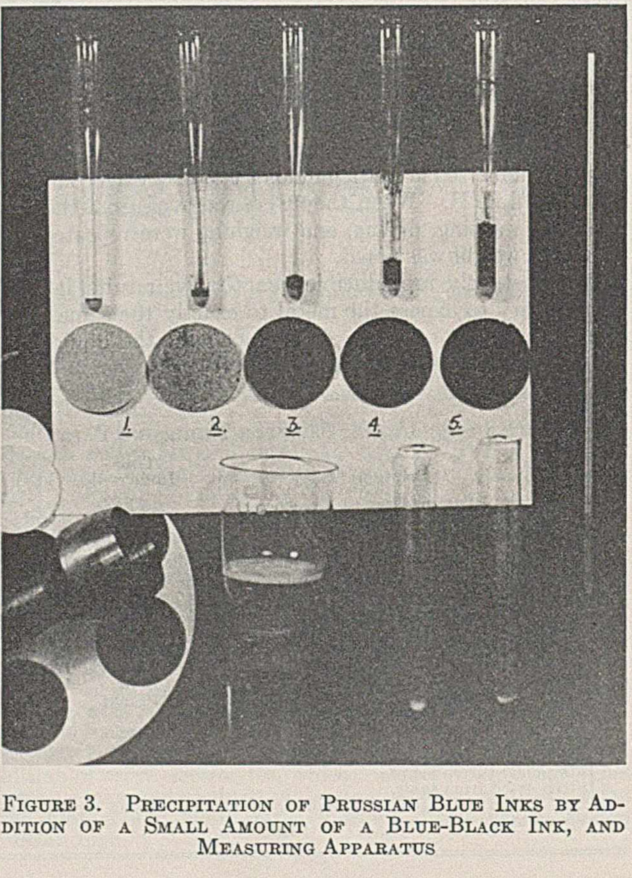

Figure 3. Precipitation of Prussian Blue Inks by Addition of a Small Amount of a Blue-Black Ink, and Measuring Apparatus

are able to control the yield of our blends. By that we mean we turn out a strong batch and then a weak batch, thus giving us leeway so as to be able to standardize to strength by mixing the two blends. In the few cases where we have had to add a standardizing material we have used Glauber salt.

The soluble forms of iron blue are generally made by treating the water-insoluble form with sodium ferrocyanide or oxalic acid. Such products are not truly soluble but they are colloidal when added to water and can be used like soluble dyestuffs.

Soluble iron blue is precipitated from its colloidal solutions by small amounts of certain metallic salts such as those of calcium, aluminum, and an excess of iron salts such as iron sulfate or iron chloride.

Most permanent blue-black inks will contain sulfate or chloride, or both, from the use of ferrous sulfate (which, with the tannic and gallic acids present, forms the insoluble deposit on the paper which makes the writing "permanent") and from hydrochloric or sulfuric acids, and from any standardizing salts which may be present in the dyes used. However, there are writing fluids to which have been added no acid or salt, and which use only dyes for the color. In such inks the only source of chloride and sulfate is material that the dye manufacturer may have used for standardizing the dye or small amounts from the water supply.

Thus, it is conceivable that certain kinds of inks may contain no chloride or sulfate and also that the same brand and formula may contain different amounts with different batches of dye.

Acknowledgment

We wish to express our thanks to the W. A. Sheaffer Pen Company for permission to publish these results, to the dye manufacturers (*1*) for the information they furnished, to John E. Hauck for the photography and assistance in the experimental work, and to Roger Macdonald for helpful suggestions.

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Nomograph for Surface Tension of Ethyl Alcohol–Water Mixtures

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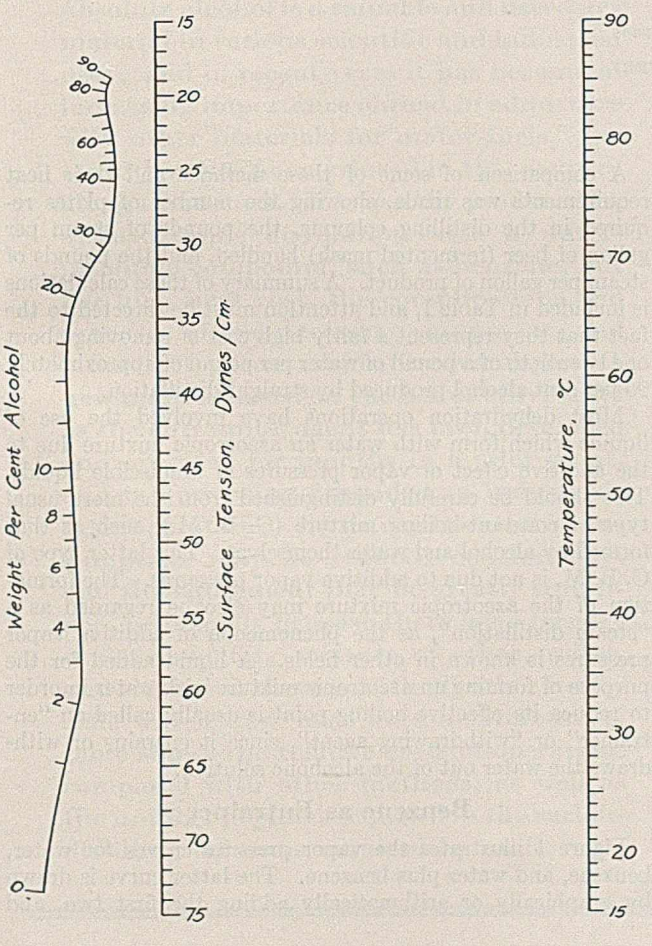
BONNELL, Byman, and Keyes (*1*) presented excellent data covering the surface tension of ethyl alcohol–water mixtures. The solutions studied had concentrations of 2.33, 5.94, 15.93, 29.67, 43.64, 61.10, 75.68, and 92.72 per cent ethyl alcohol by weight while the temperatures were at uneven intervals between 20° C. and the atmospheric boiling points.

In view of the importance of the data it seems worth while to provide a convenient and accurate means of interpolation. Surface tension, γ, can be plotted linearly with temperature, t, according to the expression,

$$\gamma = a + bt$$

where a and b are specific for each concentration. A close study of the variation of a and b with concentration, using the La Grange interpolation formula (*2*) where necessary, enables construction of the accompanying line coordinate chart.



The chart permits ready percentage and temperature interpolation, a straight line cutting the three axes in values consistent with the original data. As an illustration, a solution containing 10 per cent ethyl alcohol by weight has a surface tension of 44.0 dynes per cm. at 59° C.

Surface tension data for pure water are from the International Critical Tables (*3*).

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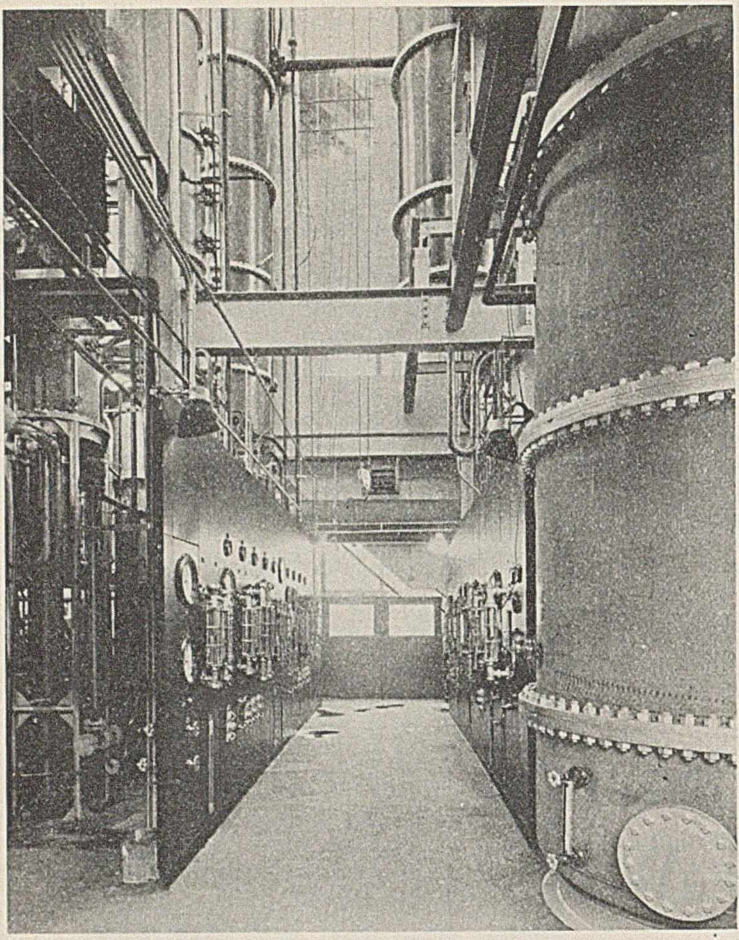

Courtesy, Vulcan Copper & Supply Company

Control Stations and Continuous Column Stills for the Recovery of Ethanol and Other Solvents

ABSOLUTE ALCOHOL

An Economical Method for Its Manufacture

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AT THE turn of the century, Young (*6*) developed a method for the manufacture of absolute alcohol which may be regarded as the forerunner of modern processes of azeotropic distillation. This was a batch process, and was patented and used (in Germany, at least, up to the time of the first World War) in about its original form.

Keyes (*1*) gave a history of the azeotropic process for the first thirty-odd years of its life as applied to alcohol dehydration and showed that Americans (among other, Keyes himself) were not only large contributors toward putting this process on an efficient continuous basis, but actually operated the first continuous industrial process. Many others since that time have worked to improve the process and to make it more economical; e. g., other entraining agents than the benzene first used by Young have been tried, additional columns have been used to make continuously the separations otherwise made in subsequent fractionation in batch units, and additional decanters, washers, etc., have been utilized to apply the tools of the distillation engineer most effectively. Klar (*2*) surveyed the literature and methods in use and gave some statistics and legal regulations for various countries, up to 1937. His small monograph is the most complete history and bibliography which has appeared to date.

Many improvements in distillation technique may be applied to the distillation procedures necessary for accomplishing this dehydration process. One of them is the vapor re-use method, patented by Wentworth (*4*) and described by Othmer (*3*), which results in considerable heat economy.

A comparison of some of these methods and their heat requirements was made, showing the number of plates required in the distilling columns, the pounds of steam per gallon of beer (fermented mash) handled, and the pounds of steam per gallon of product. A summary of these calculations is included in Table I, and attention must be directed to the fact that they represent a fairly high cost of removing about one twentieth of a pound of water per pound of approximately 95 per cent alcohol produced by straight distillation.

Most dehydration operations have involved the use of liquids which form with water an azeotropic mixture due to the additive effect of vapor pressures of immiscible liquids. This should be carefully distinguished from the more usual type of constant-boiling mixture (C. B. M.), such as that formed by alcohol and water themselves. This latter type of C. B. M. is not due to additive vapor pressures. The formation of the azeotropic mixture may also be regarded as a "steam distillation", as the phenomenon of additive vapor pressures is known in other fields. A liquid added for the purpose of forming an azeotropic mixture with water in order to reduce its effective boiling point is usually called an "entrainer" or "withdrawing agent", since it entrains or withdraws the water out of the alcoholic solution.

Benzene as Entrainer

Figure 1 illustrates the vapor pressure curves for water, benzene, and water plus benzene. The latter curve is drawn by graphically or arithmetically adding the first two, and intersects the normal atmospheric pressure abscissa at 69° C. (156.2° F.) which is thus the boiling point for a mixture of the two. The effective boiling point of water has in this manner been reduced by 31° C. (55.8° F.) from 100° to 69° C. (212° to 156.2° F.) where it is over 9° C. (16.2° F.) lower than the boiling point of pure alcohol or of the C. B. M. of alcohol and water. Thus it would be expected that this 9° C. difference between the boiling point of alcohol and the effective boiling point of water would allow the water to be rectified out of the alcohol mixture. Unfortunately the simple addition of partial pressures is not all that is involved, since alcohol itself forms a C. B. M. with benzene and a ternary mixture with benzene and water. This ternary system, the first to be discovered, has a composition of about 18.5 per cent alcohol, 7.4 per cent water, and 74.1 per cent benzene. The boiling point is, however, 64.85° C. (148.73° F.) rather than 69° C. (156.2° F.), that of the benzene-water azeotropic mixture. Thus, although the boiling point of the water is reduced (even more than at first anticipated), it may not be brought over the top of the column without more than twice as much alcohol coming with it.

After condensation, the benzene-alcohol-water ternary mixture consists of two very insoluble liquids (water and benzene) which form a lower layer and an upper layer, respectively, and a third liquid (alcohol) which is soluble in each layer and tends to bring both layers into a common solution. If properly rectified in an efficient column with ample reflux, the ternary mixture may be obtained at the head of the column, condensed, and separated into two layers. In some instances it has been found desirable to add water to promote this decantation; and in every case it is necessary to pass the water layer to another column still for the concentration of the alcohol up to a strength where it may be fed back to the azeotropic process. Thus no water is eliminated as such from the azeotropic system, but it goes out as a fairly strong alcoholic solution.

Absolute alcohol is a valuable and necessary material in various scientific and industrial uses; and in recent years it has become of increasing importance abroad in admixture with other materials for motor fuels. Interest has also been evinced in this country along these lines. It is usually produced by an azeotropic distillation with a water-insoluble compound, such as benzene, but the high heat cost, the complications and expenses of the necessary equipment, and other factors are major disadvantages. A new method based on the use of ethyl ether as the entraining agent has been developed and operated for months in a pilot plant, and is now being expanded to industrial-scale operations. By its use the steam consumption may be reduced considerably; and the equipment may be greatly simplified, principally because there is no ternary constant-boiling mixture of ether, water, and alcohol as there is with all other materials which have been used heretofore. A table shows the relative costs of operation, compared with other methods, as well as the number of plates required in the various distilling columns required by each.

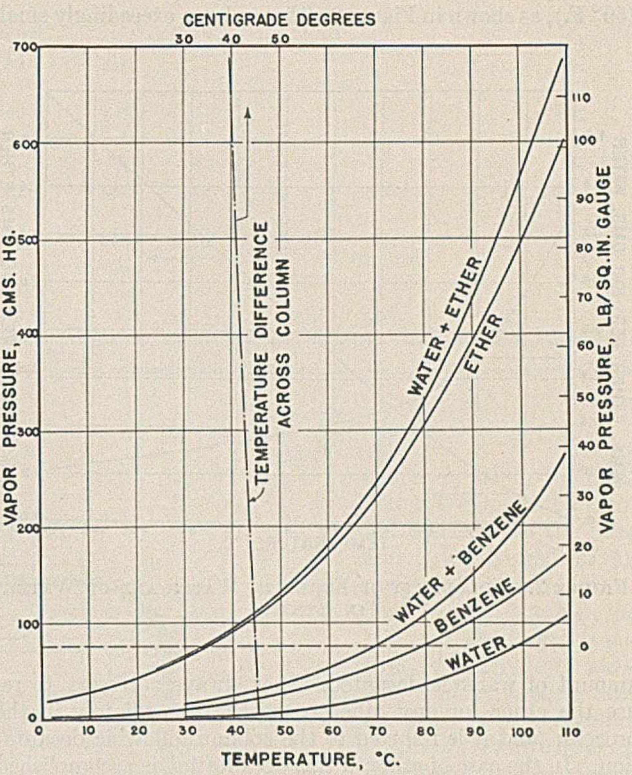


Figure 1. Vapor Pressure Curves for Water, Ether, Benzene, and for the Steam Distillation of Ether and of Benzene

Broken line shows the temperature drop across the dehydrating column in the ether dehydration system operating at various pressures.

The decantation of the condensate and the subsequent separation of the components of the two layers have been the basic steps of the several dehydration processes mentioned. These processes have also utilized other entraining agents than benzene; for example, the more recent Drawinol process uses chlorinated hydrocarbons such as trichloroethylene. All of these other entrainers have the same disadvantage as does benzene—i. e., of forming ternary mixtures with alcohol and water together. Search has been made to find a liquid which would give an azeotropic mixture with water, caused by the additive partial pressures or steam distillation effect, but which would have no binary C. B. M. with alcohol (and therefore no ternary C. B. M. with alcohol and water). If such a liquid, having suitable properties and giving a suitably effective boiling point for water, could be found, it would enable the separation of water from the alcohol at the base without bringing alcohol over the top of the column at the same time. Up to the present, no such liquid had been found as the ideal entrainer.

Ethyl Ether as Entrainer

Recently one of the authors (*5*) found that ethyl ether is such a liquid. It has long been known that ethyl ether forms no C. B. M. with alcohol but does steam distill with water at 760 mm. and 34.15° C. (93.47° F.), which is over 65° C. (117° F.) lower than the boiling point of water, and almost 45° C.

(81° F.) lower than the boiling point of alcohol. This azeotropic mixture has a composition of 98.75 per cent ether and 1.25 per cent water (by weight) at atmospheric pressure. As mentioned above, in the practical application of an azeotropic distillation process the entrainer brings over the water which, after condensation, is decanted. With ether, however, the solubility of water in ether is so high—1.15 per cent at 15° C. (59° F.), as shown in Figure 2—that only an exceedingly small amount of water is decanted. It is always necessary to reuse the ether (or any other entrainer) immediately in the process; and it is refluxed to the column following decantation. In the case of ether, if this decantation is accomplished at 15° C., approximately 1.25 minus 1.15 per cent, or only 0.1 per cent water is decanted. In other words, the ether reflux to the column would have to be approximately one thousand times as much as the water separated out, or 1000 pounds of ether would be distilled per pound of water removed; this prohibitively high ratio has undoubtedly prevented previous consideration of ether as an entrainer.

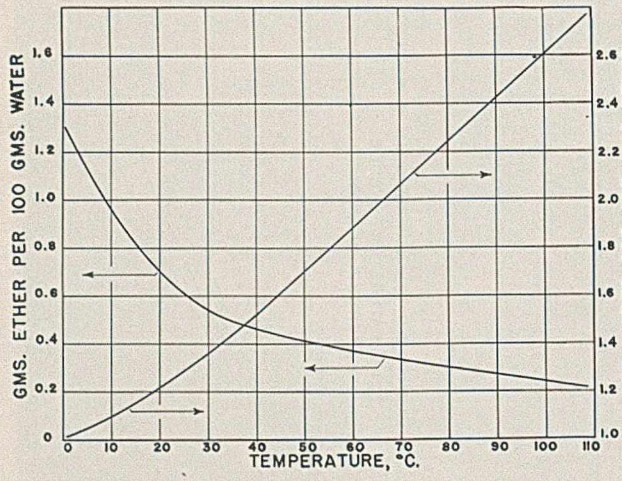


Figure 2. Solubility of Ether in Water and of Water in Ether

At pressures above atmospheric, the ratio of the azeotropic mixture is much more favorable. This is shown in Figure 1, which illustrates the vapor pressure relations for ether and water separately and additively. The water vapor pressure becomes a larger ratio of the total vapor pressure at higher temperatures and total pressures. This is equivalent to saying that the mole fraction of water in the vapor of the azeotropic mixture also increases at higher pressures and at higher temperatures. The mole fraction of water is plotted against azeotropic boiling temperatures in the upper curve of Figure 3. The center curve gives the weight per cent of water in the azeotropic mixture, as calculated from the top curve.

Following condensation of an azeotropic mixture of this sort, the condensate is decanted into two layers. Because of the small size of the water layer, the solubility of ether in water is not important, although, as mentioned above, the solubility of water in the ether layer is of prime importance. From Figure 2 it is apparent that the lowest practicable temperature in the decanter would be desirable to minimize the amount of water returned to the column due to its solubility in the ether-layer reflux. Under plant conditions a desirable minimum temperature may be taken at 15° C. At this point the water solubility is 1.16 grams per 100 grams of ether (0.0116 gram per gram); and if the number of grams of ether in the ether layer is multiplied by 0.0116, the product is the amount of water dissolved in the ether layer in a decantation conducted at 15° C. If this is subtracted from the values for the amount of water in the azeotropic mixture, the data for the lower curve in Figure 3 are obtained. This gives the weight per cent of water in the water layer passing from the decanter, based on the total amount of vapors passing from the column.

Heat Requirements

An example will serve to show the use of these data in estimating the heat required in an actual operation. If 100 pounds gage is taken as the operating pressure, Figure 1 shows that the temperature at the top of the column will be 102° C. (215.6° F.); from Figure 2 this corresponds to 3.76 per cent of water by weight in the azeotropic mixture. If, from this amount, there is subtracted the solubility of water in ether at 15° C., a net of approximately 2.5 per cent water will be separated out in the decanter and so removed. On this basis, 40 pounds of ether must be distilled to remove 1 pound of water.

This might seem to represent a comparatively high reflux to the column, or a relatively expensive distillation from the heat standpoint. Such is not the case, however, when it is considered that ether has a relatively low latent heat, 121 B. t. u. per pound at 102° C.; and 1 pound of steam (at 75 pounds per square inch gage, a usual steam pressure which might be used in the operation of a plant-scale dehydrating unit) will vaporize approximately 7.4 pounds of ether. Thus only about 40 ÷ 7.4, or 5.4, pounds of steam are required to vaporize the ether needed to bring over and separate out 1 pound of water. Furthermore, since this vaporous heat is available at a temperature of at least 100° C., it may be almost entirely used in other distillation operations of the plant—e. g., heating the preliminary beer still.

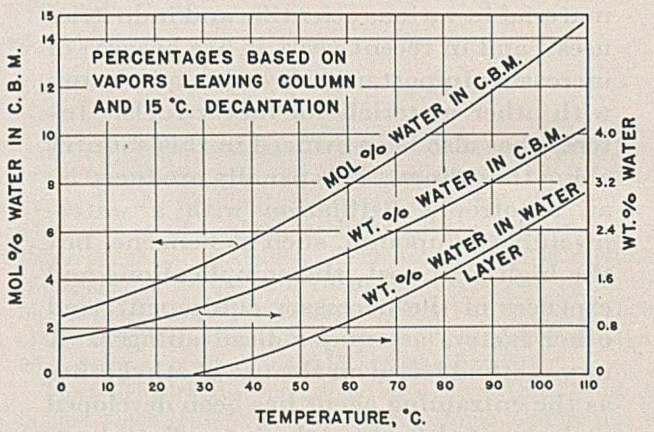


Figure 3. Mol Per Cent Water in Constant-Boiling Mixture, Weight Per Cent Water in Constant-Boiling Mixture, and Weight Per Cent Water in Water Layer (Solubility of Water in Ether at 15° C.)

Figure 4 is a flow sheet for the operation of a column accomplishing this process at a working pressure of 100 pounds per square inch gage. The temperature at the base of the column is the boiling point of absolute alcohol at this pressure, 142° C. (287.6° F.); and at the top of the column the temperature is 102° C. (215.6° F.), the azeotropic temperature at this pressure. The widths of the bands represent the number of moles of liquid or vapor flowing throughout the system. These widths, as is usual in distillation calculations, are based on the number of moles rather than the number of pounds or other weight units, because of the usual assumption

Table I. Comparison of Methods

Type of Process and Method of Operation (Alc. Concn. in Vol. %)	Feed Concn. Vol. % Ethanol	Approx. No. Plates Required in: Exhausting column (beer still)	Purifying column	Rectifying column	Dehydrating column	Water-layer stripping column	Supplementary rectifying column (dehydration unit)	Steam^a Consumption: Lb./gal. of feed	Lb./gal. of product
Continuous exhaustion and rectification to produce crude 96% alc.	6.25	20	Not required	30^b	..	..	...	1.3	20
Continuous exhaustion, purification, & rectification to produce refined 96% alc. (neutral spirits); Barbet system	6.25	20	30	54^c	..	..	...	2.21	34
Continuous exhaustion, purification, & rectification to produce refined 96% alc. (neutral spirits); vapor re-use system	6.25	20	45	54^c	..	..	...	1.3	20
Continuous dehydration of refined 96% alc.; benzene system at atm. pressure	96.0	..	..	..	50	30	45^c	8.16	8.5
Continuous exhaustion, purification, rectification, & dehydration to produce refined anhydrous alc.; Barbet system + benzene dehydration	6.25	20	30	54^c	50	30	45^{c,d}	2.74	43.9
Continuous exhaustion, purification, & dehydration to produce refined anhydrous alc.; vapor re-use system with ether dehydration at 125 lb./sq in.	6.25	20	45	54^c	30	20	Not required	1.31	21

[a] Calculations based on appropriate heat interchanging in each instance.
[b] Enriching section only.
[c] Enriching and exhausting sections.
[d] The main rectifying column may be used for concentrating aqueous alcohol from the stripping column, provided sufficient excess capacity is present.

that the molal latent heats of evaporation of the several components are equal and that thus the same total number of moles of vapor rise from plate to plate, regardless of the changes in composition. Likewise, there would be the same number of moles of liquid flowing down from plate to plate. Figure 4 is so drawn; and the bands are of uniform width, as would be expected from this assumption of "constant molal vaporization" and its corollary "constant molal overflow". The assumption is justified as far as alcohol and water are concerned, since their molal latent heats are approximately equal; but, particularly at higher pressures, the molal latent heat of ether diverges. For simplicity in this somewhat idealized and schematic diagram, the assumption is made; but it is not made in the calculations resulting in Table I.

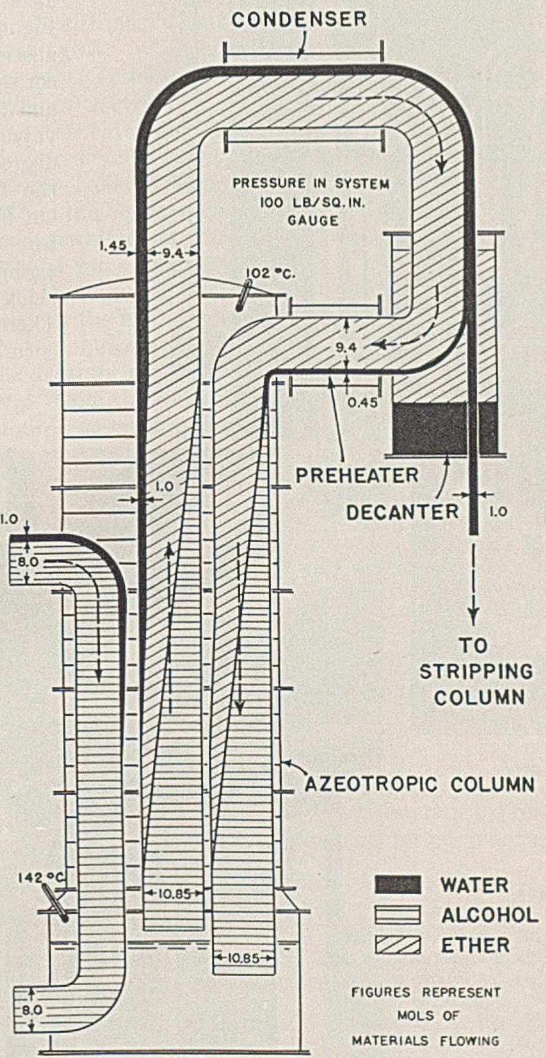


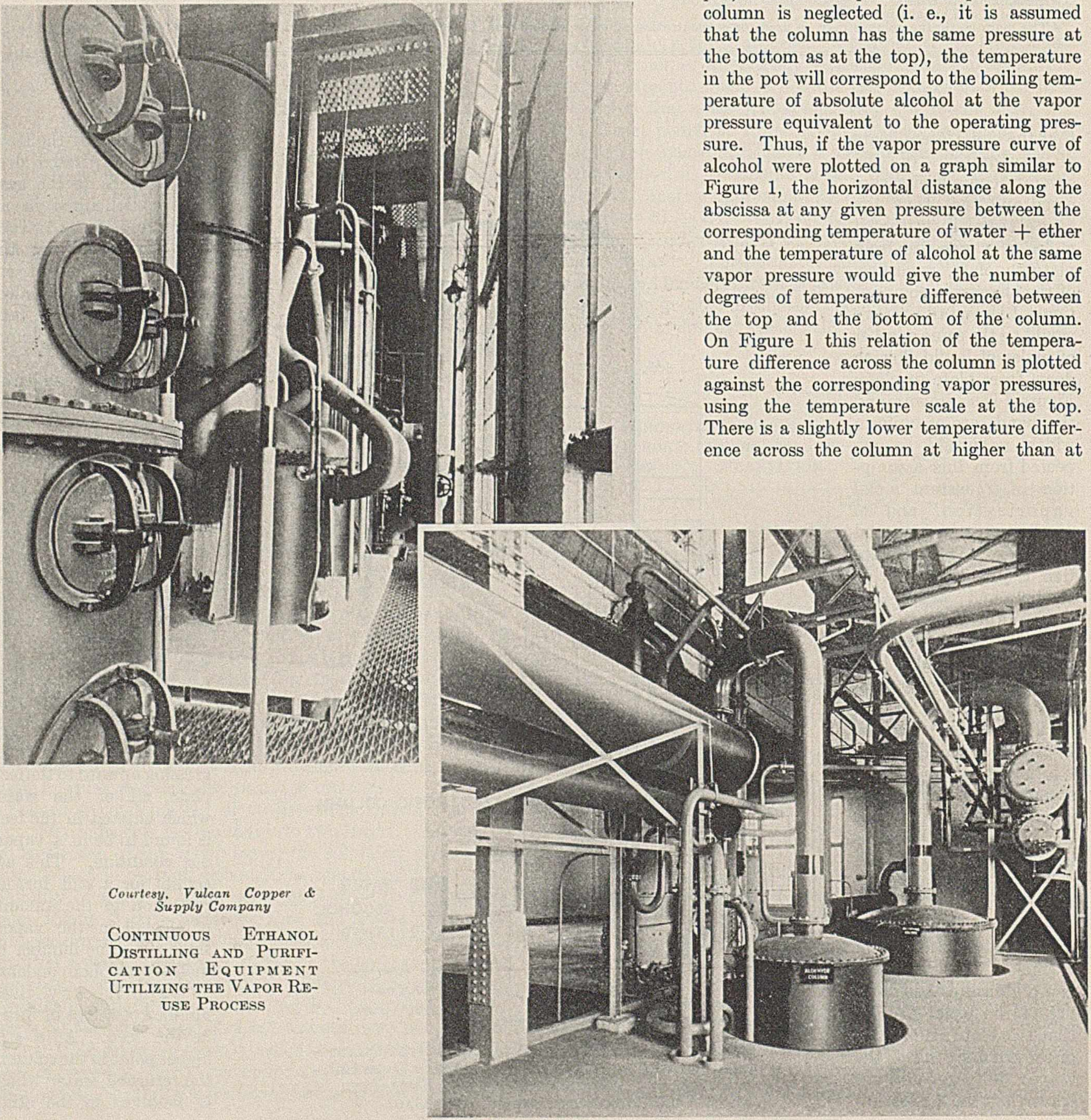
Figure 4. Approximate Molar and Heat Quantities Flowing in an Azeotropic Column Dehydrating Ethanol, Using Ether as the Entrainer at 100 Pounds per Square Inch Gage

The diagram shows that the C. B. M. of alcohol and water containing approximately 8 moles of alcohol to 1 mole of water and obtained as the product of the usual distillation, is fed into a mid-plate of the column; all of the water is removed in traversing the plates immediately below the feed; and the dehydrated alcohol descends to the base and is discharged in an anhydrous condition. The vapors leaving the still pot also consist entirely of anhydrous alcohol; and at a plate near the base of the column, ether is encountered which, by the condensation and revaporization continually taking place in a distilling column, is vaporized at the expense of the condensation of a theoretically equal number of moles of alcohol vapor. At a somewhat higher point, although still below the feed plate, water is encountered and likewise vaporized in conjunction with the ether in the azeotropic mixture since ether and water together have the lowest boiling point of any constituent. Progressing upward to the feed plate, all of the water which entered in the feed is found to be in a vaporous condition. This accounts for a still further reduction in the amount of alcohol in the vapor, since the same number of moles of alcohol condense to vaporize any given number of moles of water in the feed. At a still higher point in the column, the returned water which is dissolved in the ether from the decanter is met and removed in the same fashion; and at the top plate of the column a vapor mixture results which is substantially free of alcohol and contains water and ether in the azeotropic ratio which exists at the pressure involved. This vapor stream is condensed and decanted at a suitably low temperature, and at either the same high pressure as that of the column or at atmospheric pressure, whichever is preferable.

The water layer leaves the decanter saturated with ether but containing such a small total amount that it is not included in this simplified flow sheet. The water dissolved in the ether layer, however, is appreciable; and this, with the ether, is carried back through the preheater to the top of the column where it enters as reflux. In the ordinary case a pump is necessary to return the liquid to the pressure of the column if the decantation is not done under the high pressure of the column, as well as to overcome the friction of the preheater. The descent in the column of the ether layer as reflux liquid while it washes the rising vapor has been referred to; and the loss of the water from the liquid flowing down, with consequent condensation of alcohol vapors, is illustrated in the plates near the top. As the ether reflux descends, it meets the rising alcohol vapors; and more and more ether is vaporized with resulting condensation of an equivalent number of moles of alcohol, until at a plate near the base of the column no ether is present and pure alcohol descends into the pot.

Equipment

A dehydrating unit utilizing this system would have a temperature at the top corresponding to the temperature of the water + ether curve in Figure 1 at the operating pressure employed. If there is pure alcohol in the still pot, and if the pressure drop across the column is neglected (i. e., it is assumed that the column has the same pressure at the bottom as at the top), the temperature in the pot will correspond to the boiling temperature of absolute alcohol at the vapor pressure equivalent to the operating pressure. Thus, if the vapor pressure curve of alcohol were plotted on a graph similar to Figure 1, the horizontal distance along the abscissa at any given pressure between the corresponding temperature of water + ether and the temperature of alcohol at the same vapor pressure would give the number of degrees of temperature difference between the top and the bottom of the column. On Figure 1 this relation of the temperature difference across the column is plotted against the corresponding vapor pressures, using the temperature scale at the top. There is a slightly lower temperature difference across the column at higher than at



Courtesy, Vulcan Copper & Supply Company

Continuous Ethanol Distilling and Purification Equipment Utilizing the Vapor Re-use Process lower pressures. This function may be used to indicate the relative ease of separating the pure alcohol at the bottom of the column from the azeotropic mixture of ether and water at the top since, in general, the temperature difference across the column indicates roughly the relative ease of separation of the components of the mixture being distilled.

It appears, then, that while the heat economy due to the higher percentage of water in the water layer improves with increasing pressures, the ease of separation decreases slightly; and the number of plates in the azeotropic column may have to be increased very slightly, with increasing pressure, to compensate for decreased temperature difference between the boiling point of alcohol and the temperature of the steam distillation of water and ether.

Furthermore, it is obvious that for a given capacity of alcohol dehydrated, the column may be made much smaller in cross section with each increase in operating pressure, not only because of the greater amount of water removed for a given amount of ether distilled, as shown in Figure 3, but also because the volume of the vapor is inversely proportional to the pressure; and the same weight of vapors may thus be handled in smaller equipment when operating at higher pressures.

Table I indicates the number of plates required for the dehydrating process using ether, as well as the number required in the dehydrating column of a modern and efficient system of the usual type having a ternary C. B. M. with alcohol and water and using benzene as an azeotropic agent. While the benzene system requires fifty plates, the ether system needs only thirty. The column for stripping the water layer free of benzene after decantation and before reconcentrating has thirty plates, as compared to a maximum of only twenty plates needed for the easier separation of dissolved ether from the corresponding water layer. In addition, the benzene system requires for concentrating the water layer after stripping of benzene a supplementary column still of some forty-five plates, while no such still is needed for the ether process; although if there is ample excess capacity in the main rectifying column, this column may handle the aqueous alcohol obtained in the benzene process from the decanter after passing through a benzene stripping column. While the sums of the number of plates required (one hundred twenty-five for the benzene process and fifty for the ether process), are meaningless in themselves, they do indicate the relative complications and cost of equipment, controls, and operation for the two processes.

Besides requiring smaller and less efficient equipment, this process uses the theoretical minimum number of pieces of equipment for any azeotropic process—i. e., a main azeotropic column still, a second stripping still, a single condenser, and a decanter, together with necessary pumps, connections, etc. As Klar (*2*) indicated, no other azeotropic system proposed for dehydrating alcohol can operate with so few pieces of equipment because of the necessity of additional dephlegmators, condensers, decanters, washers, columns for separating the entrainer and alcohol from the water layer, or alcohol from the solvent layer, etc.

The vapor re-use system (*3*, *4*) may readily be applied to this process in a modified form to give low steam costs. Table I lists these costs under various conditions. An obvious heat-saving method used in the design of the first industrial installations is the use of a low-pressure evaporator or boiler as the condenser to give steam (or other vapor) immediately usable in other steps of the alcohol refinery.

Economies Effected

Thus, this dehydrating process, in combination with other methods demonstrated by years of economical operation with proved savings, makes possible the production of a refined, anhydrous alcohol, at an over-all steam cost from the dilute distiller's beer of 21 pounds per gallon. This is only 1 pound of steam per gallon more than the usual practice for producing a crude 96 per cent alcohol, and less than half as much as is required for producing a comparable product by other standard methods in use.

The alcohol produced by this system has been made, for all practical and scientific purposes, entirely free of ether—i. e., not more than a few parts per million. Because of the close chemical similarity of ether to alcohol, it is inconceivable that this minute trace would be of any consequence in even the most exacting work. The product is rigorously anhydrous, since the water is entirely removed at a higher level in the column than the ether. This practically perfect separation is possible because of the very large temperature differences (*a*) between the boiling point of the azeotropic mixture, ether-water, and that of alcohol, and (*b*) between the boiling point of the azeotropic mixture of ether-water and that of water, as compared to the respective boiling point differences for systems using benzene, trichloroethylene, etc.

This process is based on the mutual physical relations of ether, water, and alcohol. Solubility, vapor pressure, and vapor composition studies on these materials and their mixtures under the elevated pressures and temperatures involved are being made and will be reported, so that a full heat and material balance may be made around any part of the system. Operating data from one or more dehydrating units using this process (now under construction) will also be reported. The process as outlined here and as used in the design of equipment shortly to be placed in commercial operation has resulted from, and has been tried and proved by, the operation of a pilot plant over an extended period of time. This pilot plant has demonstrated advantages which may be summarized as follows:

1. Alcohol-free water and water-free alcohol are easily produced in one column. All of the alcohol entering the azeotropic rectifying column as feed is delivered directly as anhydrous or absolute alcohol from the base. All of the water is withdrawn from the top of the column free of alcohol in the form of the constant-boiling mixture with ether, and is discharged from the base of the water-layer stripping column free of both alcohol and ether.
2. Lower steam and water consumption is required in conjunction with the preliminary distillation operations than is required by any of the existing dehydrating processes, including those which employ ternary azeotropes.
3. Comparatively small and simple equipment is necessary, owing to the absence of a ternary C. B. M. and to the wide difference in boiling points between the ether-water azeotropic mixture and alcohol and the ether-water azeotropic mixture and water.
4. The added economy of the vapor re-use process, or other related systems, is readily adaptable to this process.
5. The process is simple to operate and can be made fully automatic.

Acknowledgment

Appreciation is expressed to The Vulcan Copper & Supply Company for permission to publish this work.

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Measurement of Static and Dynamic Foams in Characteristic Units

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METHODS of measuring the foaminess of liquids have been considerably influenced by the ultimate industrial application to which the foam-producing liquid is to be put. By far the greatest attention has been paid to the "dynamic" method of foam measurement, a term first coined by Hansley (*20*), in 1928, to describe a system in which the foam is continually produced by a current of gas passing through the liquid. The application of foams in ore flotation appears to be the cause for this method of foam measurement. An apparatus of this type was used by Aleinikov (*1*) for methylaniline and cresol foams, by Foulk and Miller (*16*) for inorganic salt solutions, and by Ostwald and Siehr (*30*) to investigate the relation between the height of the foam, gas pressure, and blowing time. Finally a unit of foaminess for dynamic foams was established by Bikerman (*7*), based on the hypothesis that the capacity for the formation of foam is a physical property of a liquid.

Dynamic and static foam meters, for use with any gas which will produce foam in any liquid, are described. The results of measurements of dynamic and static foams of egg albumin sols are tabulated for both air and carbon dioxide in the gaseous phase, and comparison is made with corresponding beer foams.

Evidence for a reaction between carbon dioxide and egg albumin sol is deduced from foaminess data. Units of foaminess for both static and dynamic foams are discussed, and methods of foam measurement classified and correlated.

The apparatus used by Bikerman was of the type recommended by Foulk and Miller (*16*) and by Lederer (*25*). A measured volume of air is forced through a porous membrane and through a layer of liquid above it. The volume of foam which is formed is measured in a calibrated tube. It was found that the average foam volume was proportional to the rate of streaming of the air. Hence, if V is the volume of air forced through the membrane in time t, and v is the average volume of the foam,

$$v = f(V/t)$$

where f is a constant independent of the rate of streaming. It was found that the value of vt/V observed for large amounts of liquid was independent of the size or shape of the apparatus or the rate of air flow; hence Bikerman proposed the use of this function as the unit of foaminess. In the centimeter-gram-second system it has the dimensions of time (seconds), and the symbol Σ was proposed for it (from the Greek *saponos*, meaning "lather"). It has been shown that the physical significance of Σ is the lifetime of a unit volume of foam.

The work of Bikerman, however, has left out of account a large number of methods for foam measurement, already reported in the literature, which are based on the uses of foams for industrial purposes other than ore flotation. Brewers, bakers, and soap, paper, and glue manufacturers, etc.—in fact, all industries in which the production of a foam is either a desirable or an undesirable occurrence—have reported methods of foam measurements which do not correspond to the dynamic method investigated by Bikerman. Foams can be produced in any one of several possible ways, but these nondynamic or static methods are characterized by the fact that measurements are made after the production of the foam and not during its formation.

Static methods vary among themselves chiefly in the manner in which the foam is produced. In the case of egg whites (*4*, *5*), albumin (*13*), and casein (*32*) a foam was produced by whipping; foaming of saponin solutions was promoted by forcing them through a fine filter into a vessel maintained at low pressure (*2*); foams have been produced by pouring the liquid from a height (*21*, *22*, *23*, *36*), by bubbling a gas through it (*8–11*, *24*, *25*), by pouring sand into it (*34*), or merely by shaking it (*37*). All these methods agree in that measurements are not made until after the foam is formed. There is an even greater diversity between the units used to express the results. In fact, it is not possible to find any two methods employing the same units; in at least one case where four investigators used the same method, they each employed totally different units (*8*, *10*, *22*, *24*).

The present work is an attempt to establish a unit for static foams, comparable to the Bikerman unit for dynamic foams, and if possible to establish a correlation between the methods.

The attempt to evaluate the average life of a bubble in a static foam can be made for any system in which the rate of collapse is known or where sufficient data are available to enable its calculation.

It has been found empirically for beer and saponin foams that

$$f(t) = f_0(t)e^{-kt} = f_0(t)e^{-t/k'} \qquad (1)$$

where f_0 may be assumed for convenience to be zero, and $f(t)$ is the integral life of a unit of foam volume. Then the average life of a unit volume of foam, $\overline{\Sigma}$, up to complete collapse (or time infinite) may be represented by

$$\overline{\sum} = \frac{\int_0^{\infty} f'(t)\ t\ dt}{\int_0^{\infty} f'(t)\ dt} = k' \qquad (2)$$

where $f'(t)$ denotes the derivative of Equation 1.

In order to evaluate this equation, it is assumed that the number of bubbles present at any given instant is proportional to the weight of the foam. This applies to a static foam when no great height is present and hence presents no large error for variation in the number of bubbles per unit of volume at the top and at the bottom of the foam. The validity of this assumption is not affected by the well-known fact that a gradation of bubble sizes exists in the foam. It is supposed that large bubbles are collapsing at much the same rate as small bubbles are coalescing to form larger ones; hence, a similar gradation of sizes would exist in the foam even after it has been standing for several minutes. It is also recognized that a familiar equation expresses the number of bubbles, N, in unit mass:

$$N = \frac{1}{\rho}\frac{p^2}{64\pi T^2 \Delta r}$$

where p = gas pressure within bubbles
T = surface tension of bubble substance
Δr = bubble wall thickness
ρ = density

The right-hand member can be constant only if the ratio p/T is independent of pressure and Δr is invariable. This is obviously a special case; but the quantity of liquid at the bubble interfaces may be so large that the material of the actual bubble wall contributes only a small weight fraction to the whole. This may be the explanation of the validity of the assumption empirically established by the experimental results to be described. Thus suppose N_0 bubbles are initially present in a weight W_0, and N bubbles are present finally in a weight of foam W after time t. Then,

$$W/W_0 = N/N_0;\ N = N_0 f(t) = N_0 e^{-kt} = N_0 e^{-t/k'} \qquad (3)$$

Using $\Sigma = 1/k = k'$ as the unit of measurement for static beer foams, the authors demonstrated (*33*) that the results are independent of the method of producing the foam. It can be formed by bubbling the gas through the liquid, by pouring the liquid from a height (if carbonated), or merely by shaking the liquid in the presence of the gas, and in each case the value of Σ is found to be the same. This establishes the usefulness of the unit for static foams and leaves only the question of the possibility of a correlation between static and dynamic foam units.

Dynamic Foam Measurement

An apparatus for the measurement of dynamic foams was constructed as shown in Figure 1; it is a modification of the one used by Lederer (*25*). The chief improvements are the addition of a device for a constant head of water and the extension of the function of the apparatus to allow foams made with gases other than air. The apparatus is made ready for use by closing stopcocks *C*, *D*, *E*, and *F* and opening stopcocks *A* and *B*. This allows the first, or reservoir, part of the system to be evacuated. The gas cylinder is connected, stopcock *E* is opened, and the reservoir fills with the gas to be used in the foam. When the pressures have been equalized, as indicated by a suitable manometer, stopcock *F* can also be opened and the second part of the system flushed with the gas. This process is repeated three times at least, to assure only a small concentration of air left in the system. To obtain measurements, the liquid to be investigated is placed in column *G*, and the level observed. Stopcocks *A*, *B*, *C*, and *E* are closed, and stopcocks *D* and *F* are opened; at the same time a stop watch is released. Water flows into reservoir *R*-2 under constant pressure and forces the gas through the membrane in a steady stream, which soon reaches a constant rate of flow. The foam in column *G* begins to build up and reaches a maximum height which is observed as recommended by Bikerman (*7*)—i. e., every 5 seconds for slightly foaming substances, every maximum height for strongly foaming substances. (Obviously the ideal heights which would have been attained if no collapse had occurred during formation cannot be measured.) When a sufficient number of observations has been made, stopcock *D* is closed, and simultaneously the stop watch is arrested. The volume of air passed through the membrane in the recorded time is found by opening stopcock *C* and siphoning the water out of reservoir *R*-2 into a measuring cylinder. The volume divided by the time taken for the experiment gives the rate of flow of the gas through the membrane.

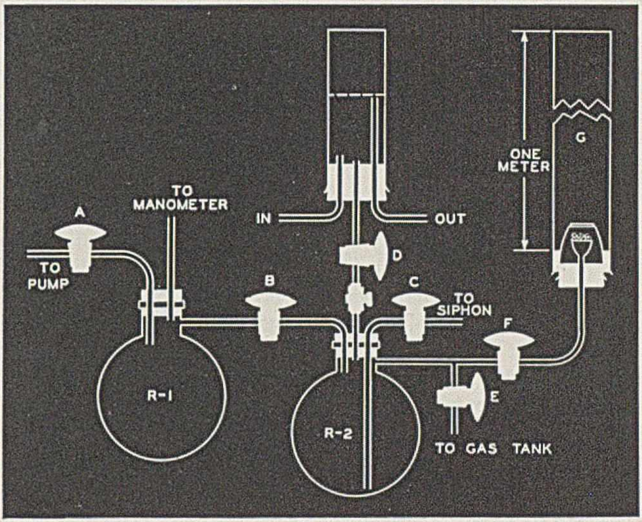


Figure 1. Dynamic Foam Meter

Egg albumin solutions of 2 per cent concentration were stored in an icebox under a mixture of xylene and paraffin oil. The method of storing and withdrawing the solution was that recommended by Bernhart and Arnow (*6*). Solution was removed from the bottom of the bottle when required and diluted with volumetric accuracy to 0.01 per cent. Table I gives the data on these solutions, using air as the gas with which to form the foam. Two U-tubes packed with ascarite were employed to remove carbon dioxide from the air. Different volumes of solution were used in separate runs, as recorded, to determine if changing the volume after 100 cc. had any effect on the result. Column *G* was cleaned with an alkaline cleaning solution (2 per cent sodium carbonate and 0.5 per cent sodium hydroxide) between each run, and when not in use, it was kept filled with distilled water. A preliminary rinsing with the solution whose foaminess was to be determined was made prior to each run. The values of Σ are calculated from Equation 1.

Table I. Dynamic Air Foams of 0.01 Per Cent Albumin

Foam No.	1	2	3	4	5	6
Av. max. ht., cm.	13.3	13.1	13.0	17.8	22.6	12.8
Vol. of soln., cc.	100	100	100	200	300	100
Initial ht. of liquid, cm.	8.2	8.3	8.3	13.6	19.4	8.4
Max. foam ht., cm.	5.1	4.8	4.7	4.2	3.2	4.4
Vol. of air, cc.	500	500	550	675	560	540
Time, sec.	184	185	214	312	320	217
Rate of flow, cc./sec.	2.7	2.7	2.57	2.16	1.75	2.49
Σ, sec.	34.2	32.3	32.8	36.3	33.8	32.2

Measurements in Tables I and II*A* were made on the same solution, using an air foam in the first and a carbon dioxide foam in the second case. The results are directly opposite to what might be expected in the case of a static foam, indicating totally different rates of coagulation for the two methods of measurement. Aleinikov (*1*) made the suggestion that in dynamic foam measurements coagulation takes place with the rupture of newly formed surfaces which are continually being replenished, but that in static foam measurements, coagulation involves the rupture of surface films which have already been standing for some time. Consequently, it was of interest to observe whether aging the protein solution had any effect on its foam stability. The concentrated protein solution was kept at a low temperature for three weeks, and then further measurements were made. These data (Table II*B*) show that a change in the foam stability does take place on aging.

TABLE II. DYNAMIC CARBON DIOXIDE FOAMS OF 0.01 PER CENT ALBUMIN

	A. Fresh Albumin				*B.* Aged Albumin			
	1	2	3	4	1	2	3	4
Av. max. ht., cm.	33.0	32.6	50.2	37.0	36.8	36.8	32.4	29.8
Initial ht. of liquid, cm.	15.1	17.4	15.2	11.4	17.0	15.6	15.8	15.4
Max. foam ht., cm.	17.0	15.2	35.0	25.6	19.8	21.2	16.6	14.4
Vol. of gas, cc.	1635	1550	2027	1860	1655	1570	1255	1160
Time, sec.	967	1043	598	776	1090	969	973	1014
Rate of gas flow, cc./sec.	1.69	1.49	3.38	2.40	1.52	1.62	1.29	1.14
Σ, sec.	193	186	189	194	237	238	234	229

An obvious difference in the appearance of air and carbon dioxide foams produced by this method exists. The air foam rises only to a small volume and is composed of relatively large bubbles; coagulation at the surface is not observable, and when the foam subsides, it leaves no solid scum sticking to the walls. The carbon dioxide foam rises to a much greater height, has smaller bubbles, and deposits a solid scum on the wall when it subsides. Occasionally, in such foams the coagulated protein seems to form a rigid film on top of the foam and prevents the proper rise of the froth above it. Results in experiments where this was observed were lower than the others and were consequently discarded. If the rate of flow of the gas through the membrane is very slow, there is more chance for it to take place, owing to the length of time required for the experiment. On the other hand, if the flow of the gas is very fast, the foam rises rapidly and continues to rise throughout the course of the experiment, apparently not reaching its constant maximum value before the gas in the reservoir is completely used up. Results from experiments of this type are again too low and must be discarded. These two factors fix the possible rates of gas flow within rather narrow limits, as shown in Tables I and II, and prevent adequate investigation of a possible variation of Σ with the rate of flow. Within the experimental range observed such a variation did not occur.

Static Foam Measurement

An apparatus for the investigation of static foams was constructed as shown in Figure 2. Exactly 100 cc. of the liquid are poured into the graduated bottom of the apparatus, and the foam is produced by means of a Chamberland filter. When the liquid has been dispersed into a foam, a stop watch is released and the filter withdrawn. The time taken for the advance of the liquid level between each 5-cc. graduation mark on the cylinder is noted. When, as sometimes happens, the rise of the liquid is very rapid the time between 10-cc. marks is taken instead.

Results for both air and carbon dioxide foams on the same sample of beer are given in Table III*A*. The calculation of Σ is by the following equation, derived from $N = N_0e^{-kt}$ and $\Sigma = 1/k$,

$$\sum = \frac{t}{2.3 \log \dfrac{100}{100 - V}} \qquad (4)$$

where V is the volume reading of the graduated tube.

The data of Table III*A* obtained by means of the static foam measuring apparatus are in agreement with the logarithmic formula for a carbon dioxide beer foam. In the case of the air foam, the logarithmic law, as evidenced by the constancy of the values for Σ, applies until about 50 per cent of the foam has disappeared, when the values of Σ begin to increase. This is precisely what would be expected from the escape of the more soluble gaseous constituents first leaving the less soluble gaseous constituents in the foam. The logarithmic law for carbon dioxide foams holds for at least 90 per cent of the lifetime of the foam. From the data of Helm and Richardt (*22*) the ratio of the stabilities of air and carbon dioxide foams can be calculated and compared with the ratio found in the present investigation. The results are 3.8 for the former and 4.5 for the latter method. When it is remembered that Helm and Richardt used the Carlsberg method and different samples and units of measurement, this is a satisfactory agreement.

Table III*B* gives data for static air and carbon dioxide foams of 0.2 per cent egg albumin. The stop watch was not released until the volume reading was 20 cc.; consequently Σ is calculated from the equation:

$$\sum = \frac{t}{2.3 \log \dfrac{80}{100 - V}}$$

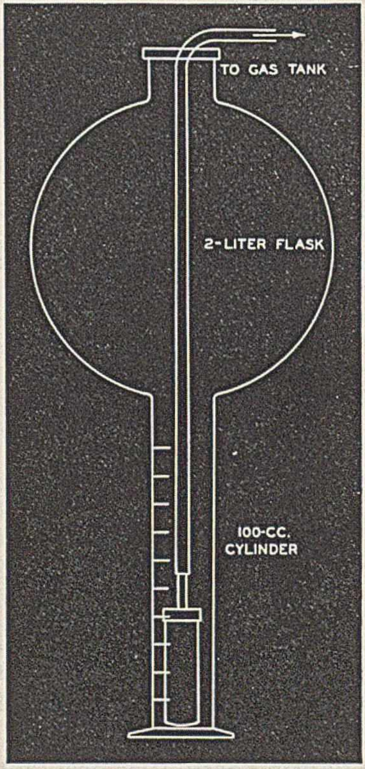


FIGURE 2. STATIC FOAM METER

It is apparent that egg albumin foams do not obey a logarithmic law. This is also in accordance with the data of Barmore (*5*) which do not indicate any logarithmic decline. However, as is the case with static foams of beer, the air foam is considerably more stable than the carbon dioxide foam.

Experimental Results

SUMMARY. Measurements of dynamic foams of egg albumin show that the carbon dioxide foam has a higher value for Σ than the air foam.

Measurements of static foams of egg albumin show that the air foam has a higher value for Σ than the carbon dioxide foam.

Dynamic foam measurements give higher values for Σ than static foam measurements for egg albumin.

Foams of egg albumin do not follow a logarithmic subsidence.

Beer foams obey a logarithmic rate of subsidence for 50 per cent of the lifetime of the foam if the foam is produced with air, and for 90 per cent of the lifetime of the foam if the foam is produced with pure carbon dioxide.

TABLE III. STATIC AIR AND CARBON DIOXIDE FOAMS FOR BEER AND ALBUMIN

A. Beer					B. 0.2% Albumin				
	Time, sec.		Σ			Time, sec.		Σ	
Vol., cc.	Air foam	CO_2 foam	Air foam	CO_2 foam	Vol., cc.	Air foam	CO_2 foam	Air foam	CO_2 foam
5	10	..	195	...	20	0	0	...	...
10	24	..	228	...	25	4	3	60.6	45.4
15	36	..	222	...	30	11	9	82.5	67.5
20	51	11	229	49.4	35	21	14	101	67.6
25	64	..	225	...	40	35	19	122	66.2
30	80	17	225	46.6	45	52	27	139	72.2
35	96	..	223	...	50	79	34	168	72.5
40	115	24	227	47.4	55	116	44	202	76.7
45	138	..	231	...	60	169	54	244	78.0
50	164	31	237	44.8	65	251	67	304	81.1
55	195	..	244	...	70	373	83	381	84.7
60	228	39	249	42.6	75	566	103	487	88.7
65	271	45	258	42.9	80	...	128	...	92.4
70	321	53	269	44.5	85	...	162	...	96.9
75	385	61	278	44.0	90	...	216	...	104
80	462	74	287	46.0	93	...	283	...	116
85	...	90	...	47.5	94	...	328	...	127
90	...	114	...	49.6	95	...	388	...	140

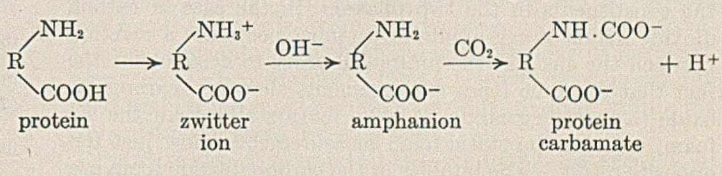
DISCUSSION. The basic assumption in the derivation of Σ in Equation 4 for static foams is the postulate that the volume of the liquid formed from the foam is a measure of bubble decay. It involves the supposition that this liquid does not come partially from a mere thinning of the bubble walls but is derived *in toto* from the collapse of the bubbles. The observations of carbon dioxide foams can be interpreted to lend some support to the assumption, based upon an argument originally employed by Barmore (*5*). Barmore found a simple linear relation between the specific gravity of egg white foams (a measure of the bubble size) and the rate of drainage. In view of this simple relation, it does not seem probable that the liquid draining from the foam can be derived from more than one source. If this source is the drainage from between the two liquid-air interfaces without any breaking of the bubbles, then on the basis of Poiseuille's equation,

$$V = Pr^4/8l\eta$$

the rate of drainage should be proportional to the fourth power of the cross section of flow. With foams composed of small bubbles, this cross section, which is the thickness of the liquid layers between the bubbles, must be decreased and hence drainage from the foam would be decreased. The observed effect is just the opposite. As shown in Table III*B*, the carbon dioxide foam, which has the smaller bubble size, drains more rapidly than the air foam. Barmore (*5*) found that foams which were finely whipped (small bubbles) drained faster than loosely whipped foams. These results bear out the contention that the liquid volume which is measured originates in the collapse of the bubbles and so considerably strengthens the claim that Σ for static foams is a real measure of the average life of the bubble.

The use of Equation 4 for static foams is, of course, also dependent on the logarithmic subsidence of the foam. Such a relation has been found to exist for beer foams (*10*) and solutions of different concentrations of saponin (*2*) where no chemical reaction takes place between the gas and the liquid. In the present study of static foams of egg albumin an increase of Σ as the foam ages (Table III*B*) may well be explained by the fact that egg albumin denatures in surface films, partially (according to Gorter, *17*), completely (according to Bull, *12*), and that the reaction is not immediate (*26*, *29*). The denatured and, in some cases, coagulated film has a superior tensile strength; consequently, as the foam subsides, those surface films which have been standing for a longer period resist rupture more and more effectively and cause an increase in the average life of the bubble as the foam ages.

In the case of air foams, only denaturation of the surface egg albumin appears to take place. This is in accordance with the x-ray study of Astbury (*3*), as well as Bull's study of protein films (*12*), in which he found the amount of denaturation to be proportional to the rate of formation of new surfaces. However, when carbon dioxide is used to produce the foam, a solid scum sticks to the walls of the tube when the foam has disappeared. This and other evidence reopens the unsettled question as to whether carbon dioxide gas reacts with albumin sols. It was so affirmed by Mellanly and Thomas (*28*), by Groak (*19*), and by Pauli (*31*), but denied by Gregorie (*18*) on the basis of a lack of increase in the conductivity measurements. If, however, the reaction is of such a nature as to produce coagulation of the protein molecule, the conductivity need not be affected. Also, Stady and O'Brien (*35*) proved a carbamate reaction between carbon dioxide and hemoglobin and serum albumin, based on analysis for carbamate by the method of Ferguson and Roughton (*15*). Therefore, strong presumptive reasons exist to suggest a reaction between egg albumin and carbon dioxide, which forms foams composed of very fine bubbles breaking rapidly and leaving a coagulated residue. The difference of foam measurements of the two foams, when first a dynamic and then a static foam meter is used, is satisfactorily explained only on the basis of a reaction between carbon dioxide and egg albumin. If we assume a carbamate reaction as the most probable one, based on the analogy of serum albumin, the carbon dioxide reacts with the amphanion and not with the protein zwitter ion. The nature of the reaction is expressed in the following equation:



$$R\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} \longrightarrow R\begin{matrix}\diagup NH_3^+\\ \diagdown COO^-\end{matrix} \xrightarrow{OH^-} R\begin{matrix}\diagup NH_2\\ \diagdown COO^-\end{matrix} \xrightarrow{CO_2} R\begin{matrix}\diagup NH.COO^-\\ \diagdown COO^-\end{matrix} + H^+$$

The reaction with carbon dioxide is rapid in the case of amino acids, hemoglobin, and the serum proteins (*35*). The decrease in the pH of the solution due to the liberation of H^+ ions on dissociation of the carbamate may well account for the presence of the observed coagulation.

A reasonable a priori assumption that the value for the average life of the bubble in the foam would remain constant whether the measurements be made by a static or a dynamic foam meter is shown by the present study to be unjustified, at least for egg albumin foams; further consideration of the mechanism of foam formation and decay will show that it is probably invalid in all cases. Foaminess as measured by the static foam meter is based on the rate of decomposition of the foam. In the case of the dynamic foam meter the measurement depends upon an equilibrium between the rates of formation and decomposition. For identical results to be obtained by the two methods, not only must the rates of decomposition be the same in both cases, but the ultimate value of Σ, in the case of dynamic foam measurements, must be independent of the rate of formation. The reason for the second condition is that the rate of formation is not taken into account in static foam measurements; the results of a previous paper (*33*) offer proof that the value of Σ is independent of the gas pressure, which determines the rate of formation.

The first condition, that the rates of foam decomposition be identical, can never be obtained in practice; the degree of deviation between the values depends on the nature of the constituent in the surface layer. As already stated by Aleinikov (*1*), the coagulation of a dynamic foam involves the rupture of newly formed surfaces, whereas the coagulation of a static foam involves the rupture of surfaces which have had time to age and, moreover, continue to age even while measurements are being made. While this factor may not be significant in many cases, it certainly has an effect in the case of egg albumin foams where, as shown by Bull (*12*), denaturation, and possibly ultimate coagulation, takes place on the surface layer. It has also been claimed that these changes in the surface layers of proteins are not immediate but take place over a period amounting to several minutes (*26*, *29*). That the aging of solutions affects the foaminess can be observed from the results of Table II*B*, where the solution was aged under conditions which tended to minimize any chemical reaction. A much greater effect would be expected when the aging of the solution takes place in the large surface areas which exist in the foam. The result of denaturation appears to be an increase in the foaming property of the protein sol, as manifested by the increase in Σ for aged solution (Table II*B*) and the continuous increase of Σ (Table III*B*) as the foam ages. This is in accordance with the results of Loughlin (*27*) who found an increase in the capillary activity of protein sols on denaturation. The work of Duce (*14*) on the aging of protein sols showed a series of maximum and minimum changes in the values of surface tension and viscosity as the sol aged. It is well known that these properties also influence the foaminess. In such circumstances a correlation between the static and dynamic foam measurements cannot be expected.

In his work on the unit of foaminess for dynamic foams, Bikerman (*7*) demonstrated that the value of Σ was independent of the rate of flow of the gas through the membrane—in other words, independent of the rate of formation of the foam—but his investigation was conducted on air foams of butyl alcohol solutions where no reaction took place between the constituents in the two phases. In the case of carbon dioxide foams of egg albumin, we must postulate a reaction between the gas and the protein in order to account for the fact that dynamic foam measurements show the carbon dioxide foam of egg albumin to be more stable than the air foam, whereas the static foam measurements show just the opposite result. The bubbles in the carbon dioxide foam are much finer than in the air foam; consequently, the volume of foam per unit volume of gas would be slightly greater. At the same time, some of the gas is absorbed by the protein sol and hence plays no part in the formation of the foam. The result is that even when the same rate of flow of gas through the membrane is used, the rate of formation of the foam in carbon dioxide differs from the value it has when the gas is air. This violates the second condition for a parity in results for the two methods. The measurements by the static method indicate the difference in the rates of foam decomposition, and the measurements by the dynamic method indicate that the difference in the rates of formation is more than enough to overcome the difference in the decomposition rates between air and carbon dioxide foams of egg albumin.

There can be no doubt that the use of air and carbon dioxide foams of egg albumin exhibits the deviation between the two basic methods of foam measurement to a maximum degree. The results of the present study show that methods of foam measurement can be correlated, even when the foam is produced in different ways, if only static methods of measurement are used. In this connection, a unit of foaminess for static foams is provided. The work of Bikerman (*7*) has provided a comparable unit for dynamic foam measurements. It is now apparent that with these two broad distinctions all the methods of foam measurement can be classified and methods within each group correlated, apparent inconsistencies between the two classes can be explained, and, it is believed, a sounder basis established for the development of further methods.

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Correspondence—Evaluation of Nitrocellulose Lacquer Solvents

Sir: A statement in our article [Ind. Eng. Chem., 32, 78 (1940)] regarding the mixed aromatic-aliphatic naphtha used indicates that it is "a commercial material with a distillation range of 95–132° C., containing approximately 30 per cent aromatics". Recently we have been informed that considerable improvement in the product has been made during the last few years. The sample in question, used throughout our work, was procured a little over four years ago. Its aromatic content was based upon the dimethyl sulfate solubility of the material, a method generally accepted at that time.

V. W. Ware and
W. M. Bruner

Properties of Coal Surfaces

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Among the properties of coal surfaces that are of scientific and practical importance the wetting characteristics are particularly significant in the selective flotation of coal components and the separation of coal particles from liquids as well as in a study of the fundamental properties of coal.

One of the most important phases of this problem involves the question of the degree of wetting; that is, the extent to which a given liquid will spontaneously wet a solid surface. The extent to which such action takes place may be quantitatively expressed in terms of the angle of contact. This subject and its related topics have received a greater part of the attention in the work here reported.

VARIOUS methods of measuring contact angles have been reviewed, and their applicability to a study of the wetting characteristics of coal surfaces has been investigated. The work includes experimental measurements of contact and interfacial angles in the two systems coal-liquid-gas and coal–organic liquid–water.

Six coals were used: one anthracite of the hard burning type; three medium volatile Pennsylvania bituminous coals (one from Lower Freeport seam in Jefferson County and two from Upper Freeport seam in Indiana County, the two latter coals being referred to in the text as Pennsylvania bituminous coal No. 1 and No. 2); one Illinois No. 6 vein bituminous coal from Franklin County; and one sample of lignite from Mercer County, N. Dak.

The liquid components of the coal-liquid-gas systems studied include distilled water and aqueous solutions of potassium permanganate, stannous chloride, and hypophosphorous acid. The gaseous phase in each case consists of one of the following: carbon dioxide, propane, oxygen, nitrogen, or air.

Investigations on the coal–organic liquid–water system have been limited to the two organic liquids carbon tetrachloride and benzene.

Methods of Measuring Contact Angles

From the numerous methods which have been described for the experimental determination of contact angles, the following have been selected for use in the study of coal surfaces and supplementary work here reported: spheroidal segment, tilting plate, and protractor measurements.

SPHEROIDAL SEGMENT. The spheroidal segment method of determining contact angles is a special case of the sessile drop method. The advantages of calculating contact angles from the dimensions of small drops were recently cited by Mack (*13*), who demonstrated that as the size of sessile drops of the same liquid is decreased, the shape progressively approaches that of a spheroidal segment. At that stage where the shape of the drop does not deviate appreciably from that of a spheroidal segment, the contact angle can be calculated from the relative values of height and base of the drop. Obviously the factors which determine the amount of deviation from a spherical shape are gravity, which tends to distort the drop, and surface tension of the liquid, which tends to resist the distortion.

If the drop is so small that it will not be materially deformed by gravitational forces, Mack's results indicate that the advancing contact angle is developed and is not in any way disturbed by mechanical vibration, as in the case of a larger drop which may assume an angle intermediate between the advancing and receding angles.

Bartell and Zuidema (*4*) found the method to be satisfactory for use in investigating solids of low surface tension which exhibit finite contact angles with both water and organic liquids. It also proved to be applicable to a study of the wetting characteristics of galena (*2*).

Even in the case of two fluids of relatively low interfacial tension values, the spheroidal segment method may be applicable to a study of interfacial angles developed at a solid surface by the two fluids, if they are immiscible and of approximately the same density (*21*).

TILTING PLATE. Various modifications of the tilting plate method have been used and adequately described by different investigators during the course of the past thirty years (*1*, *5*, *9*, *10*, *11*, *14*, *19*, *28*). Application to the study of coal surfaces was found to have inherent disadvantages. Serious difficulties were encountered in obtaining test specimens of the necessary shape and dimensions. It was, however, used on paraffin surfaces in some supplementary work which arose during the course of the present investigation.

PROTRACTOR MEASUREMENTS. In many instances it is possible to estimate the contact angle with sufficient accuracy from measurements of the angle formed between the tangent to the curve of the gas-liquid interface and the properly chosen reference plane at the point of three-phase contact. Various modifications of the method are closely interrelated in that they all involve measurements made on an enlarged image of a profile of a drop or bubble (*8*, *12*, *15*, *16*, *17*, *20*, *22–27*). The difficulty in estimating the position of the tangent by visual inspection constitutes the principal source of error, particularly when the angle is very large or very small—i. e., in the vicinity of 180° or 0°.

The so-called captive bubble machine introduced by Taggart, Taylor, and Ince (*20*) has been used extensively by a number of investigators in connection with flotation studies (*18*, *22–27*). The bubble machine consists essentially of an assembly of apparatus arranged to facilitate the accomplishment of triple-phase contact in the system solid-liquid-gas by adjusting the position of a gas bubble, until it comes in contact with a solid surface which is submerged in a liquid. The contact angles may be measured by means of a protractor on an enlarged image of the bubble.

Contact Angles in Coal-Air-Water System by Spheroidal Segment Method

Apparatus. Figure 1 illustrates the general arrangement of the various units which composed the apparatus used for manipulating and observing dimensions of small gas bubbles on a solid surface immersed in a liquid. The liquid under investigation was contained in a cube-shaped optical cell, *G*, with internal dimensions of 3 × 3 × 3 cm. The cell is described by the distributors as being made of clear glass plates, ground, polished, and cemented with a special acidproof cement. The optical cell was supported by a specially constructed stage designed to permit vertical movement of the cell by means of a rack, *H*, operated by a screw attached to the milled head, *J*. Movement of cell in a horizontal direction was accomplished by the adjustable clamp, *K*.

In those cases involving the use of air bubbles or liquid droplets of lower specific gravity than the liquid contained in the cell, it was necessary to have the underside of the immersed solid free so that the bubbles or drops could be released under the solid surface with which the bubbles or drops would make contact on rising. For this reason it was necessary to suspend the solid specimen in the cell liquid by means of clamp *F*, which was attached through a special adapter to a standard microscope mechanical stage equipped with adjusting screw *E* for movement of the specimen in a horizontal direction and adjusting screw *D* for raising or lowering the specimen.

In most cases specimen clamp *F* was replaced by a support which rested on the bottom of the cell. The support was made of platinum wire bent into the form of a frame which supported the specimen in such a way as not to interfere with transmission of the light by means of which the bubbles were observed through a microscope.

The specimen clamp proved to be more satisfactory than the other support from the standpoint of ease and precision in manipulating the specimen. However, the latter type was more desirable on the basis of its freedom from all possibility of contaminating the cell solution.

The small bubbles were produced by a micropipet constructed from Pyrex capillary tubing of 1-mm. bore. The tubing was drawn into a thread with an outside diameter of approximately 0.1 mm. The bore of the resulting thread was about 0.02 mm. The small tapered end of the capillary tubing was then bent through an angle of 90° if the pipet was to be used for placing bubbles on the under surface of an immersed solid. Small bubbles or drops of the fluid in the pipet were extruded from the small tapered end by applying pressure, by means of a screw clamp, to a piece of rubber tubing; one end of the tubing was attached to the large end of the glass capillary while the other end was closed.

To facilitate manipulation of the micropipet, it was clamped in a mechanical stage which was provided with screw adjustments for movement in horizontal and vertical directions. The dimensions of bubbles were estimated by a graduated ocular in a microscope at a magnification of 62 diameters. The light source was so arranged as to produce a reflection of the image of the bubble from the polished solid surface. The exact position of the gas-solid interface was indicated by a line common to both the image and its reflection.

It is obvious that the three-phase system, solid-liquid-gas, could be realized in the case of a bubble of gas on a solid surface surrounded by water as well as in the case of a liquid drop resting on a solid surface surrounded by gas.

In the present application of the spheroidal segment method of measuring contact angles, the use of bubbles proved to be preferable to the use of small drops in a number of ways. Because of the abnormally high vapor pressure of a small drop as compared with that of a plane liquid surface, it was virtually impossible to maintain an atmosphere which was saturated with respect to the small drops. Consequently the drops evaporated rapidly. Moreover, it was observed that the height of the drop decreased more rapidly than the base during evaporation. Mack's original method (*13*) of noting the volume of the drop from a buret so that it was necessary to observe only its base in order to calculate the contact angle, would not permit a study of the shape of the drop over a period of time. This seemed to be desirable in the case of coal surfaces.

In the case of a small air bubble in distilled water saturated with air, the volume of the bubble can be increased or decreased by proper regulation of the temperature.

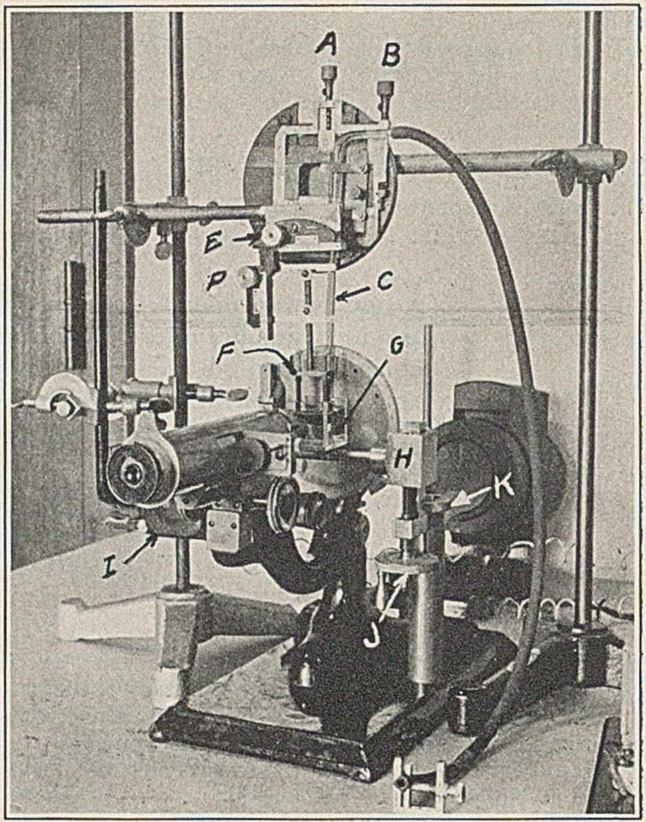

Figure 1. Apparatus for Manipulating and Observing Dimension of Small Gas Bubbles on Coal Surfaces under Water

A.	Screw head for vertical movement of bubble pipet
B.	Screw head for horizontal movement of bubble pipet
C.	Bubble pipet
D.	Screw head for vertical movement of solid specimen
E.	Screw head for horizontal movement of solid specimen
F.	Specimen clamp
G.	Optical cell
H.	Screw rack for raising or lowering optical cell
I.	Magnetic coil for vibrating cell stage
J.	Milled head attached to screw which operates *H*
K.	Clamp for permitting horizontal movement of cell stage

From a review of the factors which influence the value of the contact angle, it must be concluded that exposure of a solid surface to air often has a variable and unpredictable effect on its contact angle with water. From this fact alone it is possible to foresee some of the difficulties which may arise from the procedure of placing liquid drops on solid surfaces in air to determine contact angles.

Another disadvantage in the use of small liquid drops arose from accidental contamination of the liquid-air interface which is extremely difficult to avoid for extended periods of time. In the specific case of coal surfaces considerable improvement resulted from the use of small bubbles of gas rather than drops of liquid. Gas bubbles were used exclusively in all the work here reported where the system coal-liquid-gas was concerned.

Selection of Specimen. The work on bituminous coal was confined largely to the jet black bands of bright coal. This selection was based on the assumption that from the standpoint of both petrographic and chemical analysis the anthraxylon portion of a banded coal is more nearly homogeneous than the main bulk of the coal as a whole. Each test specimen of bituminous coal was in the form of a parallelopiped with approximate dimensions of 2 × 2 × 2 cm. One requirement was that the specimen contain at least one continuous, well-defined, jet black band of bright coal. The parallelopipeds were cut with a silicon carbide wheel from lump coal.

Preparation of Polished Surface. In preparing the polished coal surfaces, an effort was made to duplicate as nearly as possible the method used by Wark and Cox (*6*, *25*) in preparation of polished mineral surfaces to be used in flotation research. The surface to be tested was ground and polished under water in three stages by the use of the abrasive powders Crystolon (silicon carbide) 2F, Crystolon 600, and levigated alumina, in the order named. The first two stages were accomplished on ground-glass plates which were cleaned with chromic acid before use on each specimen. The surface was finally polished with levigated alumina on a glass plate covered with linen which had been subjected to a treatment designed to remove, as far as possible, any foreign material which may have been present. A different linen covering was used for each specimen.

All of the abrasive powders used were previously ignited for at least 8 hours at 850° C. to preclude the possibility of their introducing grease or oil contamination.

The surface to be tested was not allowed to become dry through exposure to the air during the grinding and polishing process or during the interval between polishing and testing.

It is not maintained that unaltered coal surfaces can be prepared by the procedure described above. It is merely the result of an attempt to prepare coal surfaces under reasonably uniform conditions.

Deposition and Measurement of Small Bubbles. The end of the micropipet was lowered into the test solution and adjusted to bring the small tip into focus in the lower half of the microscope field. The specimen was then manipulated into a position such that the band of bright coal was directly above the pipet tip. Thus the small bubbles on being extruded from the tip, by application of pressure on a rubber tube connected to the large end of the pipet, would rise through the liquid and contact the coal surface at the desired position. By horizontal movement of the specimen in a direction either to the right or left of the field of view, it was possible to deposit a row of bubbles throughout the entire length of the particular band of coal under investigation. Utmost cleanliness of the pipet was essential in order that the liquid in the cell should wet the glass tip in such a way as to clip the small bubbles off as they were formed. The slightest amount of contamination on the pipet invariably resulted in losing all control over the size of the bubble produced. The procedure and apparatus here described permit the use of bubbles of any desired size larger than 10^{-7} cc. in volume.

Table I. Contact Angle of Small Air Bubbles on Bituminous Coal Surface Immersed in Water

Observation No.	Specimen No.	Conditions of Test	No. of Bubbles	Av. Height of Bubbles, Mm.	Contact Angle θ, Degrees Max.	Min.	Av.
1	1	Freshly exposed black band in surface produced by fracture in air	5	0.284	62	49	54
2	1	Duplication of obsvn. 1; cell water renewed	4	0.335	50	45	49
3	1	Repetition of obsvn. 2 after 3.5 hr.	4	0.348	55	50	52
4	2	Black band in polished surface	10	0.336	30	23	27
5	2	Repetition of readings in obsvn. 4 after 20 min.	10	0.403	31	22	27
6	3	Black band in polished surface	10	0.333	39	18	29
7	3	Readings repeated after 20 min.	10	0.370	37	22	29
8	3	Portion of dull surface	16	0.332	33	21	26
9	3	Readings repeated after 1 hr.	16	0.341	35	20	26
10	3	Readings again repeated immediately	16	0.339	35	20	26
11	3	Readings again repeated after 2 hr.	16	0.297	42	21	30
12	4	Black band in polished surface	11	0.399	34	17	21
13	5	Black band in polished surface	10	0.200	22	17	20

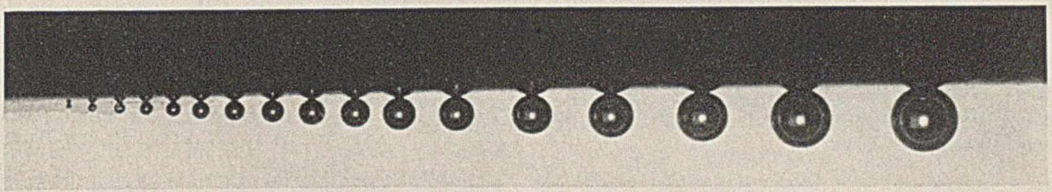

Figure 2. Various Sized Air Bubbles on Coal Surface under Water (× 11)

Figure 2 illustrates the general appearance of various sized air bubbles in distilled water on a bright band in a polished surface of bituminous coal. This photomicrograph portrays bubbles ranging in actual size from 0.06 to 0.8 mm. in diameter.

For routine measurements the bubbles were of approximately the same size and, in general, were less than 0.5 mm. in diameter. An exception to the general rule (reported in Table II) has been included for comparison with the results obtained by the adopted procedure.

Experimental Results. In application of the spheroidal segment method the contact angles may be calculated from the dimensions of height and base of the bubble (*13*) by the formula:

$$\tan \frac{\phi}{2} = \frac{2h}{b}$$

where height h and base b may be expressed in any convenient linear units, and ϕ is the contact angle measured through the fluid of which the bubble or drop is composed. Thus in the case of an air bubble in water,

$$\phi = 180° - \theta$$

where θ is the contact angle conventionally measured through the liquid.

The results from the observations of contact angles by the spheroidal segment method are recorded in Table I. The coal used throughout these tests was taken from the Lower Freeport seam, Jefferson County, Penna. All measurements were made in distilled water. The bubbles were formed from air.

The last two observations from Table I are reported in detail in Table II to demonstrate the distribution of the various values of the contact angle about the average values recorded in the condensed Table I.

The bubble dimensions in Tables I and II were calculated to millimeters from measurements made in terms of ocular scale divisions at a magnification such that 54.3 scale divisions were equivalent to 1 mm. The readings were taken to an estimated one tenth of a scale division. Hence the dimensions reported in Tables I and II represent measurements estimated to approximately ±0.002 mm.

Considerable variation in the value of the angle of different bubbles on the same coal surface was observed in most of the specimens investigated. For bubbles smaller than 0.5 mm. in diameter the value of the angle was not influenced by variations in bubble size.

From Table I it is obvious that the affinity of a coal surface for water in preference to air depends to an appreciable extent on which one is first present after the surface is produced. It is not implied that grinding and polishing a surface under water prevent the access of air which may be dissolved in the water.

The actual reason for the difference in wetting characteristics of the surfaces produced by the two methods is unknown. However, it is possible that the adsorption of air may have a marked effect on the free surface energy of a coal surface.

TABLE II. DETAILED DATA FROM OBSERVATIONS 12 AND 13 (TABLE I)

Bubble No.	Height, Mm.	Base, Mm.	$2h/b$	$\phi/2$	θ, Degrees
		Observation 12			
1	0.147	0.052	5.66	80.0	20
2	0.199	0.074	5.38	79.5	21
3	0.239	0.077	6.21	80.9	18
4	0.258	0.079	6.53	81.3	17
5	0.315	0.092	6.85	81.7	17
6	0.354	0.111	6.38	81.1	18
7	0.405	0.131	6.18	80.8	18
8	0.457	0.147	6.22	80.9	18
9	0.499	0.146	6.84	81.7	17
10	0.722	0.396	3.65	74.7	31
11	0.794	0.482	3.29	73.1	34
		Observation 13			
1	0.201	0.077	5.22	79.2	22
2	0.201	0.066	6.09	80.7	19
3	0.190	0.063	6.03	80.6	19
4	0.188	0.068	5.53	79.8	20
5	0.184	0.066	5.58	79.9	20
6	0.184	0.066	5.58	79.9	20
7	0.182	0.068	5.35	79.4	21
8	0.184	0.070	5.26	79.3	21
9	0.181	0.055	6.58	81.4	17
10	0.304	0.111	5.48	79.7	21

Observations 9 and 10 in Table I may be cited as examples of the degree of precision which may be expected of measurements made by the method here described.

An attempt was made to test specimens of an anthracite and a lignite by the spheroidal segment method. In both cases, however, no angles were measured since the bubbles did not seem to make sufficient contact to attach themselves to the surface, but drifted at random over it until striking an irregularity or escaping at the edge.

Contact Angles in Paraffin-Water-Air System

The work reported in this section was conducted primarily to provide additional information concerning the nature of the contact angle which is developed by a small bubble of air on a solid surface. The method consists, in general, of a comparison of the angle assumed by a small bubble with the values observed on the same solid surface by the tilting plate method which permits direct observation of both the advancing and receding angles.

Paraffin was selected as the solid because its physical characteristics permit its use in many of the methods for the study of wetting characteristics. Moreover, paraffin is known to have finite advancing and receding contact angles with water in air, and the angles have been found to remain constant on exposure of the paraffin surface to air (*28*).

SPHEROIDAL SEGMENT METHOD. The apparatus and procedure used for the deposition of small bubbles on paraffin were those described in the foregoing section.

TABLE III. ANGLE OF CONTACT BETWEEN PARAFFIN, WATER, AND AIR BY SPHEROIDAL SEGMENT METHOD

Plate No.	No. of Bubbles	Contact Angle θ, Degrees		
		Max.	Min.	Av.
1	7	104	99	101
2	6	104	99	102
3	4	104	100	102
4	11	105	99	102
5	12	107	102	104
6	10	105	98	103
7	12	110	104	107
8	7	107	98	102
9	10	110	100	105
10	8	108	100	105
11	10	111	103	108
12	10	109	100	104
13	11	101	99	99
14	9	107	100	104
			Weighted average	103.6

TILTING PLATE METHOD. The apparatus embodied the essential features of the equipment and procedure described by Wenzel (*28*).

The average value found by the spheroidal segment method for the contact angle of 127 small air bubbles on fourteen different paraffin surfaces in water was 103.6°. The maximum, minimum, and average values from tests on the individual plates are given in Table III.

By the tilting plate method average values of 116.8° for the advancing angle and 103.5° for the receding angle were found in fifty-two tests on thirty paraffin plates. Results from the individual tests are recorded in Table IV; in those instances where more than one test is reported on one single plate, the tests were made on different sections of the same plate.

From the results recorded in Table IV, it appears that paraffin surfaces prepared in an apparently uniform way from the same material may vary perceptibly in surface properties. Moreover, the properties of a single plate may not be entirely uniform at all sections. Deductions from the results are in agreement with Bartell's conclusion (*3*) that the advancing contact angle is a sensitive criterion of the condition of a solid surface.

The satisfactory agreement between the average value of the receding angles as determined by the tilting plate method and the average value obtained by the spheroidal segment method demonstrates that the contact angle developed by a

TABLE IV. ANGLE OF CONTACT BETWEEN PARAFFIN, WATER. AND AIR BY THE TILTING PLATE METHOD

Plate No.	θ, Degrees		Plate No.	θ, Degrees	
	Advancing	Receding		Advancing	Receding
20	114	102	30	118	108
20	117	105	31	115	101
20	116	106	32	121	104
20	111	99	33	121	105
20	112	101	34	116	102
20	111	103	35	122	105
20	115	102	36	121	101
20	114	103	37	117	101
20	115	102	38	114	105
21	116	105	39	123	104
21	114	103	40	124	105
21	116	103	41	121	106
21	115	105	42	117	105
21	115	104	43	119	106
21	113	102	44	121	108
21	112	104	45	116	101
21	115	105	46	116	102
21	114	104	46	115	102
22	118	101	46	116	103
23	115	108	47	117	103
24	113	103	48	118	103
25	122	105	48	121	103
25	123	105	49	116	103
26	114	101	49	117	102
27	115	105	49	119	102
28	117	103	Average	116.8	103.5
29	120	105			

small air bubble on a paraffin surface under water is the receding one. In the absence of contradictory evidence it seems reasonable to accept this as an indication that small air bubbles on other solid surfaces will also develop the receding contact angle.

Contact Angles in Coal-Liquid-Gas System by Captive Bubble Machine Method

The construction of the bubble machine was based on the original description by Taggart, Taylor, and Ince (*20*). Full advantage was also taken of the detailed descriptions later published by Del Giudice (*7*) and Wark and Cox (*6, 25*). The information obtained from the study of coal surfaces by the use of the bubble machine was largely of a qualitative nature.

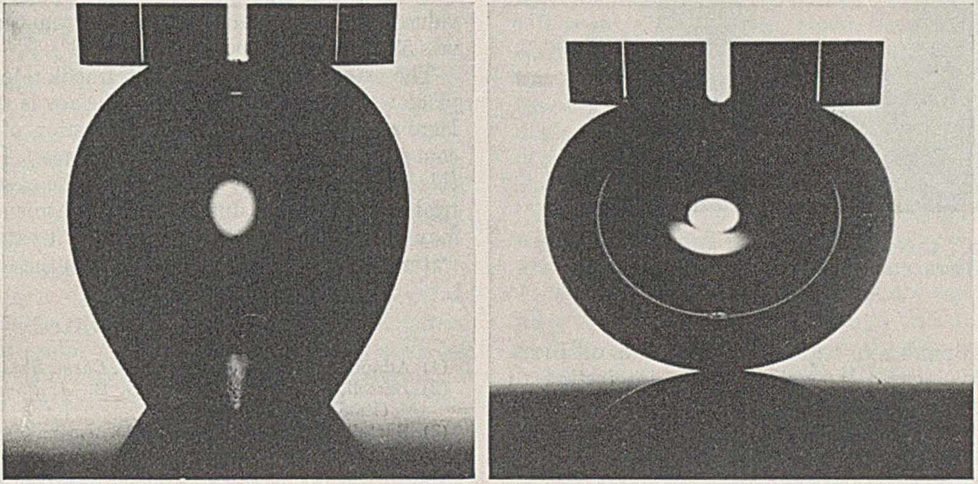

Figure 3 (*Left*). Nitrogen Bubble on Surface of Bituminous Coal in Water
Figure 4 (*Right*). Nitrogen Bubble in Water, Receding from Specimen Shown in Figure 3 after Treating with 3 Per Cent Hypophosphorous Acid

Dependence of Observed Angle on Method of Approach. With gas bubbles on polished coal surfaces under distilled water, all experimental attempts to arrive at concordant values of the angle from the advancing side and from the receding side of the equilibrium angle were unsuccessful. Consequently it may be assumed that at present there is not sufficient justification for considering the observed angle as measured by the adopted procedure to be the true equilibrium one. For this reason the terms applied to the contact angle measured at coal surfaces by the bubble machine will refer merely to the observed characteristic angle.

It was necessary that the observed angle be approached with extreme caution, for if it were reduced to a value smaller than that required for theoretical equilibrium conditions, then the difficulties of trying to approach it from the receding side would be encountered.

It follows that the value of the observed angle may actually be affected by the manner and magnitude of the vibration used to induce the attainment of conditions necessary for development of the characteristic angle. This was adequately demonstrated by experience. However, by resorting to the use of mild uniform vibration induced by a magnetic coil, uniform and apparently characteristic values of the contact angle were obtained, as shown in the following example: In twelve measurements on two different bright bands in a specimen of Pennsylvania bituminous coal No. 1 in water, nitrogen developed an average angle of 60°. The values varied between 58° and 62°. On a second specimen of the same kind of coal under similar conditions, an average value of 61° was derived from six measurements varying between 60° and 63°.

The time of contact required to give a constant value for the angle varied with different coals and also with different gases on the same coal. For example, after being in contact for 5 minutes, a bubble of nitrogen showed no tendency to displace water from a polished surface of anthracite. On being slowly released, the bubble receded from the surface without distortion or the slightest tendency to adhere. However, when the time of contact was increased to 30 minutes, the observed contact angle was measured as 34° (average of four measurements varying between 30° and 36°). When the time of contact was further lengthened to 1.5 hours, an average value of 48° (varying between 45° and 50°) was obtained. Additional time increases did not result in higher values of the angle.

In the case of bituminous coals immersed in water, some adhesion between a nitrogen bubble and coal was always observed at the instant of contact, and a constant value of the characteristic angle was reached in a shorter time than that required by the anthracite. Thus on a bright band in Pennsylvania bituminous coal No. 2 in water, a nitrogen bubble developed an angle of 59° (average of four measurements varying between 57° and 60°) after a contact period of 15 minutes. Before detachment, the bubble was again pressed down in the same position where it was kept in contact for 2 hours. The resulting angle was again 59° (average of four measurements varying between 58° and 60°).

Influence of Nature of Gas on Contact Angle. No appreciable difference in the value of the contact angle was observed with bubbles of carbon dioxide, propane, oxygen, air, and nitrogen on the same coal surface. However, there was a perceptible difference in the length of contact time required to develop the maximum angle. The various gases are listed above in the order of increasing time of contact necessary to obtain reproducible values.

Comparison of Contact Angles on Coals of Various Ranks. Although the group of coals investigated does not comprise a comprehensive list of representatives from each rank, the following results are submitted as an introduction to the subject:

The average value found for nitrogen at the polished surfaces of an anthracite under distilled water was 48°.

Numerous tests on various specimens of Pennsylvania bituminous coals 1 and 2 under similar conditions yielded an average value of 60°. At the surface of an Illinois bituminous coal the average value of the contact angle between nitrogen and distilled water was found to be 57°.

After a contact period of 30 minutes neither nitrogen nor air showed any tendency to adhere to the polished surface of undried North Dakota lignite in water.

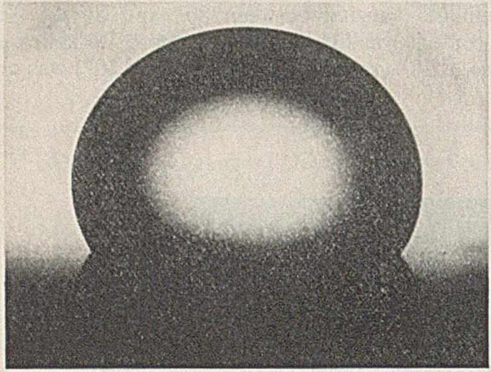

Figure 5. Contact between a Drop of Carbon Tetrachloride and Anthracite in Water

Effect of Oxidizing and Reducing Solutions on Bituminous Coal Surfaces. It is particularly interesting to compare the effects of the action of oxidizing and reducing solutions on the wetting characteristics of a bituminous coal surface. The contact angle between water and nitrogen or air at bituminous coal surfaces was reduced to zero by pretreatment of the specimen with 0.2 per cent solution of potassium permanganate. Similar results were also obtained by pretreatment of the specimen with a 3 per cent solution of stannous chloride or a 3 per cent solution of hypophosphorous acid.

The effect of a reducing agent on the wettability of a bituminous coal surface is illustrated graphically in Figures 3 and 4. Figure 3 shows a nitrogen bubble on a bright band of Pennsylvania bituminous coal in distilled water. The photograph was taken during the course of a routine measurement made by the adopted procedure.

Figure 4 shows a nitrogen bubble receding from the same coal specimen portrayed in Figure 3 after the specimen had been conditioned one hour in a 3 per cent solution of hypophosphorous acid. Before the photograph of Figure 4 was taken, the bubble had been pressed down on the treated coal surface and retained in that position for 30 minutes before being slowly withdrawn. As seen from Figure 4, the nitrogen bubble did not show the slightest tendency to adhere to the treated coal surface but receded with a zero angle when the bubble was permitted to withdraw slowly from the coal surface.

Interfacial Angles in Coal–Organic Liquid–Water System

By methods previously described, various sized drops of carbon tetrachloride were applied to polished surfaces of anthracite immersed in water. For relatively large drops (5-mm. diameter) of carbon tetrachloride where the form is perceptibly influenced by gravity, the angle as measured with a protractor averaged 59° (measured through the water), varying between 53° and 63°. It did not seem to be important whether the drop was attached to the bubble holder or entirely supported by the coal surface. The important requirement was that the area of the carbon tetrachloride–coal interface be not forcibly increased beyond the extent required for development of the characteristic angle. When the drop was placed in contact with the coal surface at a small angle (measured through the water) and then carefully vibrated, it spread rapidly to give the characteristic value of the angle, but if it were forcibly spread further over the coal surface, it could not be induced to return spontaneously to the original position. A drop of carbon tetrachloride supported by a surface of anthracite in water is shown in Figure 5.

Drops of benzene under the above conditions developed an average angle of 46°, varying between 44° and 47°.

A specimen of the same anthracite was tested with smaller drops (average height 0.44 mm.) of carbon tetrachloride. In this case vibration of the specimen did not affect the value of the angle. Assuming a spheroidal segment form, the average value of the contact angle calculated from the drop dimensions was 53° (varying between 50° and 58°).

The extent to which carbon tetrachloride and benzene displace water from an anthracite surface is surprisingly small. Here again it appears to be a question of which fluid first comes in contact with the coal surface. It is possible that this phenomenon may be related to the observation in industrial practice that a dust-proofing treatment with mineral oil may be less effective on coal which is treated when wet with water than on the same coal treated in the air-dried condition.

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Extraction of Natural and Artificial Coals with Solvents

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QUALITY and quantity of the bitumen, the material which can be extracted more or less from natural and artificial coals with solvents, determine the technical value of these fuels. Bitumen which distills off at higher temperatures without being strongly decomposed is the cause of sandy coke formation from certain bituminous coals. If decomposition of bitumen below its boiling point under formation of larger molecules takes place, then these compounds cement the residual coal particles (the nonsoluble organic part of coals) together, and hard coke is obtained.

In the following study different solvents were used for the extraction of different coals. This has been done to get some insight into the nature of those coals and of the resulting residual coals, and to obtain some data concerning the extraction capacity of different bitumen solvents.

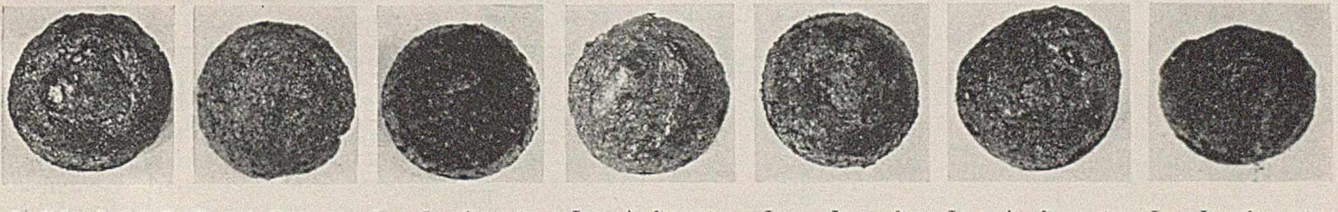
These coals were ground to 200 mesh and extracted as completely as possible with the following solvents: acetone, benzene, dioxane, acetophenone, acetophenone followed by extraction with benzophenone, tetrahydronaphthalene (above its boiling point under pressure), and benzophenone at different temperature and pressures. Twenty-five grams of each coal quality were extracted during 24 hours at room temperature or at the boiling temperature of the solvent. The extracts were separated from the residual coal by filtration over porous glass filters, the residual coals were washed with acetone, and this solution was combined with the solution containing the chief amount of bitumen. The solvents were evaporated in vacuum. Repeated boiling with water was carried out to remove these amounts of solvent which, through the formation of molecular compounds (for instance between phenols and ketones) at their boiling temperature cannot be eliminated from the residual coal. In this way the solvent can be removed completely. The bitumen was dried at room temperature over phosphorus pentoxide in vacuum. When benzophenone was used as a solvent, the adhering benzophenone was eliminated from the bitumen by extraction with benzene.

The extractions with acetone, benzene, and dioxane were carried out in a Soxhlet extractor. The extraction temperature, therefore, was somewhat below the boiling temperature of the solvents. The amount of extracted bitumen was determined by the weight of the extract and by the amount of residual coal. Those figures checked within a difference of about 5 per cent.

The bitumens of artificial coals extracted below 100° C. were solid. At higher temperatures very viscous oils resulted. A small amount of cracking may have taken place.

Different solvents extract different components from natural coal. Extraction of Pittsburgh coal with benzophenone at 310° C. produces 12.6 per cent bitumen. The remaining residual coal gives sandy coke. The same coal extracted with tetrahydronaphthalene under pressure at 300° C. yields 18.8 per cent bitumen. In spite of the higher amount of extracted bitumen, the residual coal gives a hard coke. Polar solvents with partial valences on their oxygen atoms (dioxane, acetone, acetophenone) have a selective affinity toward the phenolic components of bitumen. Those phenolic substances are responsible for the caking properties of coal. Less polar substances, such as tetrahydronaphthalene, extract more of the neutral substances of bitumen which have little to do with the caking properties of this bitumen.

Acetophenone (proposed in this laboratory by Regis Raab) is the best extracting solvent at normal pressure. Its use



I. Coke of original coal A

I_{A_1}. A after extn. of 0.3% bitumen with acetone at 20° C.

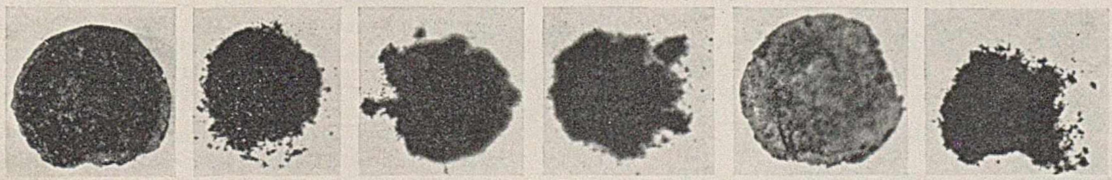
I_{A_2}. I_{A_1} after extn. of 0.7% bitumen with acetone at 56° C.

I_{B_1}. A after extn. of 0.01% bitumen with benzene at 20° C.

I_{B_2}. I_{B_1} after extn. of 0.21% bitumen with benzene at 80° C.

I_{C_1}. A after extn. of 0.6% bitumen with dioxane at 20° C.

I_{C_2}. I_{C_1} after extn. of 1.0% bitumen with dioxane at 100° C.



I_{D_1}. A after extn. of 4.0% bitumen with acetophenone at 20° C.

I_{D_2}. I_{D_1} after extn. of 22.6% bitumen with acetophenone at 100° C.

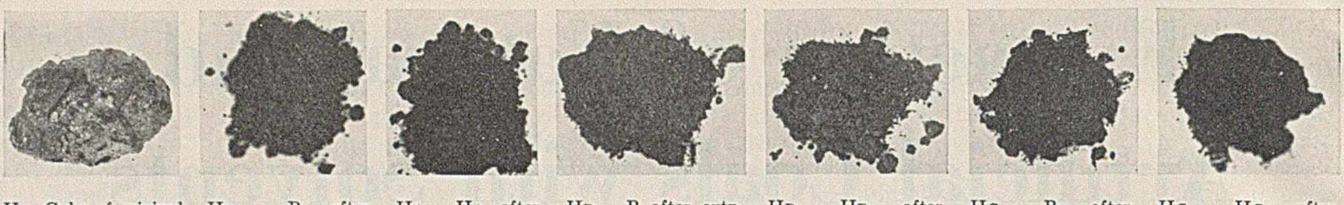
I_{D_3}. I_{D_2} after extn. of 32.8% bitumen with acetophenone at 205° C.

I_{D_4}. I_{D_3} after extn. of 0.0% bitumen with benzophenone at 310° C.

I_E. A after extn. of 18.8% bitumen with tetrahydronaphthalene at 300° C. under pressure.

I_F. A after extn. of 12.6% bitumen with benzophenone at 310° C.

FIGURE 1. COKES FROM PITTSBURGH BITUMINOUS COAL A



II. Coke of original coal B

IIA$_1$. B after extn. of 35.2% bitumen with acetone at 20° C.

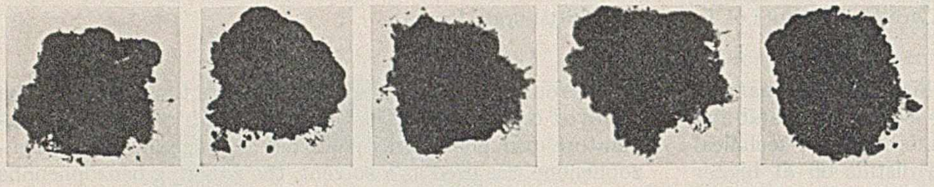
IIA$_2$. IIA$_1$ after extn. of 39.6% bitumen with acetone at 56° C.

IIB$_1$. B after extn. of 21.5% bitumen with benzene at 20° C.

IIB$_2$. IIB$_1$ after extn. of 36.3% bitumen with benzene at 80° C.

IIC$_1$. B after extn. of 16.5% bitumen with dioxane at 20° C.

IIC$_2$. IIC$_1$ after extn. of 19.2% bitumen with dioxane at 100° C.



IID$_1$. B after extn. of 22.0% bitumen with acetophenone at 20° C.

IID$_2$. IID$_1$ after extn. of 31.6% bitumen with acetophenone at 100° C.

IID$_3$. IID$_2$ after extn. of 57.6% bitumen with acetophenone at 205° C.

IID$_4$. IID$_3$ after extn. of 58.4% bitumen with benzophenone at 310° C.

IIE. IID$_4$ after extn. of 59.6% bitumen with benzophenone at 310° C.

Figure 2. Cokes from Alkali-Cellulose Coal B

Table I. Carbon and Hydrogen Contents of Coals

Coal No.	Coal Description	C	H	O(N, S)
I	Pittsburgh bituminous coal, composition on ash and water-free basis	80.02	5.75	14.23
II	Artificial cellulose coal produced in presence of alkali	82.5	5.43	12.07
III	Artificial cellulose coal produced in presence of pure water	82.8	5.1	12.1
IV	Lignin coal	81.0	5.38	13.62

has the advantage that there is no combination with a hydrogenation effect as is the case with tetrahydronaphthalene[1] at elevated temperature. Tetrahydronaphthalene, alone or with phenols, is now widely used in industry and in scientific research work as an extraction agent for bitumen. Acetophenone decomposes at its boiling point in the presence of coal, with the formation of a brownish liquid. It shows its superiority over the low-boiling solvents (acetone, benzene, dioxane), over the higher boiling solvents (tetrahydronaphthalene at 250–300° C.) under pressure, and over benzophenone. It removes mostly the phenolic components of the coals which are responsible for their caking qualities.

Table I lists the carbon and hydrogen content of the different coals which give the cokes shown in Figures 1 and 2.

Table II shows the results of this study. Artificial cellulose coal produced by heating cellulose with water at 320° C. and artificial lignin coal (lignin and water at 320° C.) give, before and after extraction, sandy coke always.

Conclusions

Polar substances such as ketones preferably remove substances of phenolic character from natural and artificial bituminous coals. These phenolic substances are the cementing substances which bind together the residual coal particles during the coking process. Less polar substances (such as tetrahydronaphthalene and benzene) remove preferably neutral substances which evaporate without strong decomposition during the coking process. Therefore, the coking properties of coals by this extraction are not changed.

Table II. Extraction of Coals

			Pittsburgh Bituminous Coal, I			Artificial Coals: OH–Cellulose Coal, II			Artificial Coals	
				Coke of Residual Coal			Coke of Residual Coal			
No.	Solvents	Temp., ° C.	% Weight of ext.	Appearance[a]	Yield, %	% Weight of ext.	Appearance[a]	Yield, %	H$_2$O–cellulose, III, % wt. of ext.	Lignin, IV, % wt. of ext.
A	Acetone 1	20	0.3	+	64.4	35.2	–	77.2	13.3	0.8
	2	56.5	0.4	+	64.5	4.4	–	78.6	2.1	0.6
			0.7			39.6			15.4	1.4
B	Benzene 1	20	0.01	+	64.2	21.5	–	72.0	11.9	0.04
	2	80	0.2	+	64.6	14.8	–	78.2	2.0	0.08
			0.21			36.3			13.9	0.12
C	Dioxane 1	20	0.6	+	64.6	16.5	–	70.2	5.3	0.0
	2	100	0.4	+	63.8	2.7	–	70.7	1.9	0.4
			1.0			19.2			7.2	0.4
D	Acetophenone 1	20	4.0	+	65.5	22.0	–	71.3	6.2	0.2
	2	100	18.6	–	71.9	9.6	–	79.6	2.5	1.1
	3	205	10.2	–	73.9	26.0	–	81.8	11.6	0.2
			32.8			57.6			20.3	1.5
D$_4$	D$_3$ extd. with benzophenone	310	0	–	74.0	0.8	–	82.5	0	0
E	Tetrahydronaphthalene twice under pressure	300	18.8	+	..	..	..	..	..	..
F	Original coal with benzophenone	310	12.6	–	73.7	59.6	–	83.3	20.6	1.5

[a] Hard dense coke, +; sandy coke, –.

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[1] First proposed by E. Berl, H. Schildwächter, and W. Schmidt, *Brennstoff-Chem.*, 7, 149, 181 (1926); 9, 105, 212 (1928).

Benzene is a poor extraction agent for natural bituminous coals compared with acetophenone and tetrahydronaphthalene.

Artificial carbohydrate coals give much more soluble bitumenlike materials after extraction with any of the used solvents compared with natural bituminous coals.

Artificial cellulose coals produced in weak alkaline medium show more soluble bitumen than artificial cellulose coal produced in neutral or weak acid medium.

Lignin coals give very little soluble bitumen. Its results probably from the small amounts of carbohydrates which are difficult to separate from the isolated lignin. This is one more important reason why natural bituminous coals could not have been formed extensively from lignin and its derivatives.

In another publication it will be shown that by a special treatment the amount of soluble bitumen of artificial carbohydrate coals, which for the coals described in this paper is much higher than that of natural coals, can be reduced to the amount which the latter coals show. This is due to a conversion of lower molecular phenols and phenol-carbonic acids into more complex and therefore less soluble higher phenols and phenol derivatives.

AEROGEL CATALYSTS

Dehydrations and Decarboxylations[1]

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A comparison is made of the activities of aerogels, xerogels, and precipitates as catalysts for the dehydration of alcohols, the esterification of acetic acid with ethanol and the dehydration and decarboxylation of aliphatic acids. The aerogels were often, but not always, the most active catalysts. The advantages of the aerogel form are found to be of smaller magnitude than was predicted from earlier work.

THIS communication is an extension of the general problem of evaluating aerogels as catalysts, which is being carried out in this laboratory. Kistler, Swann, and Appel (*11*) showed that thoria aerogel was a more active catalyst than the xerogel (ordinary dried gel) or precipitate for decarboxylating aliphatic acids and esters to ketones. In a study of the vapor-phase oxidation of acetaldehyde to acetic acid over silica and platinized silica, Foster and Keyes (*7*) showed that the best aerogels and xerogels have about the same activity. These gels appear to be the best vapor-phase contact catalysts known for this reaction, and the best aerogel seems to be a slightly better catalyst than the best xerogel, although the difference is so small that such factors as method of preparation or impurities could easily reverse the order of relative activity. Bliss and Dodge (*4*) found that alumina aerogel was less active than some precipitated forms of alumina for the dehydration of ethanol. Kearby, Kistler, and Swann (*9*) showed that a mixed aerogel of alumina and chromic oxide gave the best conversions of *n*-butanol and ammonia to butylamine. A xerogel of the same composition gave lower conversions to monobutylamine but a higher conversion to total amines and to nitrile, which is the dehydrogenation product of butylamine.

General Experimental Operation

The reactions selected for study were: dehydration of alcohols over alumina, thoria, and a mixed alumina-chromic oxide catalyst; esterification over silica; and dehydration and decarboxylation of acetic acid over thoria. All of these catalysts were prepared in the form of the xerogel and aerogel. The porosities of silica and thoria gels were varied, and precipitated silica and alumina were also prepared.

A suitable temperature was selected for each reaction, and the conversions were determined for varying times of contact. The results thus show the relative times of contact necessary to obtain the same conversions with the different catalysts. Data at various temperatures are desirable, but work in this laboratory has indicated that the order of relative activity does not change much with temperature. This is shown by a comparison of Figures 1 and 2; the experiments of Figure 1 were carried out at a higher temperature than those of Figure 2. The higher temperature resulted in an upward displacement of the curves of Figure 1, but the same general shape and relative order of activity was retained.

The apparatus used for the reactions was described previously (*9*). In all experiments 50 cc. of 8-20 mesh catalyst rested in a bed 7.5 cm. deep in the annular space between 28-mm. and a 43-mm. o. d., thin-walled Pyrex tube. In order to avoid errors in temperature measurement due to the heat of reaction, the reaction temperature was recorded as the temperature of the reactants as they entered the catalyst.

The temperature changes accompanying dehydration reactions have too often been disregarded. An example of the magnitude of this effect is an experiment in which 3 grams per minute of ethanol were passed through precipitated alumina (catalyst 3), the temperature of the entering reactants dropped from 385° to 336° C. after passing through 3.5 cm. of the catalyst. The usual method of measuring the reaction temperature with a thermocouple embedded in the catalyst could thus have given any temperature between 336° and 385° C., depending on its location. In the absence of any reaction as in passing nitrogen over the catalyst, the temperature was constant through the catalyst bed.

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[1] For previous papers in this series, see literature citations *9* and *11*.

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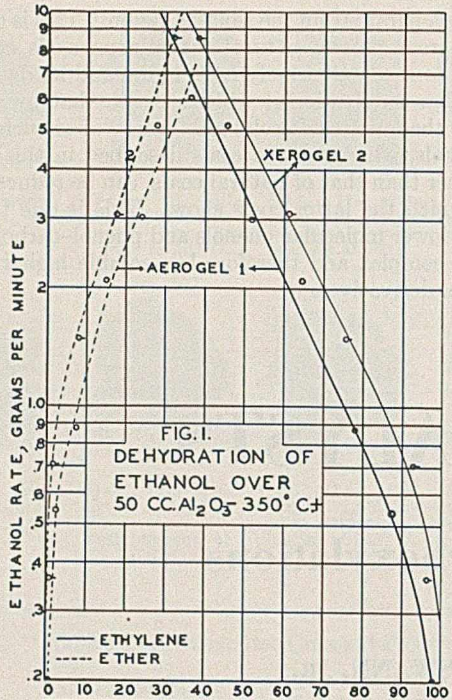

FIG. 1. DEHYDRATION OF ETHANOL OVER 50 CC. Al_2O_3-350° C.

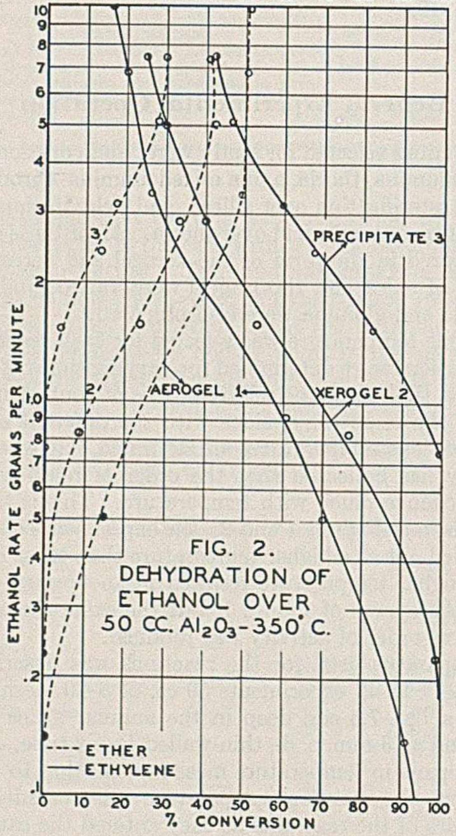

FIG. 2. DEHYDRATION OF ETHANOL OVER 50 CC. Al_2O_3-350° C.

This effect is appreciable even on less active catalysts. Thus, Figures 1 and 2 illustrate the differences in conversions obtained because of a change in the location of the thermocouple. The increased temperatures of Figure 1 resulted in the aerogel being 2.7 times more active, and the xerogel 2.3 times more active than at the lower temperature of Figure 2. Since it is unlikely that the temperatures of the aerogel and xerogel of Figure 2 were exactly the same, because of the difficulty of reproducing the exact position of the embedded thermocouple, one would not expect these relative activities to check more closely. It is recognized that the method of maintaining the temperature of the entering reactants constant does not result in the same temperature within the catalyst bed for different catalysts, but the differences are entirely dependent on the activity of the catalysts, and the heat absorbed by the reaction merely tends to reduce the differences observed in their activities. In the single-tube catalyst chambers, usually used in work of this type, greater core effects might easily permit even greater differences than the above.

In this work temperatures were measured by two calibrated chromel-alumel thermocouples. In order to show that a catalyst remained at constant activity during its use, the last run was made at a rate between those of two of the first runs. The fact that it fell on the same curve as the earlier runs was considered evidence of constant activity.

Catalyst Preparation

Catalyst 1, Alumina Aerogel. Into 2600 cc. of an aqueous solution containing 822 grams of aluminum chloride hexahydrate, cooled to 0° C., were stirred 790 cc. of liquid ethylene oxide. The solution set to a firm, transparent hydrogel in 10 hours. Two thirds of this hydrogel was extracted thoroughly in a Soxhlet extractor with ethanol (initially containing 2 per cent ammonium hydroxide). About 400 cc. of this alcogel were autoclaved (*10*) at 260° C. to give the aerogel [apparent density (Ap. D.), 0.127 gram per cc.].

Catalyst 2, Alumina Xerogel. The remaining alcogel was dried slowly at room temperature until it had shrunk to about half of its volume. Drying was continued at increasing temperatures to 375° C., giving the xerogel (Ap. D., 0.368 gram per cc.).

Catalyst 3, Precipitated Alumina. The other third of the hydrogel was stirred with a large volume of distilled water to form a colloidal sol. This was coagulated with ammonium hydroxide, filtered, washed, and dried. Since it was observed to contain carbon, it was covered with fuming nitric acid, dried, and ignited at 375° C.; a gritty, porous, white precipitate resulted (Ap. D., 0.765 gram per cc.).

Catalysts 4 and 5. The details of preparing these catalysts were given previously (*9*). They contain 90.6 per cent alumina and 9.36 per cent chromic oxide. Catalyst 4 is an aerogel (Ap. D., 0.185 gram per cc.). Catalyst 5 is a xerogel (Ap. D., 0.728 gram per cc.).

Catalyst 6, Silica Aerogel. A solution of 600 cc. of ethanol, 600 cc. of water, and 150 cc. of concentrated hydrochloric acid was cooled to 0° C. and poured with stirring into a cold solution of 1200 cc. of tetraethyl-*o*-silicate and 600 cc. of ethanol. This solution set to a firm gel when placed in an oven at 50° C. It was extracted with ethanol, and a portion was autoclaved to give the aerogel (Ap. D., 0.189 gram per cc.).

Catalyst 7, Partly Dried Silica Aerogel. The remainder of the silica alcogel was dried at room temperature until it had shrunk to about half of its volume. A portion was autoclaved with ethanol to give an aerogel (Ap. D., 0.320 gram per cc.).

Catalyst 8, Silica Xerogel. The remaining partly dried alcogel was dried to a xerogel (Ap. D., 0.966 gram per cc.).

Catalyst 9, Microcrystalline Silica. This so-called amorphous silica or tripoli, mined near Cairo, Ill., was moistened with water containing a small amount of ethyl silicate as a binder, compressed, and dried to a hard cake. This was broken into 8–20 mesh pieces (Ap. D., 1.00 gram per cc.).

Catalyst 10, Thoria Aerogel. The thoria hydrogel was prepared by method I of Kistler, Swann, and Appel (*11*) with two changes. The precipitated thoria was peptized with dilute hydrochloric acid, and the 30 per cent colloidal sol was coagulated to a gel by the addition of one tenth its volume of liquid ethylene oxide. The hydrogel was extracted with methyl alcohol, initially containing 2 per cent ammonium hydroxide, and a portion was autoclaved to give aerogel 10 (Ap. D., 1.33 grams per cc.).

Catalyst 11, Low-Density Thoria Aerogel. This catalyst was prepared by extracting the above alcogel with ether, followed by liquid propane and autoclaving with propane at 120° C. to form the aerogel (Ap. D., 0.589 gram per cc.).

Catalyst 12, Thoria Xerogel. This was prepared from the thoria alcogel by a method identical with that for catalyst 2, (Ap. D., 2.56 grams per cc.).

All of the catalysts were screened to 8–20 mesh and heated for 3 hours at 375° C. in a stream of oxygen before any density or catalytic measurements were made with them. A 50-cc. tared

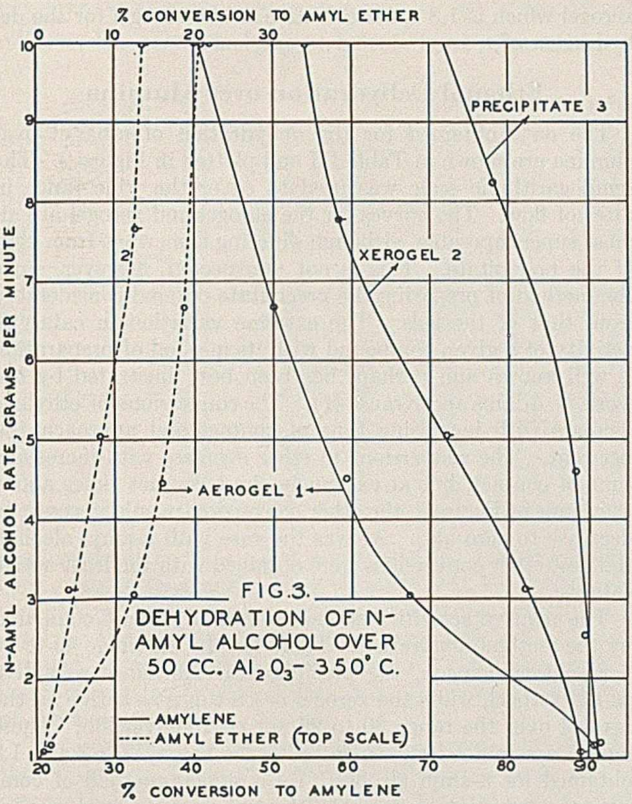

FIG. 3. DEHYDRATION OF N-AMYL ALCOHOL OVER 50 CC. Al_2O_3- 350° C.

volumetric flask was filled with each of the catalysts. The samples were packed to substantially constant volume by tapping the flask two hundred times and were then weighed. The apparent densities recorded in grams per cc. are one fiftieth of these weights.

Dehydration of *n*-Amyl Alcohol

About 100 grams of a well-fractionated *n*-amyl alcohol, boiling between 136° and 139° C., entered the catalyst chamber at 350° C. for each run. The weight of alcohol delivered, the time, and the lowest temperature in the catalyst were recorded for each run. The products were delivered into a one-liter Florence flask in a bath of crushed ice, and then passed through a trap at −80° C. to a gasometer. Only negligible amounts of gas were formed, the weight of product received in the two traps approximating the weight of alcohol delivered. The product was extracted at 0° C. with a saturated solution of potassium carbonate and dried over solid anhydrous potassium carbonate. Twenty cubic centimeters of butyl Carbitol were used to wash the carbonate and were added to the dried product which was then fractionated in a precision column. The fractions collected were weighed and recorded as follows: 20–40° C. amylene, 130–145° amyl alcohol, and 160–190° diamyl ether. A small correction factor obtained from determinations on known mixtures was added to the amylene conversions to correct for its loss by evaporation during the separation.

Dehydration of Ethanol

About 120 grams of 99.5 per cent ethanol entered the catalyst at 350° C. for each run. The products passed successively through a one-liter Florence flask at 0° C., two traps at −80° C., and a gasometer which had previously been calibrated against ethylene. The lowest temperature in the catalyst was recorded for those active enough to cause it to fall below 340° C. At the completion of the run the flask and the traps were warmed successively to 20° C. to expel dissolved gaseous products through the gasometer. The amount of gas with its temperature and pressure were recorded and a composite sample analyzed by means of a standard copper oxide apparatus (*5*). The ethylene was determined by absorption in aqueous bromine–potassium bromide solution with two final rapid absorptions in fuming sulfuric acid. Over the alumina catalysts about 99 per cent of the gas was ethylene, the remainder being about 4 parts methane to 1 part ethane. No hydrogen or carbon monoxide was present in these products.

The liquid products were washed into a distilling flask and distilled in a precision column. The fraction boiling below 40° C. was weighed, corrected for its water content, and recorded as ether. The remainder was distilled completely free of alcohol, and the recovered alcohol was determined from the weight and specific gravity of the distillate. The liquid products from most of these dehydrations had an odor of higher molecular weight olefins, but only traces of these were present. The fact that the ethylene conversions amounted to 98–99 per cent at the slowest rates over the alumina catalysts indicates that their probable error was only 1 to 2 per cent.

Esterification of Acetic Acid

The reaction of ethanol and acetic acid was studied over four silica catalysts at 450° C. Since some of the ethanol might be dehydrated or dehydrogenated under these conditions, a 10 per cent excess was used over that theoretically required by the acetic acid. A freshly prepared solution of the two reactants was metered to the catalysts. The use of a fresh solution ensured the absence of liquid-phase esterification since this was shown to amount to only 0.5 per cent in 4 hours. Preliminary determinations showed that the weight of products received was practically equal to those delivered and justified the calculation of rates of flow from the weight of product received.

The procedure followed was developed to complete the study in a minimum time to avoid changes in catalyst activity. Delivering the reactants at the highest rate, the product was by-passed for 3 minutes and then about a 10-gram sample was collected in a tared flask while measuring with a stop watch the time for its collection. The flow was then cut to the next lower rate and by-passed for 3 minutes, and an approximate 10-gram sample was collected as before. This procedure was continued until all of the runs were completed; four runs required about 70 minutes of which about 40 minutes were required by the lowest rate run. The increase in the weight of the tared flasks showed the amount of reactants delivered in the measured time. The products were diluted with 100 cc. of distilled water and titrated with 1 *N* sodium hydroxide, using phenolphthalein as an indicator to determine the unreacted acetic acid. The amount of acid esterified was taken by difference, a procedure previously reported satisfactory (*14*). Saponifications of the product of the lowest rate runs for each catalyst checked these conversions within one per cent.

Dehydration and Decarboxylation of Acetic Acid

The decomposition of acetic acid into acetone, carbon dioxide, and water was studied over three thoria catalysts at 275° C. About 100 grams of acetic acid were allowed to pass over the catalysts for each run. A slight rise in temperature (5° C.) of the reactants as they passed through the catalyst indicated an exothermic reaction. The products passed into a one-liter Florence flask at 0° C., thence through a trap at −80° C. and into a gasometer. At the completion of the run the flask and trap were successively brought to room temperature to expel dissolved carbon dioxide. The volume, temperature, pressure, and analysis of the gas were recorded. The amount of unreacted acetic acid in the condensed products was determined by titrating an aliquot with standard 1 *N* sodium hydroxide. The amount reacted was determined by difference. This procedure had previously been shown to agree with determinations of the acetone formed (*11*). In the present work the conversions were also calculated from the less precise measurements of the carbon dioxide formed, to check the titrations. The average deviation between the two methods was 1.4 per cent with a maximum deviation of 3.7 per cent, the differences being about equally distributed between positive and negative values.

n-Amyl Alcohol Dehydration over Alumina

The data obtained for the dehydration of *n*-amyl alcohol over the alumina catalysts (1, 2, and 3) are given in Table I plotted in Figure 3.

TABLE I. DEHYDRATION OF *n*-AMYL ALCOHOL OVER ALUMINA AT 350° C.

Run No.	Alumina Catalyst (50 Cc.)	Lowest Temp., ° C.	*n*-Amyl Alcohol, G./Min.	Space Velocity, Hr.$^{-1}$	% Conversion to: Amylene	% Conversion to: Amyl ether	% Alcohol Recovered
1	Aerogel 1	336	10.5	3200	38.5	20.0	37.6
2		324	10.4	3180	40.8	22.0	29.8
3		333	6.66	2030	49.9	18.7	28.4
4		329	4.48	1370	59.1	15.8	20.9
5		335	3.03	925	67.5	12.4	16.8
6		334	1.16	354	91.2	1.8	3.0
7	Xerogel 2	324	10.6	3240	53.6	13.7	27.1
8		328	7.76	2370	58.2	12.5	20.5
9		327	5.05	1540	71.8	8.0	12.4
10		331	3.11	950	82.0	3.8	7.0
11		341	1.07	327	89.0	0.8	3.0
12	Ppt. 3	318	8.24	2520	78.0	..	10.1
13		318	4.61	1405	88.3	0.0	4.4
14		322	2.54	775	89.7	0.0	3.4
15		338	1.17	357	91.3	0.0	3.1

In Table I the third column shows the lowest temperature in the catalyst bed. This is a measure of the magnitude of the cooling effect of the endothermic reaction, since the reactants entered the catalyst at 350° C. in all of the runs. The space velocities tabulated are the cc. of vapor (standard temperature and pressure, S. T. P.) per cc. of catalyst per hour, and are equal to the moles of amyl alcohol delivered per hour, divided by the cc. of catalyst (50 cc.) and multiplied by 22,400 cc. per mole. Much of the work which has been reported on the dehydration of *n*-amyl alcohol has made no mention of amyl ether as a product. In this work the amounts of amyl ether were small but definite. The ether was identified by boiling point, density, and refractive index as well as odor. The largest amount of ether was formed with the least active catalyst, indicating that the more active catalysts dehydrate the ether so rapidly that it does not appear in the reaction products.

The conversion curves of Figure 3 are useful in evaluating the relative activity of the catalysts. This is done by determining how fast the vapors must be passed over the xerogel to give the same conversion as the aerogel, at various conversions. Similarly, the precipitate is compared with the xerogel. The computation of the relative activities is illustrated in Table II, the values of the flow rates being taken from Figure 3.

TABLE II. COMPUTATION OF RELATIVE ACTIVITIES OF ALUMINA CATALYSTS

% conversion to amylene	55	60	65	70	75	80	85	Av.
Rate of alcohol, grams per min.:								
Aerogel	5.3	4.2	3.3	2.8	2.35	2.0	..	..
Xerogel	9.3	7.3	6.2	5.35	4.5	3.6	2.5	..
Precipitate	..	..	..	..	9.07	7.7	6.25	..
Xerogel ÷ aerogel	1.75	1.74	1.88	1.91	1.91	1.8	..	1.82
Ppt./xerogel	..	..	..	..	2.02	2.15	2.5	2.22

The relative activity of these catalysts, particularly the gels, remained fairly constant over a wide range of flow rates. As an average the precipitate is 2.2 times as active as the xerogel which is 1.8 times as active as the aerogel for the dehydration of *n*-amyl alcohol to amylene.

Ethanol Dehydration over Alumina

The data obtained for the dehydration of ethanol over alumina are shown in Table III and plotted in Figure 2. The semilogarithmic scale was used to cover the wide range in rates of flow. The curves for the aerogel and xerogel are almost superimposable, although differing somewhat from that of the precipitate. This is not unexpected, however, since the method of preparing the precipitate differed considerably from that of the gels. The extreme variation in catalytic activity of a given compound with its method of preparation is well known and perhaps has been best illustrated by the work of Adkins and Krause (*1*). The conversions of ethylene increase with increasing time of contact and approach 100 per cent. The conversions to ether decrease with increasing time of contact, but at extremely short contact times above the range of Figure 2, the ether conversions would necessarily decrease to zero also. As was the case with *n*-amyl alcohol, the best ether conversions were obtained with the least active catalyst.

The relative activities of the three catalysts are compared by the method illustrated in Table II. In the range 40 to 90 per cent conversion, the precipitate is 2.3 times as active as the xerogel, while the xerogel is 1.8 times as active as the aerogel over the range 30 to 90 per cent conversion. These figures are in good agreement with the values of 2.2 and 1.8 obtained for *n*-amyl alcohol. By a similar method of comparison, the relative ease of dehydration of *n*-amyl alcohol compared to ethanol can be determined. The *n*-amyl alcohol rates were multiplied by 0.523 (46.05/88.1) before comparison with the ethanol rates. This furnishes an equimolal basis for the comparison of contact times, 1 gram of amyl alcohol having the same contact time as 0.523 gram of ethanol. Comparing rates for the aerogel conversions between 40 and 90 per cent, it is found that *n*-amyl alcohol is 3.4 times more easily dehydrated than ethanol. A similar comparison for the rates of xerogel conversions between 55 and 80 per cent shows a value of 3.5. This means that the same per cent conversions to olefins were obtained from ethanol and *n*-amyl alcohol when the contact time of the ethanol was 3.45 times that of the *n*-amyl alcohol.

The data for *n*-amyl alcohol and ethanol are in good agreement, and show that for these reactions over alumina catalysts the aerogel is inferior to the xerogel and the precipitate. The order of activity in this case is the same as that of the apparent densities. Alumina aerogel, then, does not possess the advantages found previously for other aerogel catalysts.

Dehydration of Ethanol over Alumina–Chromic Oxide at 350° C.

The dehydration of ethanol was also studied over the amination catalysts, aerogel 4 and xerogel 5, composed of 9.36 per cent chromic oxide and 90.6 per cent alumina. The data obtained are plotted in Figure 4 and given in Table IV. These differ from Figure 2 and Table III in that they show the extent of dehydrogenation also. This was negligible over the pure alumina catalysts. The values shown for acetaldehyde were calculated on the assumption that all of the hydrogen was formed by dehydrogenation of the alcohol to acetaldehyde, and may therefore not be an accurate estimate of its extent in the product. Direct determinations of acetaldehyde showed that very little was present in the reaction products, and it seems probable that it entered into secondary reactions, since the product usually had an odor of aldehyde

Table III. Dehydration of Ethanol over Alumina at 350° C.

Run No.	Alumina Catalyst (50 Cc.)	Lowest Temp., ° C.	EtOH G./Min.	Space Velocity, Hr.$^{-1}$	% Conversion to: Ethylene	% Conversion to: Ether	% EtOH Recovered
16	Aerogel 1	338	10.4	6080	16.5	50.2	30.0
17		338	6.82	3980	20.1	50.0	26.3
18		334	3.36	1960	26.5	49.0	23.2
19		334	0.917	535	60.8	22.0	16.3
20		334	0.507	296	70.0	14.6	13.8
21		331	0.138	80.6	91.4	0.3	1.4
22	Xerogel 2	324	7.41	4330	24.8	41.0	25.9
23		322	5.00	2920	30.3	42.0	23.3
24		324	2.86	1670	39.8	33.2	20.2
25		325	1.56	911	52.9	23.7	17.8
26		326	0.828	484	76.8	8.4	11.8
27		338	0.225	131	98.8	0.0	0.4
28	Ppt. 3	324	7.39	4320	42.1	29.2	19.7
29		322	5.11	2980	46.7	28.2	18.8
30		320	3.16	1850	59.6	17.2	15.7
31		322	2.40	1400	67.3	14.0	13.7
32		324	1.52	889	82.4	3.8	8.5
33		328	0.746	436	98.2	0.0	1.7

condensation products. It is noticeable that a marked difference exists in the specific catalytic activity of the aerogel and the xerogel. The aerogel is the most active dehydration catalyst and the xerogel the most active dehydrogenation catalyst. Each catalyst appears to give a definite ratio of dehydrogenation to dehydration, which is fairly independent of the time of contact.

The evaluation of the relative dehydration activities by the method of Table II (between conversions of 20 and 50 per cent) shows that the aerogel is 2.0 times as active as the xerogel. The failure of the dehydrogenation curves to overlap and the low precision of the measurements at such low conversions make a similar quantitative evaluation of dehydrogenation activity impossible. A comparison of dehydration activities shows that pure alumina aerogel (No. 1) is 2.6 times more active than the aerogel containing chromic oxide (No. 4). Pure alumina xerogel (No. 2) is 7.1 times as active as the xerogel containing chromic oxide (No. 5). Since the aerogels have more nearly the same apparent densities, the figure 2.6 is probably a better criterion of the effect of 10 per cent chromic oxide than 7.1. The fact that the aerogel is the best dehydration catalyst in this instance is probably less significant than the converse case with pure alumina gels because of the existence of a fundamental difference in the specific activity of the chromic oxide–alumina gels.

Dehydration of Ethanol over Thoria

Sabatier (*15*) listed thoria as a better and more specific dehydration catalyst than alumina. This consideration made it seem desirable to compare the relative activity of the thoria gels for the dehydration of ethanol. The data obtained on the first catalyst studied, xerogel 12, showed that the evaluation of the relative dehydration activities of these gels would not be practical because of the excessive side reactions. The xerogel had very low activity, requiring a temperature of 400° C. to give volumes of gas comparable to those obtained over the not highly active alumina–chromic oxide catalysts 4 and 5 at 350° C. The data obtained are shown in Table V.

The fraction listed in Table V as ether had a strong odor of olefins and may also have contained acetaldehyde. The values for the alcohol recovered may also be somewhat in error, owing to the presence of products of secondary reactions. A product insoluble in water was formed to the extent of 7 cc. for run 1 and 30 cc. for run 2 (total feed, 100 grams). This product boiled smoothly over the range 40° to 150° C., was highly unsaturated, and gave no reaction with sodium, acetic anhydride, benzene sulfonyl chloride, sodium bisulfite, or phenylhydrazine. It appears to consist of olefinic hydrocarbons and to represent 10 to possibly 30 per cent of the ethanol reacted. This product may result from the dehydration of higher alcohols formed by condensation of simple alcohols as observed by Kistler, Swann, and Appel (*11*). It is probably not formed from the direct polymerization of ethylene, since runs with pure ethylene over these gels gave no liquid products.

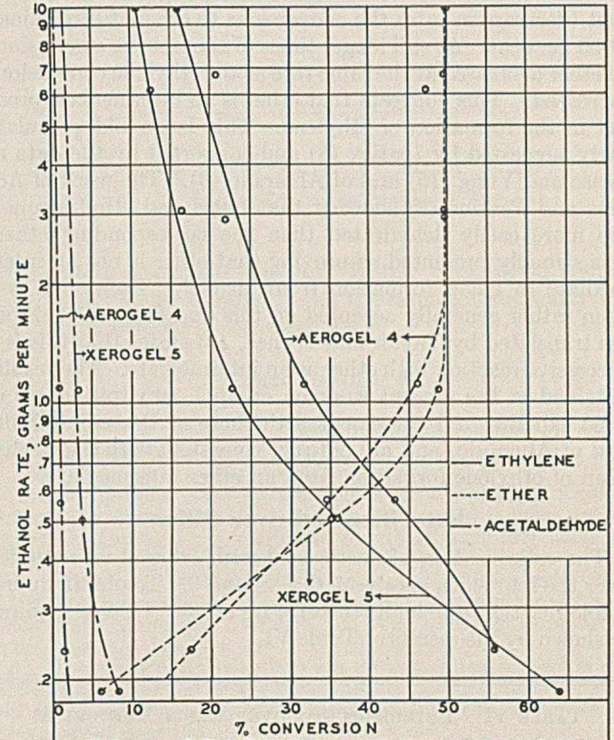

FIG. 4 DEHYDRATION OF ETHANOL OVER 50 CC. Al_2O_3-Cr_2O_3 AT 350° C.

Table IV. Dehydration of Ethanol over Alumina–Chromic Oxide Catalyst at 350° C.

Run No.	Catalyst	EtOH, G./Min.	Space Velocity, Hr.$^{-1}$	% Conversion to: C_2H_4	% Conversion to: Ether	% Conversion to: Acetaldehyde	% EtOH Recovered	Gas Analysis: % C_2H_4	Gas Analysis: % H_2
1	Aerogel 4	9.85	5750	15.9	49.7	0.5	33.6	94.5	3.3
2		6.72	3930	20.9	49.5	0.6	30.7	95.3	3.0
3		2.94	1720	21.7	49.7	0.7	24.1	95.5	3.0
4		1.11	649	31.7	46.0	0.9	20.8	95.5	2.9
5		0.564	330	43.1	34.4	1.0	19.0	96.1	2.3
6		0.237	138	55.9	17.5	1.5	15.2	95.6	2.6
7	Xerogel 5	10.15	5940	10.7	49.5	1.4	38.7	85.8	11.5
8		6.18	3820	12.4	47.2	1.8	33.6	84.2	11.9
9		3.08	1800	16.3	49.7	2.2	26.5	85.6	11.3
10		1.08	631	22.6	48.7	3.3	22.4	86.7	10.7
11		0.505	295	35.8	35.1	3.3	19.8	89.0	8.2
12		0.185	108	64.0	6.0	8.1	11.1	85.0	10.7

The gas analyses show that at 400° C. this catalyst is slightly better as a dehydrogenation catalyst than as a dehydration catalyst. At 350° C. the converse is true to about the same extent. The gel is much less active than the corresponding alumina gel. This catalyst differs markedly from the thoria studied by Sabatier (*15*). The relatively high percentage of carbon dioxide in the gas is rather unusual. A possible explanation for its formation is that the aldehyde formed by dehydrogenation of the ethanol condenses to ethyl acetate, which is then decarboxylated and dehydrated to acetone, carbon dioxide, and ethanol. These are all well-known

Table V. Dehydration of Ethanol over Thoria Xerogel 12

Run No.	Temp., ° C.	EtOH, G./Min.	% EtOH Coverted to: C_2H_4	% EtOH Coverted to: Ether	% EtOH Recovered	Cc. Gas (S. T. P.) per G. EtOH	CO_2	C_2H_4	O_2	H_2	CO	C_2H_6 + CH_4
1	400	1.22	20.5	7.9	25.5	220	10.1	45.2	0.4	..	...	...
2	400	0.628	25.3	4.7	4.3	363	8.5	34.0	0.1	51.9	2.5	2.2
3	350	0.658	9.8	5.9	69.9	90	2.9	52.9	0.3	39.9	1.7	2.0
4	400	0.621	24.9	8.5	7.7	310	7.7	39.2	0.2	49.5	1.0	1.6

reactions. The results show clearly the diverse action of thoria as a catalyst. Dehydration, dehydrogenation, decarboxylation, and condensation are illustrated here. When considered with its known amination activity (*9*, *15*) and its oxidation activity in the gas mantle, it becomes evident that thoria is one of the most diverse catalysts known. Because of these predominating secondary reactions, the attempt to evaluate the relative dehydration activities of the thoria gels was abandoned.

Mechanism of Ethanol Dehydration

Figures 2 and 4 show that over the less active catalysts (alumina aerogel 1 and the alumina–chromic oxide gels 4 and 5) a 50 per cent conversion to ether was obtained at the highest rates studied. Over a fivefold increase in the time of contact (decrease in rate) the conversions to ether still remained at 50 per cent. At still longer times of contact the conversions to ether decreased at the same rate as the ethylene conversions increased. This suggests that ether is an intermediate product in the formation of ethylene. This is an old postulate early suggested by Ipatiev (*8*) and supported by the data of Pease and Yung (*13*) and of Alvarado (*3*). The work of Adkins and Perkins (*2*) showing that butyl and ethyl alcohols are more easily dehydrated than the corresponding ethers was strongly presented as proving that ether is not an intermediate in olefin formation from alcohol. Their view has been rather generally accepted on this question, but Schwab (as translated by Taylor and Spence, *16*) states that this is a successive reaction with ether as an intermediate. The results obtained in the present work on ethanol dehydration are in good experimental agreement with those of Pease and Yung and of Alvarado, and are entirely consistent with the mechanism of ethylene formation from an ether intermediate.

Esterification over Silica

The esterification of acetic acid with ethanol was studied over the four silica catalysts, 6, 7, 8, and 9. To obtain appreciable reaction, the high temperature of 450° C. was required as shown by the results of Table VI.

Table VI. Esterification over Silica Xerogel 8[a]

Temperature, ° C.	300	350	400	450
% AcOH esterified	0.5	2.5	5.1	19.1

[a] 1.3 grams of reactants passing over 50 cc. of catalyst per minute.

The silica catalysts used for this reaction showed a rapid loss in activity which could not be restored by regeneration with oxygen. Ten hours of use as an esterification catalyst followed by regeneration with air and oxygen resulted in a decrease from conversions of 30 and 60 per cent to 4.7 and 38 per cent for aerogel 6. While it gave lower conversions, the xerogel was less affected by such treatment, and showed a decrease from 5.4 and 29.6 per cent to 4.3 and 24.3 per cent. Thus, after considerable usage the aerogel remained a better catalyst than the xerogel. It was thought best for the purpose of this investigation to compare the initial activities of the catalysts. The fact that check runs, made after those at the slowest rates, showed conversions only about 2 per cent lower than those of the earlier runs, indicated that any loss of activity of the gel catalysts during the course of these rapid tests was negligible.

The data obtained for the four catalysts are shown in Table VII and plotted in Figure 5. The order of decreasing activity of the catalysts is: amorphous silica, aerogel, partly dried aerogel, and xerogel. The values for amorphous silica are unexpectedly large, since this is actually microcrystalline silica for the most part. The activity drops rapidly, falling below the two aerogels in the course of these short experiments. Evaluation of relative activities by the method of Table II shows that aerogel 6 is 2.1 times as active as the partly dried aerogel 7 in the range 20–50 per cent conversion. The partly dried aerogel is 4.7 times as active as xerogel 8 in the range 15–30 per cent conversion. Because of its rapid loss in activity and fundamental difference in structure, the microcrystalline silica is not compared quantitatively with the gels. The catalytic activities of the gels are in the ratio 9.9 to 4.7 to 1, while the apparent specific volumes have the ratio 5.1 to 3.0 to 1, the most active catalyst being the most porous and expanded gel of the group. These gels thus offer another example where the aerogel excels the xerogel.

Table VII. Esterification of Acetic Acid and Ethanol over Silica

Run No.	Catalyst	Temp., ° C.	AcOH + EtOH[a], G./Min.	Space Velocity, Hr. $^{-1}$	% AcOH Conversion to Ester
1	Aerogel 6	450	2.82	1450	30.0
2		450	1.01	517	52.0
3		450	0.559	287	58.0
4		450	0.254	130	60.9
5		450	1.107	568	49.9
6	Partly dried aerogel 7	450	2.75	1410	17.7
7		450	1.02	522	36.3
8		450	0.508	260	49.2
9		450	0.286	147	55.5
10		450	0.510	261	46.7
11	Xerogel 8	450	2.74	1400	5.38
12		450	1.14	584	11.6
13		450	0.549	282	19.7
14		450	0.284	145	29.6
15		450	0.563	288	17.6
16	Amorphous silica 9	450	2.84	1450	48.2
17		450	0.944	484	54.1
18		450	0.459	235	48.8
19		450	5.24	2680	34.3
20		450	0.252	129	42.6

[a] 10% excess EtOH over theoretical.

The amount of gas formed in this reaction as determined in longer preliminary runs over the gel catalysts was negligible when based on the total amount of product. A typical analysis of this gas showed 90.6 per cent ethylene, 2.3 hydrogen, and 6.9 methane, indicating that the ethanol and not the acetic acid was decomposing. The amorphous silica gave approximately seven times as much gas as the gels, amounting to about 80 cc. per gram of reactants. The ethylene formed by the dehydration of the ethanol may have cracked to a slight extent to form methane and carbon. This is a known reaction and is supported by the fact that carbon was deposited on the catalysts, and methane was present in the gas.

Previous work on vapor-phase esterification by Reid, Milligan, and Chappell (*14*), consisting of an equilibrium study, showed silica gel to be the best vapor-phase catalyst. Because of the high conversions they obtained, silica gel has been considered a good catalyst for this reaction. It should be pointed out that their conversions were obtained only at extremely long times of contact. The present work, showing the necessity of using a temperature of 450° C. and the rapid loss in activity of the catalysts, indicates that silica gel is not a good catalyst for this reaction.

In a study of the oxidation of acetaldehyde over these same silica catalysts, Foster (*6*) found that the aerogel and partly dried aerogel were equally active and about seven times more than the xerogel.

Decarboxylation and Dehydration of Acetic Acid over Thoria

The results obtained on converting acetic acid to acetone, carbon dioxide, and water are shown in Table VIII and plotted in Figure 6. This reaction is apparently free of any extensive secondary reactions since the gaseous product consisted of more than 99 per cent carbon dioxide in all cases. The results show that xerogel 12 and aerogel 10 (extracted with methanol) have considerably less activity than the gels studied previously by Kistler, Swann, and Appel (*11*). However, the relative activities are in the same order, the aerogel being more active than the xerogel. The considerably lower activity of aerogel 11 (extracted with propane) is additive with some of the above facts in showing that the differences in catalytic activity caused by small variations in methods of preparation of such gels may be greater than the differences due to the aerogel and xerogel porosities. The methods previously used for preparing thoria gels (*11*) were difficult to reproduce with the thorium salts used in this investigation; this indicates a possible difference in composition.

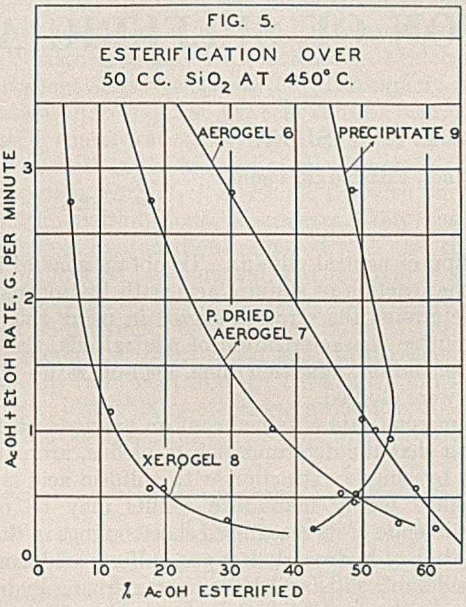
FIG. 5.

ESTERIFICATION OVER 50 CC. SiO_2 AT 450° C.

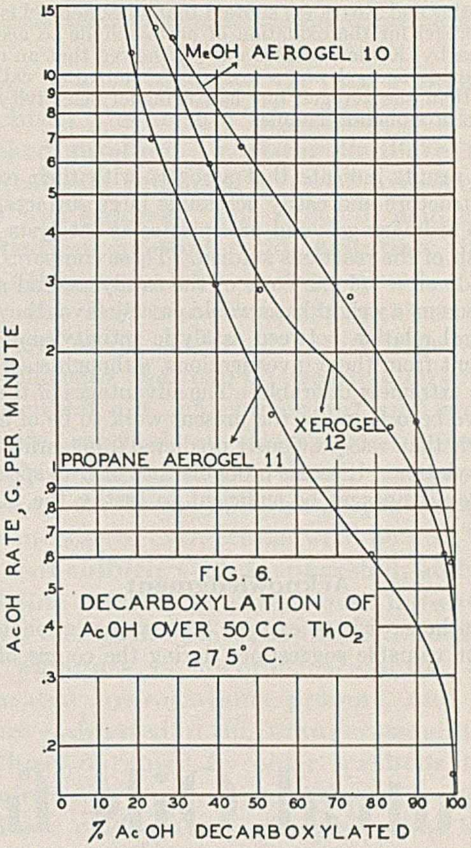
FIG. 6.

DECARBOXYLATION OF AcOH OVER 50 CC. ThO_2 275° C.

Applying the method of evaluation used in Table II over the range of 30 to 90 per cent conversion, it is seen that aerogel 10 is 1.56 times as active as xerogel 12 and 3.29 times as active as aerogel 11. The considerably lower activity of the aerogel after propane extraction is difficult to explain. It might be attributed to the lower apparent density, but is probably due to fundamental changes in surface structure caused by the low-temperature propane extraction or by higher hydrocarbons in the propane (bottled gas) during the autoclaving. On the other hand, the methanol may exert an activating effect on the thoria, as observed for copper oxide catalysts by Kostelitz and Huttig (*12*). The results show the difficulty of reproducing the same catalytic activity in different batches of the same gel.

Conclusions

The investigations of aerogels as catalysts may be summarized as follows:

1. The present investigation and especially that of Kistler, Swann, and Appel (*11*) show that thoria aerogel is more active than thoria xerogel or precipitate for decarboxylating acids to ketones.
2. The present investigation as well as that of Bliss and Dodge (*4*) shows that alumina aerogel is inferior to some xerogel and precipitated aluminas. Catalyst activities have the same order as the apparent densities.
3. The present investigation shows that silica aerogel is superior to silica xerogel for the vapor-phase esterification of ethanol and acetic acid. Activity of the catalysts has the reverse order of the apparent densities.

TABLE VIII. DECARBOXYLATION OF ACETIC ACID OVER THORIA

Run No.	Thoria Catalyst	Temp., ° C.	AcOH, G./Min.	Space Velocity, Hr.$^{-1}$	% AcOH Reacted
1	Aerogel 11 (extd. with propane)	275	11.4	5110	18.6
2		275	6.89	3090	23.7
3		275	2.94	1320	39.7
4		275	1.38	618	53.8
5		275	0.610	273	78.5
6		275	0.168	75	98.8
7	Aerogel 10 (extd. with methanol)	275	12.38	5540	28.9
8		275	6.54	2930	46.2
9		275	2.75	1230	73.6
10		275	1.33	596	90.0
11		275	0.590	264	98.3
12	Xerogel 12	275	13.05	5850	24.4
13		275	5.95	2670	38.4
14		275	2.87	1290	51.0
15		275	1.27	569	83.4
16		275	0.612	274	96.8

4. Foster and Keyes (*6*) showed that silica aerogel is superior to the xerogel for the oxidation of acetaldehyde to acetic acid.
5. Kearby, Kistler, and Swann (*9*) showed that an alumina-chromic oxide aerogel was a less active amination catalyst for alcohols than the xerogel, but had a higher selectivity for the formation of monobutylamine.

These results indicate that aerogels, with their extremely porous structure and easily accessible large surfaces, are superior to ordinary gels and precipitates as catalysts for only about half of the reactions studied. These comparisons have been made on a volume basis of the catalysts, and a similar comparison on a weight basis would greatly favor the aerogels. No general relation between catalytic activity and porosity is apparent from these investigations, although such correlations are extremely desirable. The advantages of the aerogel form have been found in the present work to be of a smaller magnitude than was previously predicted from earlier work on decarboxylation. It seems probable that only in special cases will these advantages be sufficient to justify the utilization of aerogels.

Acknowledgment

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Neutral Oils from Coal Hydrogenation • ACTION OF SULFURIC ACID

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A RAPID and convenient method of analyzing neutral oils was needed in connection with this bureau's study of the hydrogenation of coal and tar (*8*). Although a procedure that would estimate the hydrocarbon types accurately was preferred, the principal aim was to develop a rapid, convenient, and reproducible method of characterizing small samples of oil. Methods (*6, 7, 17, 18*) based upon physical constants, which can be applied best to hydrocarbon mixtures containing only two or three types of functional groups, appeared unsuitable for complex oils, such as those obtained from coal, that contain olefins and neutral oxygen, sulfur, and nitrogen compounds.

Since several workers (*4, 5, 10, 13*) have shown that sulfuric acid reacts selectively with olefins, aromatics, and saturates, usually in the order named, attention was directed to this reagent. Consideration of the literature showed that little work had been done on the reactions of sulfuric acid with oils produced by coal hydrogenation and that all attempts to develop a simple and accurate method of determining olefinic, aromatic, and saturated hydrocarbons in other neutral oils were disappointing (*4, 10*). Moreover, there are objections to classifying oils containing compounds with two or more functional groups (such as styrene and similar compounds of higher molecular weight) as mixtures of olefins, aromatics, and saturates. In spite of these faults, however, sulfuric acid is a valuable analytical tool and is widely used in the examination of neutral oils (*3*). To obtain general information on the reaction of sulfuric acid with hydrogenation oils and to determine the errors involved in using this reaction for the routine characterization of neutral oils, the effect of acid concentration, agitation time, acid-oil ratio, and other variables were studied.

The numerous data obtained confirm previous work (*4, 10*) in showing that the determination of olefins, aromatics, and saturates by simple extraction with sulfuric acid is unsatisfactory since highly inaccurate results may be obtained. However, in spite of its recognized shortcomings in the precise determination of hydrocarbon types, sulfuric acid can be used with considerable satisfaction for characterizing hydrocarbon oils conveniently, rapidly, and economically. The method of characterization adopted on the basis of the results obtained in the present work, which has been used for some time for the routine testing of coal-hydrogenation oils (*8, 9*), is described below.

Experimental Procedure

Since many of the methods previously recommended require that considerable quantities of oil (often 100 cc.) be shaken by hand with sulfuric acid, steps were taken at the beginning to improve these two features of the analysis. After experiments were made with several graduated separatory funnels, a funnel that was calibrated in 0.05-cc. subdivisions and required only 5 cc. of oil was adopted. By using this funnel and a shaking ma-

Using 5-cc. samples of oil and a shaking machine, the action of sulfuric acid on cracked gasoline, a coal-tar distillate, and neutral oils produced by coal hydrogenation was studied. The effect of acid concentration, acid-oil ratio, agitation time, and other variables were determined. Plotting the acid concentration against the amount of oil extracted gave curves with two plateaus that can be used to characterize neutral oils. A convenient and reproducible method of characterizing small samples of neutral oil, which consists in locating the levels of the two plateaus by two successive extractions with 86 and 98.5 per cent sulfuric acid, is suggested, and the probable errors involved are indicated. The levels of the plateaus indicate roughly the amounts of olefinic, aromatic, and saturated hydrocarbons present, and the values estimated in this manner are similar to those obtained by older methods that require more oil, reagents, and time. Sulfuric acid extractions show that aromatic hydrocarbons predominate in coal-hydrogenation oils and that the aromatic content increases with increase in molecular weight.

chine developed specially for the purpose, which agitates eight funnels simultaneously, considerable economy in both time and material was easily accomplished. Although only 5 cc. of oil are required, the volume of oil in the funnel can be read with an accuracy (±0.2 per cent) greater than that usually attainable with sulfuric acid extraction methods of analyzing neutral oils.

Unless otherwise indicated, the following standard procedure was used: Five cubic centimeters of oil and then 15 cc. of acid were placed in the graduated funnels. The funnels were closed with rubber stoppers ("Noair 5"), inverted, clamped to the shaking machine, and agitated mechanically for 5 minutes. The funnels were placed in an upright position and allowed to stand for at least 30 minutes. The acid layer was then drained off until the upper surface of the oil approached the zero mark of the funnel. After the funnels had stood in this position for at least 1.5 hours, more acid was run out until the upper oil level was exactly opposite the zero mark on the upper end of the graduated part of the funnel. The oil volume was recorded, and the volume of oil extracted was calculated by subtracting this value from the original volume (5 cc.).

The concentrations of the more dilute sulfuric acid solutions were calculated (*15*) from their specific gravities, which were determined with 12-inch (30.5-cm.) hydrometers. The concentrations of the acid solutions stronger than 93 per cent were determined by titration. Most of the oils studied (Table I) were prepared by the continuous hydrogenation of coal or tar in the bureau's experimental plant (*8*, *9*). The cracked gasoline was furnished by D. R. Stevens of the Mellon Institute. The coal-tar distillates, which were produced in the bureau's experimental carbonization equipment (*3*), were obtained from J. D. Davis and L. P. Rockenbach.

Extraction of Olefins

INFLUENCE OF ACID CONCENTRATION. To determine the effect of acid concentration on the amount of olefins extracted, 5-cc. portions of oil were shaken mechanically for 5 minutes with three volumes of sulfuric acid of different concentrations. The results obtained with cracked gasoline, various hydrogenated coal distillates, synthetic mixtures, and a coal-tar distillate are shown in Figure 1. The amount of oil extracted increased gradually with increase in acid concentration up to about 88 per cent acid, and then rapidly with acid concentration up to about 96 per cent sulfuric acid. Increasing the acid concentration beyond this point caused little additional increase in the amount of oil extracted.

From previous work (*1*, *4*, *5*, *10*, *11*, *13*) with pure olefinic and aromatic hydrocarbons, it appears likely that olefins are the principal hydrocarbons removed with acid concentrations up to about 88 per cent and that removal of aromatics is the main reaction occurring with acid concentrations higher than about 88 per cent. On this basis 85 to 87 per cent sulfuric acid should be useful as an analytical reagent for extracting olefins from neutral oils. Although sulfuric acid of this strength is capable of attacking aromatics, its principal role under the conditions of the present work probably is the removal of olefins, and its use gives approximate values for the first flat portion of the volume-acid concentration curves shown in Figure 1. Furthermore, 86 per cent sulfuric acid is advantageous in that slight variations in concentration have little effect on the volume of oil extracted. It is shown below that 86 per cent sulfuric acid has the further advantage of extracting approximately the same quantity of olefins as is removed by treatment with 80 per cent sulfuric acid followed by distillation to the original end point [Kester-Pohle (*13*) and similar methods].

TABLE I. DESCRIPTION OF NEUTRAL OILS[a]

Oil No.	Neutral Oil	Boiling Range, ° C.	Sp. Gr. (15.6° C.)	Volume, Per Cent: Olefins[b] 1	Olefins[b] 2	Aromatics[b] 1	Aromatics[b] 2	Saturates[b] 1	Saturates[b] 2
1	Cracked gasoline[c]	...	0.751	17.0	16.4	23.6	23.2	59.4	60.4
2	Bruceton overhead oil[d]	20–330	0.937	6.6	7.8	65.0	63.4	28.4	28.8
3	Washington overhead oil[e]	20–235	0.836	9.0	9.0	41.4	41.6	49.6	49.4
4	Same	20–330	...	11.6	...	46.0	...	42.4	...
5	Alabama overhead oil[f]	270–330	...	11.0	...	78.0	...	11.0	...
6	Hydrogenated coal tar[g]	20–235	...	1.5	1.4	65.1	65.2	33.4	33.4
7	Tar dist.	20–330	...	7.0	...	78.6	...	14.4	...
8	Synthetic mixt.[h]	...	...	12.8	...	72.1	...	15.1	...
9	Same	...	...	18.7	...	68.3	...	13.0	...
10	Montana overhead oil[i]	20–330	0.891	8.8	8.6	47.6	47.4	43.6	44.0

[a] All the oils were distillates that had been washed with dilute NaOH, H_2SO_4, and water, and dried.
[b] Estimated by successive extractions with 86 and 98.5% H_2SO_4.
[c] Raw cracked gasoline after treatment with dilute NaOH and H_2SO_4.
[d] From the continuous hydrogenation of Pittsburgh bed coal.
[e] From the continuous hydrogenation of McKay bed coal.
[f] From the continuous hydrogenation of Mary Lee bed coal.
[g] From the continuous hydrogenation of high-temperature tar.
[h] These solutions were prepared in 1937 and used in previous work (*4*).
[i] From the continuous hydrogenation of Colstrip coal.

To find the effect of increasing the sulfuric acid concentration beyond those shown in Figure 1, two of the oils (3 and 10, Table I) were treated with stronger sulfuric acid and oleum. When the results were plotted, curves with two plateaus were obtained (Figure 2). Since these oils were obtained from two different coals, it is believed that other oils prepared by coal hydrogenation would give similar curves. Although not a precise measure of the hydrocarbon types present, the levels of the plateaus probably are related to the amounts of olefins, aro-

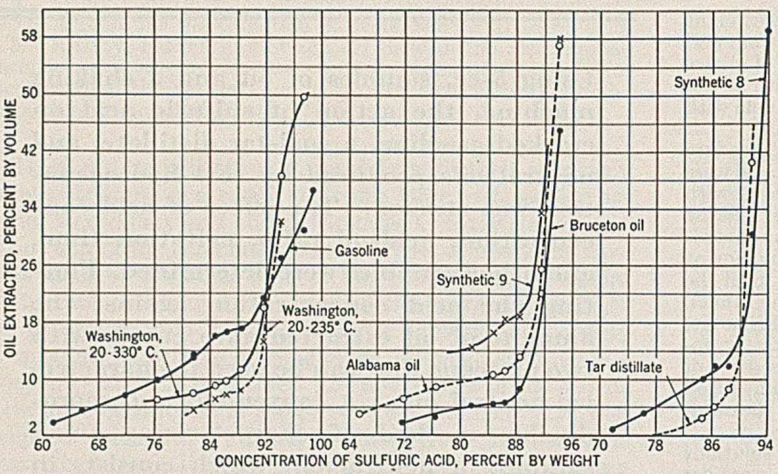

Figure 1. Effect of Sulfuric Acid Concentration on Percentage of Oil Extracted

matics, and saturates in the oil; hence it is to be expected that the curves will differ principally in the location of the plateaus. Comparison of Figure 2 with Figure 8 shows that the second or higher plateau is affected by the proportion of olefins present or by a preliminary treatment to remove olefins.

Acid-Oil Ratio

The influence of the acid-oil ratio was studied with cracked gasoline and the neutral oil (2 in Table I) prepared by hydrogenating Bruceton (Pittsburgh seam) coal. The amount of oil extracted increased rapidly with increase in acid-oil ratio up to about 2 cc. of acid (86.4 per cent) for 5 cc. of oil (Figure 3). Larger amounts of 86.4 per cent acid caused a gradual increase in the amount of oil extracted. These results indicate that great care in measuring the quantity of acid is not necessary for acid-oil ratios greater than about 1.

Figure 3 indicates also that the cracked gasoline is more sensitive to changes in the acid-oil ratio than the neutral oil obtained by hydrogenating Bruceton coal. The data in Figure 3 were collected at different times and, together with the data in Tables II to VIII, illustrate the reproducibility to be expected with the present apparatus and method when variations in room temperature are neglected and unusual care is not exercised in measuring the volume of acid and time of agitation.

Agitation Time. Cracked gasoline and Bruceton oil (samples 1 and 2 in Table I) were shaken mechanically with three volumes of 86.4 per cent acid to determine the effect of agitation time. The results (Table II) show that the time of agitation is relatively unimportant for periods of time greater than 1 minute. As shown below, these results are in marked contrast with those obtained by repeated extraction with fresh sulfuric acid, which removed considerable additional amounts of oil.

Table II. Effect of Time of Agitation on the Volume Per Cent of Oil Extracted by Sulfuric Acids[a]

Oil No.	Neutral Oil	Agitation, Minutes: 1	3	5 a	5 b	7	10 a	10 b	20
1	Cracked gasoline	18.4	...	18.0	17.0	18.4	16.6	17.0	17.8
2	Bruceton overhead oil	7.6	7.4	7.8	6.6	...	7.4	...	...

[a] Oils (5 cc.) were agitated mechanically with 15 cc. of 86.4% H_2SO_4.

The data in Figures 4, 5, and 6 show the effect of repeating the sulfuric acid treatments, which consisted of shaking the oil with 3 volumes of acid for 5 minutes. Although the largest amounts of oil were extracted by the first treatment, considerable amounts were removed by further treatment with fresh sulfuric acid. Very little oil was extracted from the Washington oil (sample 4, Table I) by the fourth and fifth treatments (Table III), but oil could be extracted from the cracked gasoline even after thirteen treatments with sulfuric acid (Figure 4). Since it is likely that 61.6, 65.6, 71.8, and 76.5 per cent sulfuric acid extracted only negligible quantities of aromatics, these results indicate that the cracked gasoline contained a much higher percentage of olefins than that indicated by one extraction with three volumes of 86.4 per cent sulfuric acid (Table I).

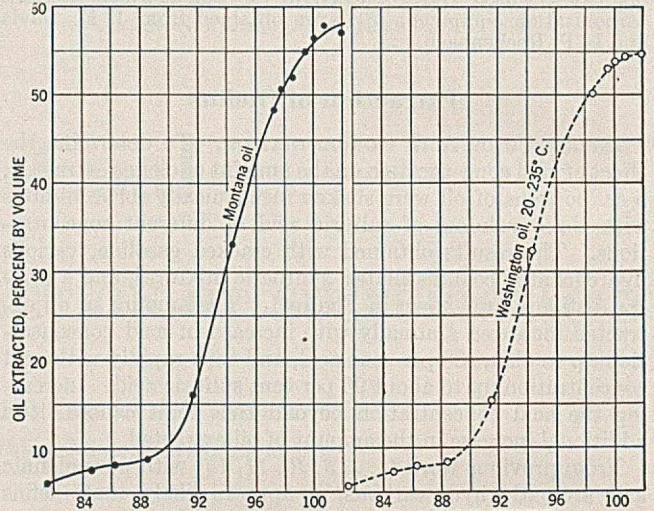

Figure 2. Extraction of Overhead Oils with Three Volumes of Sulfuric Acid of Different Concentrations

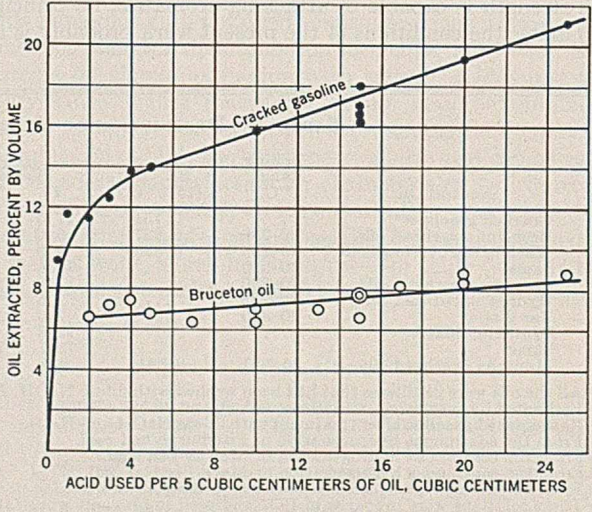

Figure 3. Effect of Acid-Oil Ratio on Olefins Extracted by 86.4 Per Cent Sulfuric Acid

Using data obtained by extracting coal with organic solvents for different periods of time, Landau and Asbury (*14*) plotted the time of extraction against the time–extraction yield ratio and found that the slope of the resulting straight line represented the ultimate extraction yield. When plotted in a similar manner, the data (Figure 5) obtained with cracked gasoline after the third or fourth extraction gave straight lines. The slopes of these lines indicate that extraction of the cracked gasoline with 60 to 75 per cent sulfuric acid for an infinite time would remove about 60 per cent of the oil (Figure 5). It cannot be stated definitely that the oil extracted is olefins; but excluding manipulative losses, this appears probable since sulfuric acid of these concentrations is known to sulfonate only negligible amounts of benzene, toluene, and xylene (*4*).

The data obtained with the Washington oil after the first extraction (Table III) were similar to those collected with the cracked gasoline, in that straight lines were obtained when the total time of agitation was plotted against the time–oil extracted ratio (Figure 6). The ultimate yields of extractable oil were estimated by Landau and Asbury's method (*14*) from the slopes of these lines. The results indicate that 76.5 per cent sulfuric acid, which is incapable of attacking appreciable amounts of aromatics under these conditions, would remove about 14 per cent of the oil if the treatment were continued indefinitely. Whether this value, which is considerably greater than the olefin value indicated by one extraction with 86.4 per cent sulfuric acid (Table I), approximates the true olefin content of the Washington oil is not known. Figure 6 also shows that larger percentages of the oil would be extracted by repeated treatment with sulfuric acid of higher concentrations.

Table III. Extraction of Washington Neutral Oil[a] with Sulfuric Acid of Different Concentrations

No. of Extractions	Vol. % Oil Extd. at Acid Concn. of: 76.5%	81.6%	84.7%	86.4%	88.5%	91.6%	94.1%
1	7.0	8.0	9.0	9.6	11.2	20.0	38.4
2	8.0	9.4	10.4	11.4	13.8	24.4	42.4
3	10.0	11.4	12.8	13.6	16.0	27.6	45.8
4	10.4	11.4	13.0	14.0	17.0	29.8	47.0
5	11.0	...	14.0	14.8	18.0	31.6	48.8

[a] Boiling point, 20–330° C.

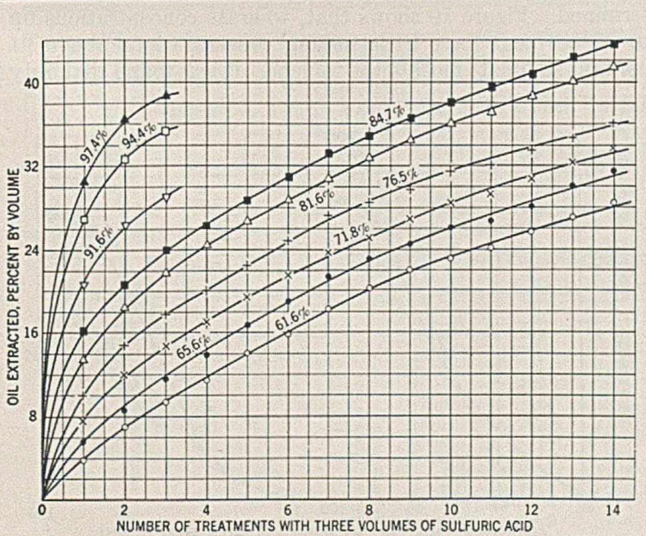

Figure 4. Repeated Extraction of Cracked Gasoline with Different Concentrations of Sulfuric Acid

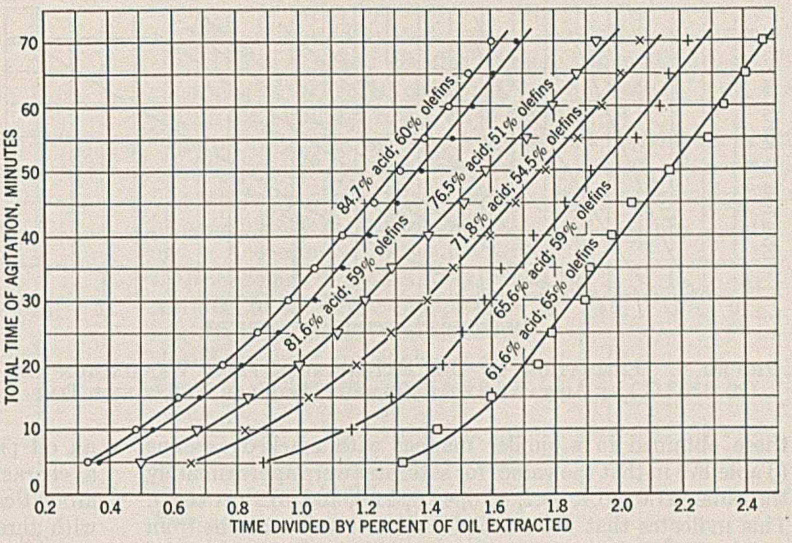

Figure 5. Estimation of Olefin Content of Cracked Gasoline from Slopes of Time–Oil Extracted Curves

Because the results obtained by repeated extraction (Figure 4) should be equivalent to using large amounts of sulfuric acid, analysis of the data by Landau and Asbury's method (*14*) to obtain the ultimate extraction yields (Figures 5 and 6) appears permissible. Whether or not the ultimate extraction yields represent the true olefin contents, it is interesting that this treatment of the data gives virtually straight lines whose slope may be used to characterize the oil.

The olefin-free oils remaining after extractions (Figure 4) with sulfuric acid of different concentrations were shaken mechanically for 5 minutes with 98.7 per cent sulfuric acid (Table IV) Straight lines were obtained by plotting the percentages of residual oil against the number of sulfuric acid treatments (Figure 7). These experiments show that the values obtained for saturated hydrocarbons by extraction with strong sulfuric acid are influenced in some instances by the methods used to estimate or remove the olefins. For example, the extrapolated values (approximately 41.5 and 58.5 per cent) for saturates in the cracked gasoline differ as much as 17 per cent (Figure 7).

Table IV. Extraction of Olefin-Free Cracked Gasoline[a] with 98.7 Per Cent Sulfuric Acid[b]

No of Extractions	Residual Oil, Per Cent by Volume A[c]	B[d]	C[e]	D[f]	E[g]	F[h]	G[i]	H[j]
1	47	45.4	44.6	43.2	40.4	40.2	48.8	59.4
2	44.4	43	42.4	41	38.6	38.4	46.6	54.8
3	...	...	...	39.4	37.2	37	44.4	52.6
4	...	...	...	37.4	35	35	42	50.2
5	...	...	...	36.4	34	34	40.8	47.2
6	...	...	...	...	...	...	...	45.6

[a] Sample 1, Table I.
[b] Shaken for 5 minutes with 15 cc. of 98.7% H_2SO_4 after removal of olefins (Figure 4).
[c] Previously extracted 14 times with 61.6% H_2SO_4.
[d] Previously extracted 14 times with 65.6% H_2SO_4.
[e] Previously extracted 14 times with 71.8% H_2SO_4.
[f] Previously extracted 14 times with 76.5% H_2SO_4.
[g] Previously extracted 14 times with 81.6% H_2SO_4.
[h] Previously extracted 14 times with 84.7% H_2SO_4.
[i] Previously extracted 6 times with 86.4% H_2SO_4.
[j] Previously extracted once with 86.4% H_2SO_4.

The oils that remained after extracting the Washington sample five times with moderately dilute sulfuric acid (Table III) were shaken mechanically for 5 minutes with three volumes of 98.7 per cent sulfuric acid. The results differed from

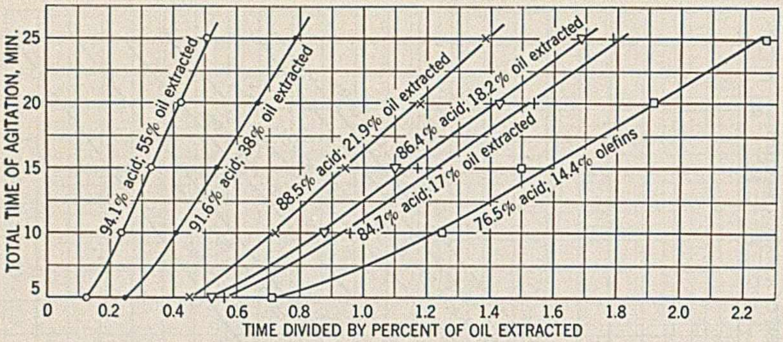

Figure 6. Estimation of Oil Extractable from Washington Oil (20–330° C.) by Agitation with Sulfuric Acid for an Infinite Time

those obtained in a similar manner with cracked gasoline (Table IV) in that the values for saturates were approximately the same (41.0, 40.4, 39.2, 40.0, 40.0, 41.0, and 40.2 per cent). This indicates that the method used to remove olefins from coal-hydrogenation oils has little influence on the subsequent determination of saturates.

Effect of Temperature

The temperatures given in Table V were read from a thermometer that extended through the rubber stopper into the graduated separatory funnels. The oil and 86.4 per cent sulfuric acid were cooled to the initial temperatures shown in Table V and then agitated manually for 5 minutes. The results indicate variations in the amount of oil extracted by 86.4 per cent sulfuric acid of about 25 per cent. Any differences in oil volume caused by thermal expansion and contraction can be calculated.

Table V. Effect of Temperature on the Extraction of Olefins from Bruceton Oil[a]

Temperature, ° C.							
Room	Initial	0.5 min.	1 min.	2 min.	4 min.	5 min.	Olefins, %
23	10	...	22.5	23.5	25	25.7	9.2
21	21	22.5	22.5	23.0	23.2	23.2	7.0
23	35	32	31.5	30.5	29.3	28.8	8.4
25	0	0.8	6	7.5	8	6	7.0

[a] Bruceton overhead oil distillate (sample 2, Table I); oil (5 cc.) shaken by hand for 5 minutes with 15 cc. of 86.4% H_2SO_4.

To get information on the effect of temperature on the extraction of aromatics, the olefin-free oil and 98.7 per cent acid were cooled or heated to the initial temperatures shown in Table VI and then shaken manually for 5 minutes; temperatures were read as before from a thermometer inserted through the rubber stopper. The heat of the reaction was enough to raise the temperature above 30°, even with an initial temperature of 0° C. In experiment 4 (Table VI) the temperature was kept at about 7° C. by pouring ice water over the funnel. The values for saturated hydrocarbons were approximately the same (within 10 per cent) for all of the experiments except No. 4.

Extraction of Aromatics

Effect of Acid Concentration. The oils used in studying the removal of aromatics were prepared by treating some of the neutral oils of Table I with 86.4 per cent sulfuric acid to remove olefins. The resulting olefin-free oils were shaken mechanically for 5 minutes with three volumes of sulfuric acid to determine the effect of acid concentration. Figure 8 shows that the amount of oil extracted increased rapidly with increase in acid concentration up to about 97 per cent. From 97 to 99 per cent sulfuric acid there was relatively little increase in oil extracted with increase in acid concentration. Previous work (*4*) showed that 98 per cent acid sulfonates aromatics rapidly but has little action on saturated hydrocarbons. Therefore, the plateau in Figure 8 that occurs at about 98 per cent acid is probably the dividing line between aromatics and saturates. Regardless of the accuracy of this demarcation, the plateau of the curves in Figure 8 should be useful in characterization of oils. Furthermore, slight variations in acid concentration at this point would have little effect on the amount of oil extracted.

Repeated extraction of different fractions (1, 20–188°; 2, 188–207°; 3, 207–235°; 4, 235–270°; 5, 270–300°; 6, 300–330° C.) of an oil produced by coal hydrogenation also indicated that a characteristic and reproducible amount of oil (probably aromatics predominate) is removed by one treatment, with three volumes of 98 per cent sulfuric acid (Figure 9). The second, third, and later extractions removed small and approximately constant amounts of oil; when the volume of the residual oil was plotted against the number of treatments, straight lines resulted. The slopes of these lines decreased with increase in molecular weight of the oil treated, which indicates that the saturates of lower molecular weight react more readily with concentrated sulfuric acid than do saturates of high molecular weight.

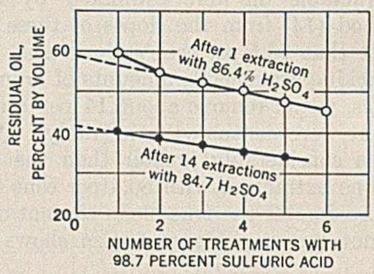

Figure 7. Repeated Extraction of "Olefin-Free" Oil with 98.7 Per Cent Sulfuric Acid

Using the present equipment, the effect of acid concentration on the sulfonation of pure toluene and benzene was determined. Figure 10 shows that, whereas concentrations up to 90 per cent have little action, concentrations above 94 per cent sulfonate most of the toluene. It was found that only

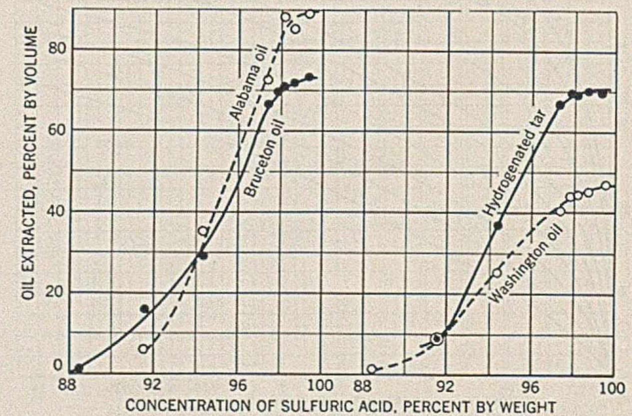

Figure 8. Extraction of Aromatics with Three Volumes of Sulfuric Acid

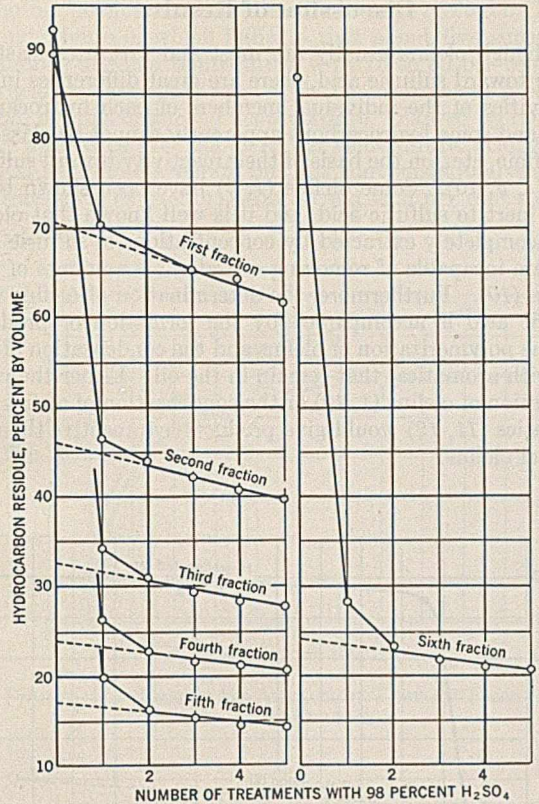

FIGURE 9. SEPARATION OF AROMATIC AND SATURATED HYDROCARBONS BY EXTRACTION WITH 98 PER CENT SULFURIC ACID

negligible amounts of xylene were attacked in the 5-cc. funnels at room temperature by 3, 4, and 5 volumes of 86.4 per cent sulfuric acid. Since toluene and xylene are comparatively reactive toward sulfuric acid, these experiments indicate that most of the oil removed by 86.4 per cent sulfuric acid from the cracked gasoline and other oils (Tables I and III) was olefinic.

Figure 11 shows that about 13.5 cc. of 98.7 per cent sulfuric acid is necessary to sulfonate 5 cc. of benzene (5 minutes of mechanical agitation). Since benzene is comparatively difficult to sulfonate, this indicates that three volumes of 98.7 per cent acid are adequate to remove the aromatics from most oils. Figure 12 shows the effect of room temperature and acid concentration when 10 cc. (pipet) of 98.7 per cent acid are shaken for 5 minutes with 5 cc. of benzene.

ACID-OIL RATIO. Figure 13 shows that the amount of oil extracted from olefin-free oil by 98.7 per cent sulfuric acid (shaken mechanically for 5 minutes) increases rapidly with increase in acid-oil ratio up to about one. Accordingly, ratios larger than one should be used in analytical methods to obtain easily reproducible results, although smaller ratios should be used in refining operations to utilize the sulfuric acid efficiently.

AGITATION TIME. Olefin-free oils were shaken mechanically with three volumes of 98.7 per cent sulfuric acid to determine the effect of agitation on the amount of oil extracted. Figure 14 shows that the amount extracted increases rapidly up to about 4 minutes and slowly thereafter. Therefore, 4 minutes or more of agitation should be employed to get reproducible results.

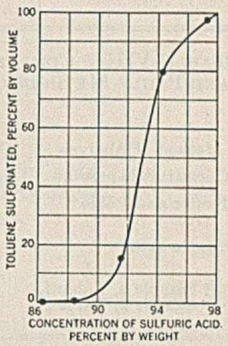

FIGURE 10. SULFONATION OF TOLUENE WITH THREE VOLUMES OF SULFURIC ACID

Synthetic Solutions

Several synthetic solutions were prepared by mixing either benzene or heptane with cracked gasoline (sample 1, Table I). The data obtained with the resulting mixtures agree moderately well with calculated values, which were derived from the analyses of the cracked gasoline shown in Table I. The olefin and aromatic values obtained with the benzene-cracked gasoline mixtures were consistently higher and lower, respectively, than the calculated values; straight lines were obtained by plotting the determined olefin and aromatic values (Table VII) against the percentage of benzene added to the cracked gasoline. The content of saturated hydrocarbons, which ranged from 6 to 95.2 per cent, was estimated within 5 per cent of its value (Table VII) by successive extractions with three volumes of 86.4 and 98.7 per cent acids. The percentages of aromatics calculated and found in Table VII agree within about 10 per cent of their values. The data for olefins are, however, subject to considerable error, amounting to as much as 30 to 50 per cent of the total.

TABLE VI. EFFECT OF TEMPERATURE ON THE EXTRACTION OF AROMATICS FROM HYDROGENATED TAR

Expt. No.	Temperature, ° C.							Saturates, %
	Room	Initial	0.5 min.	1 min.	2 min.	3 min.	5 min.	
1	22.5	9	20	27.5	33	31.5	29.5	27.8
2	24	24	37	39	38	36.8	32.5	26.0
3	24.5	30	35.5	38.9	38.5	36.5	33.2	28.2
4	25	0	9	6.5	6.5	6.0	7.0	52.0
5	26	0	21	28	32	32	31	27.0

TABLE VII. ANALYSIS OF SYNTHETIC SOLUTIONS

	Components, % by Vol.			Composition, % by Volume					
				Calculated			Found		
No.	Cracked gasoline[a]	Benzene	Heptane[b]	Olefins	Aromatics	Saturates	Olefins	Aromatics	Saturates
1	100	..	..	...	...	...	16.7	23.4	59.9
2	..	..	100	...	...	100	0	0.8	99.2
3	75	25	..	12.5	42.6	44.9	13.6	40.4	46.0
4	50	50	..	8.4	61.7	29.9	11.4	58.1	30.5
5	20	80	..	3.3	84.7	12.0	7.4	80.2	12.4
6	10	90	..	1.7	92.3	6.0	5.4	89.0	5.6
7	75	..	25	12.5	17.8	69.7	13.4	17.4	69.2
8	50	..	50	8.4	12.1	79.5	9.0	12.4	78.6
9	20	..	80	3.3	5.3	91.4	3.4	6.0	90.6
10	10	..	90	1.7	3.1	95.2	1.4	3.8	94.8

[a] Cracked gasoline previously washed with dilute NaOH and H_2SO_4 (sample 1, Table I).
[b] Prepared by washing heptane fraction with 15% oleum.

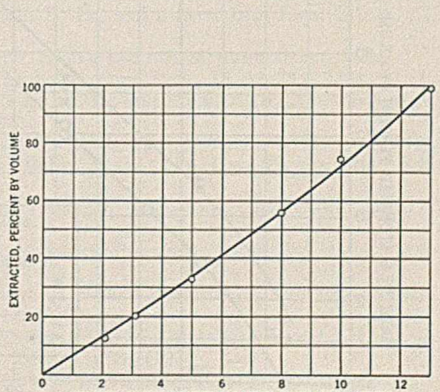

FIGURE 11. SULFONATION OF BENZENE WITH VARIOUS AMOUNTS OF 98.7 PER CENT SULFURIC ACID

Comparison with Kester and Pohle Method

Table VIII shows that successive extractions of 5 cc. of oil with 86.4 and 98.7 per cent sulfuric acids gave results with two synthetic solutions that compare favorably with data obtained by the more complicated Kester and Pohle method (100 cc. of oil) which has been used in the analysis of many coal-tar distillates. Both procedures result in 7 to 30 per cent errors in olefin content, 3 to 5 per cent in aromatics, and 3 to 30 per cent in saturates.

Table VIII. Comparison of Simple Extraction and Kester and Pohle Methods of Determining Olefins and Aromatics

	Solution 1[a]			Solution 2[b]		
Method of Analysis	Olefins	Aromatics	Saturates	Olefins	Aromatics	Saturates
Constituents present	15	70	15	25	65	10
Kester and Pohle (*13*)	16 17	69.3 68.6	14.7 14.4	18 18	68.8 70.4	13.2 11.6
Simple extn.	12.6 13.0	72.2 72	15.2 15	18.6 18.8	68.4 68.2	13.0 13

[a] Sample 8, Table I.
[b] Sample 9, Table I.

Action of Sulfuric Acid on Saturated Hydrocarbons

The oil remaining after the treatment of several overhead oils (produced by coal hydrogenation) with three volumes of 98.7 per cent sulfuric acid was shaken mechanically for 5 minutes at room temperature with three volumes of sulfuric acid or oleum solutions. The results obtained with this oil, which should consist principally of saturated hydrocarbons, show that the amount of oil extracted increases rapidly with increase in acid concentration beyond 98 per cent sulfuric acid. However, when concentrated sulfuric acid is used to determine aromatics, the acid is diluted by the water formed, and it is likely that the amount of saturates removed is less than would be expected from Figure 15.

The curve obtained by plotting the oil extracted against the total sulfur trioxide content shows a plateau at about 1 per cent oleum (Figure 15). Saturated hydrocarbons differ considerably in reactivity toward sulfuric acid; hence, a plateau in Figure 15 might be expected. Further study might show that fuming sulfuric acid or chlorosulfonic acid could be used as a reagent to estimate the proportions of reactive (usually branch-chained) and unreactive hydrocarbons present in saturated oils.

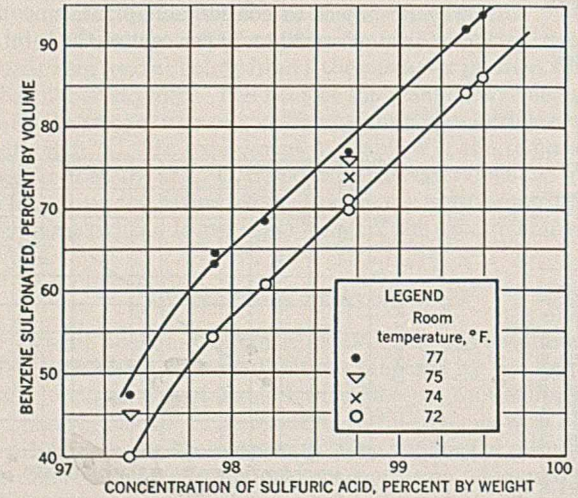

Figure 12. Sulfonation of Benzene with Two Volumes of Sulfuric Acid

Discussion of Results

Although olefins usually are most and saturates least reactive toward sulfuric acid, there are great differences in the reactivities of the individual members of each hydrocarbon type, and some hydrocarbons apparently cannot be classified as olefinic, etc., on the basis of their reactivity toward sulfuric acid (*4*, *5*, *10*). Some olefins (*1*, *2*) have been shown to be quite inert to sulfuric acid, and it is well known that olefins are incompletely extracted by concentrations of sulfuric acid that are incapable of removing considerable amounts of aromatics (*10*). Furthermore, the determination of olefins with sulfuric acid is accompanied by the formation of products (by the polymerization of olefins and the condensation of olefins with aromatics) that remain in the oil. Either the polymerization of olefins (*1*, *10*) or the condensation of olefins and aromatics (*11*, *12*) would give products less reactive than the original olefins.

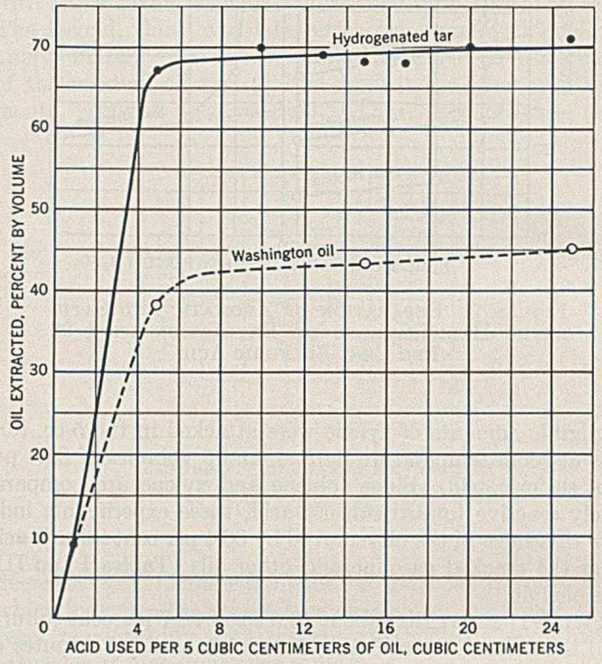

Figure 13. Extraction of "Olefin-Free" Oils with Various Amounts of 98.7 Per Cent Sulfuric Acid

The curves in Figures 1, 2, and 8, which are characteristic of the oils and related to the amounts of olefins, aromatics, and saturates present, could be used as such in analytical work to differentiate between different neutral oils. However, the curves differ most in the levels of the plateaus, and therefore the determination of these two levels should be adequate for the simple characterization of oils. This is the basis of the method adopted (described below), which consists in locating the two plateaus approximately by extracting the oil successively with two appropriate concentrations of sulfuric acid.

From Tables V, VI, and VII and Figures 13 and 14 it appears that, although the sulfonation of aromatics is markedly affected by the reaction temperature, the reaction of olefins with sulfuric acid is rapid and relatively independent of the temperature. From these observations it might be expected that an improved separation of olefins and aromatics could be achieved by treating the neutral oil with concentrated sulfuric acid for a short time at about 0° C. This possibility was not studied.

Another possible analytical method was suggested by Table III and Figure 6, which indicate that about five successive extractions at room temperature with 75 to 80 per cent sulfuric acid should remove most of the olefins from oils produced by coal hydrogenation. This procedure, followed by removal of the aromatics with about 98 per cent sulfuric acid, might be used as a more accurate but less convenient analysis than two successive extractions with 86 and 98.5 per cent sulfuric acid.

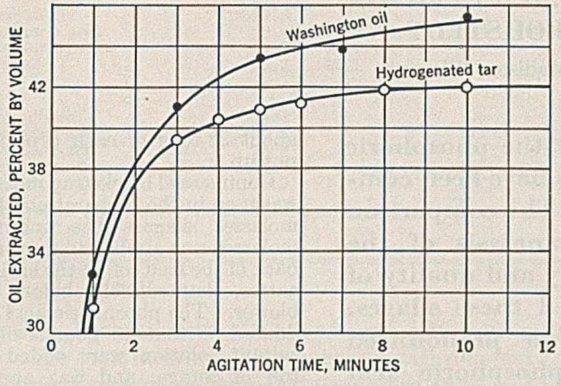

Figure 14. Effect of Agitation Time on Extraction of Aromatics

The analyses in Table I and the data in Figure 1 show that oils produced by coal hydrogenation (*8*, *9*), although quite different from cracked gasoline, are similar to coal-tar distillates (*3*), in that aromatic hydrocarbons predominate. Figure 9 indicates that the aromatic content of coal-hydrogenation oils increases with increase in molecular weight. This conclusion agrees with other analyses made with several coal-hydrogenation oils (*9*).

Method Adopted

The method adopted and used for some time to characterize neutral oils produced by coal hydrogenation (*8*, *9*) is as follows: The oil (5 cc.) is shaken mechanically for 5 minutes with 15 cc. of 86 per cent sulfuric acid. Although obviously not a precise measure of the olefin content, the oil extracted is reported as olefins. The olefin-free oil remaining in the funnel is then shaken for 5 minutes in a similar manner with 15 cc. of about 98.5 per cent sulfuric acid. The residual oil is reported as saturates, and the percentage of aromatics is calculated by difference.

Probably this simple method estimates the saturates with reasonable accuracy but gives low olefin and high aromatic values. Although the amounts of the hydrocarbon types are not indicated precisely, this method is advantageous in several respects. Less oil (5 cc. instead of the 100 cc. frequently used) and reagents are required. The oil, chiefly saturates, remaining after the second extraction is adequate for additional treatment with strong sulfuric acid and the determination of refractive indices, from which the carbon-hydrogen ratio and content of naphthenes and paraffins can be estimated (*16*). Since the only operations are two successive extractions with sulfuric acid, the method is short and well suited for routine work.

Many of the previously recommended methods (*4*, *10*) consist in extracting the oil with 80 to 91 per cent sulfuric acid, distilling the residual oil to the original end point, and extracting the distillate with 96 to 100 per cent sulfuric acid. Although the present method omits the distillation, the olefin values (Table VIII), resulting from one extraction with 86 per cent sulfuric acid, agree fairly well with those obtained by extracting the oil with 80 per cent acid and distilling the residual oil to the original end point. The distillation might be desirable with cracked gasolines and similar oils, but it is believed that this step is not profitable for coal-tar distillates and oils produced by hydrogenating coal. Owing to the fact that low-boiling polymers would be found in the distillate, the distillation step is always of questionable value for oils boiling over a wide range.

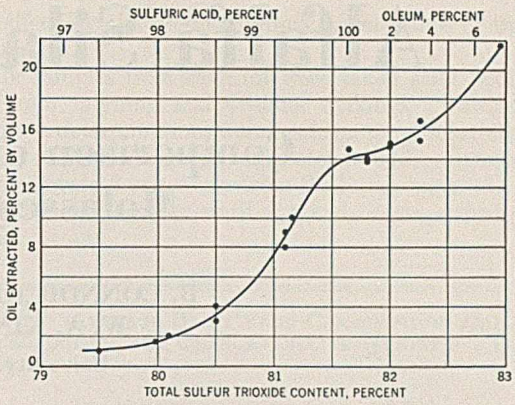

Figure 15. Action of Sulfuric Acid and Oleum on Saturated Hydrocarbons

Acknowledgment

The authors are grateful to H. H. Storch for the coal-hydrogenation oils and constructive criticism of the manuscript. The 5- and 10-cc. graduated funnels were made by glass workers at the Fisher Scientific Company of Pittsburgh.

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Alfalfa Silage Preservation

Comparison of Phosphoric Acid and Molasses as Preservatives

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Alfalfa silages prepared by the phosphoric acid and molasses methods have been compared during three years. The comparison was based on chemical analysis of the silages and on the quantity and quality of milk produced by cows fed these silages. Chemical studies show no pronounced differences between the phosphoric acid silage (20–30 pounds per ton) and the molasses (65 pounds per ton), but show poorer preservation and greater carotene losses with lower amounts of phosphoric acid.

Either is satisfactory as to palatability and milk production, and no harmful effect on milk flavor has been noted.

The carotene and vitamin A contents of milks produced on phosphoric acid (20–30 pounds per ton of forage) and the molasses silages are high as compared to averages for Wisconsin winter-market milk, while milk produced on silage made with 8–15 pounds of phosphoric acid is in the same range as average winter milk.

A PREVIOUS publication (*10*) compared the A. I. V. and the molasses methods, covering three years of experimental work on the ensiling of alfalfa. The conclusion reached was that "molasses alfalfa silage appears to be equal to A. I. V. alfalfa silage, and conditions of farm practice probably make molasses silage more suitable for general use".

A method which has certain advantages over the A. I. V. process is the use of phosphoric acid to replace the mixture of hydrochloric and sulfuric acids. Virtanen in 1932 (*24*) and later Wilson (*26*) described the use of phosphoric acid to lower the pH of forages for silage making, and compared it with the use of hydrochloric and other acids. Later a mixture of hydrochloric acid and phosphoric acid obtained from the action of water on phosphorus pentachloride (*12*), the so-called Penthesta solution, was tried in Europe (*3*, *11*, *20–23*).

No extensive articles on the use of phosphoric acid in comparison with other silage preservatives have appeared, although short reports on the use of this method have been given by several workers (*4*, *11*, *17*, *19*).

In a survey of northeastern United States farms in 1938 (*2*), thirty-two farmers out of a total of three hundred and eighty reported using phosphoric acid with satisfactory results.

A number of commercial producers have advocated the use of phosphoric acid, and have published pamphlets on the preparation of silage with it. The acid is sold under various trade names, "Phosilage", "Ensilaid", "Silo-phos", etc.

The phosphoric acid method has the great advantage, as compared with the A. I. V. method, of using a weaker acid which is much less corrosive to the equipment and hence can be applied directly to the forage at the silage cutter. In this respect it is on a par with molasses.

Preparation of Silages

Alfalfa silages prepared by the phosphoric acid and molasses methods have been compared during three years of experimental work. The silages were prepared from first-cutting alfalfa in the early bloom stage. About 14 tons of phosphoric acid silage were put up in 1937 and 23 tons of molasses silage. In 1938 and 1939 about 23 tons of each type were put up.

Commercial blackstrap molasses was used in the preparation of the molasses silage. The undiluted molasses was applied to the alfalfa back of the feed roll of the ensilage cutter, immediately before the blower. The phosphoric acid was diluted so that 40 pounds of resultant solution were added per ton of forage, and was applied in the same manner as the molasses.

The molasses was added at the rate of 65 pounds per ton, the phosphoric acid at rates varying from 8 to 30 pounds of 75 per cent acid per ton.

Analysis of Silage

At the time of ensiling, the alfalfa was analyzed for dry matter and carotene. Samples of silage were taken every 2 to 3 weeks after the silo was opened, and analyzed for pH, dry matter, ammonia, and carotene. The carotene was determined by the method of Hegsted, Porter, and Peterson (*9*). Table I gives the averages of these determinations for each of the silages.

Good alfalfa silage should have a pH below 4.5 and an ammonia nitrogen content of less than 10 per cent of the total nitrogen. Thus, 20–30 pounds of phosphoric acid per ton produced good silage while 15 pounds or less did not. In 1939 the pH was satisfactory but the odor was poor. All of the molasses silages were good and most were excellent. In 1938 the forage was not tramped at all during ensiling while in the other years it was, and this seems to have made considerable difference in the quality of the silage. However, the carotene content of the green alfalfa was lower in 1938 than in the other years.

Carotene losses varied from 3 to 15 per cent for the molasses silage, from 3 to 9 per cent for the silage preserved with 20 pounds or more of phosphoric acid, and from 24 to 44 per cent for the silages made with less than 20 pounds of phosphoric acid per ton. Thus again it is seen that the quality of the phosphoric acid silage improved markedly as the amount of phosphoric acid was increased from 8 to 30 pounds per ton of forage.

In the use of phosphoric acid for silage it is important that the fluorine content be low (about 0.05 per cent). Fluorine analyses were made by a modification of the method of Armstrong (*7*) on various samples of phosphoric acid alfalfa silage

TABLE I. COMPOSITION OF SILAGE

Silage	Preservative, Lb./Ton	Dry matter, %	Ammonia N, % of total N	pH	Carotene, Micrograms/G. Dry Matter	Quality[a]
			1937			
Green alfalfa	..	27.3	..	...	184	...
Phosphoric acid	15	25.9	9.8	4.5	139	Fair
Phosphoric acid	30	25.5	5.0	3.9	190	Excellent
Molasses	65	26.4	8.8	3.9	156	Excellent
			1938			
Green alfalfa	..	23.8	..	...	125	...
Phosphoric acid	15	22.6	13.3	4.9	64	Poor
Phosphoric acid	30	24.9	10.7	4.3	119	Good
Molasses	65	25.2	12.1	4.5	121	Good
			1939			
Green alfalfa	..	28.4	[b]	...	196	...
Phosphoric acid	8	26.8	[b]	4.2	119	Fair
Phosphoric acid	14	26.8	[b]	4.0	110	Fair
Phosphoric acid	20	26.9	[b]	4.0	177	Good
Molasses	65	25.9	[b]	4.2	177	Good

[a] Based on color, odor, and chemical analysis.
[b] Not determined.

in 1938. The university silage averaged 10.6 p. p. m. fluorine, while some farmers' silages, prepared with different grades and amounts of phosphoric acid, contained from 40 to 1050 p. p. m. of fluorine (dry basis).

Analysis of Milk

Cows from the university herd were divided into two lots, approximately equal in weight, age, breed, stage of lactation, and milk and butterfat production. Preliminary feeding trials only were made with the phosphoric acid silage in 1937, and no data on the results are given in the table. In 1938 each group of cows consisted of one Holstein, two Guernsey, one Jersey, and one Brown Swiss, and in 1939, of two Holstein, two Guernsey, one Jersey, and one Brown Swiss. Table II gives the rations, milk production, etc., of the animals. At the rate of consumption given, silage made up approximately 38 per cent of the dry matter of the rations. Both silages were equally satisfactory as to palatability and in their effect on milk production and maintenance of weight of the animals.

Milk samples from each lot were taken after pooling the milk from morning and evening milkings. Carotene and vitamin A determinations were made on the whole milk by the method of Olson, Hegsted, and Peterson (*16*). Samples were analyzed every 3 or 4 weeks from the beginning of the feeding period late in October until the end of the experiment in March.

TABLE II. AVERAGE DAILY FEED CONSUMPTION, DAILY MILK PRODUCTION, AND CHANGES IN LIVE WEIGHT PER COW

Lot	Alfalfa Hay, Lb.	Grain Mixture[a], Lb.	Silage, Lb.	Daily Milk[b] Production, Lb.	Decline in Daily Milk[b] Production, Lb.	Initial Weight, Lb.	Gain in Weight, Lb.
			1938				
Phosphoric acid	5.9	10.6	42.7	27.4	5.8	1053.2	37.2
Molasses	5.9	10.6	42.4	26.5	5.0	1049.2	44.2
			1939				
Phosphoric acid	8.3	8.4	38.5	20.9	5.5	1051.1	83.7
Molasses	8.3	8.4	38.7	21.8	5.8	1022.9	96.7

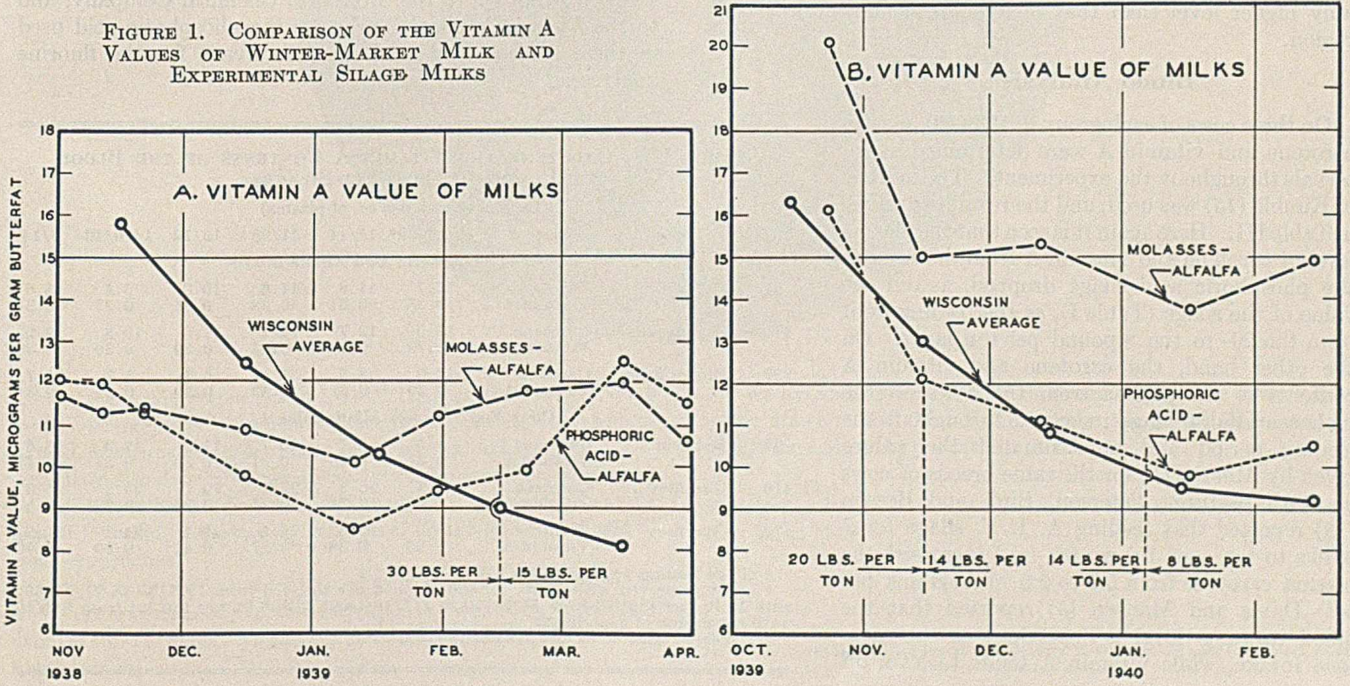
[a] The grain mixture was made up as follows:

	Phosphoric Acid Lot, %	Molasses Lot, %
Ground corn	70.1	69.4
Ground oats	27.9	27.7
$CaCO_3$	1.0	..
Bone meal	..	1.9
Iodized salt	1.0	1.0

[b] 4 per cent fat-corrected milk.

Figure 1*A* gives graphs for the total vitamin A potency for 1938, obtained by adding together the vitamin A figures and half of the carotene values (*14*) for each sample. The vitamin A value of Wisconsin market milk, as found by Dornbush, Peterson, and Olson (*6*) in this laboratory, is included for comparison. This figure indicates that in 1938–39 the molasses alfalfa silage milk about maintained its original level in February and March, which was well above the market milk. Silage preserved with 15 pounds of phosphoric acid per ton

FIGURE 1. COMPARISON OF THE VITAMIN A VALUES OF WINTER-MARKET MILK AND EXPERIMENTAL SILAGE MILKS



gave poor results, as would be expected from the low carotene content of the silage. However, with 30 pounds of phosphoric acid per ton of silage, the vitamin A value of the milk became much better and essentially equaled that of the milk produced on the molasses silage.

Figure 1*B* gives the same graphs for 1939–40. The vitamin A value of milk produced on molasses alfalfa silage was much above that of average market milk, while that of milk from the phosphoric acid silage dropped at approximately the same rate as the carotene content of the silage (Table I).

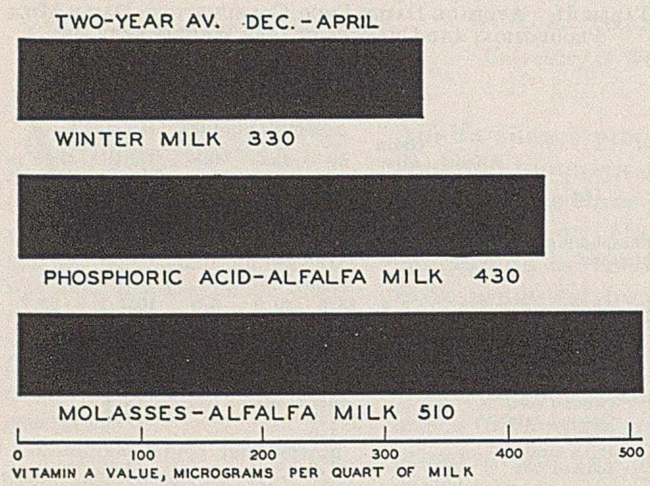


FIGURE 2. AVERAGE VITAMIN A VALUES OF WINTER-MARKET MILK AND EXPERIMENTAL SILAGE MILKS

Averaging the carotene and vitamin A contents (micrograms per gram) of the butterfats produced on these silages for the two years gave the following results: phosphoric acid, carotene 7.3, vitamin A 7.5; molasses, carotene 9.8, vitamin A 8.0.

If the total potency (carotene and vitamin A) is expressed in micrograms per quart value, and the averages for the months January to March for the two years are compared with the average for Wisconsin market milks over the same period, it is seen from Figure 2 that the feeding of these silages maintained the vitamin A potency of the milks at a considerably higher level than that of average winter milk in this region.

Blood Analysis

On three cows of each group in 1939–40, plasma carotene and vitamin A were determined at intervals throughout the experiment. The method of Kimble (*13*) was used, and the results are given in Table III. Here again it is seen that the plasma level of carotene and vitamin A from the cows on the phosphoric acid silage dropped, as did the value of the silage (Table I), as the feeding went from the 20- to the 8-pound per ton layer. On the other hand, the carotene and vitamin A contents of the plasma from the cows on the molasses alfalfa silage increased throughout the feeding period and approximated the values given by Moore (*15*) for the same breeds of cows on fresh pasture. Peterson, Bird, and Beeson (*18*) reported that feeding A. I. V. silage for 7 weeks to ten cows on winter feed increased the plasma carotene from 5.2 to 9.6 micrograms per cc. Davis and Madsen (*5*) reported that the blood carotene level is dependent on the carotene intake, while vitamin A tends to level off and does not increase proportionally with increasing carotene intake; these facts are also evident in Table III.

Discussion

This work seems to indicate that for the production of well-preserved phosphoric acid alfalfa silage with a carotene content equal to that of molasses alfalfa silage, it is necessary to use 20–30 pounds of phosphoric acid (75 per cent) per ton of forage.

Bender *et al.* (*2*) state that "the maximum amount of acid necessary to preserve legume crops seems to be 16 pounds per ton of green material. All cases of severe spoilage could be traced to the use of less acid." Sixteen pounds per ton would seem to be a minimum, and 20 pounds or over would appear to be preferable. The various commercial producers of phosphoric acid recommend 14 to 18 pounds per ton for legumes.

In 1938–39 silage put up with 30 pounds of phosphoric acid proved more palatable than the molasses silage, while in 1939–40 the molasses silage proved more palatable than that made with 14 and 8 pounds of phosphoric acid. These observations check well with the degree of preservation, and thus the palatability of good phosphoric acid alfalfa silage is approximately equal to that of good molasses alfalfa silage.

Anderson *et al.* (*1*), Garrett *et al.* (*8*), and Whitnah *et al.* (*25*) reported the relation between carotene content of the feed of the cow and the production of milk of good flavor. Low carotene was associated with oxidized flavor in the milk. A single test late in the feeding trials showed no particular effect on flavor or development of oxidized flavor in milks from cows fed these two types of silage.

Acknowledgment

The work reported in this paper is a cooperative experiment by the Departments of Biochemistry, Dairy Husbandry, and Agricultural Engineering. Various phases of the work have been done with the advice or supervision of F. W. Duffee, C. A. Elvehjem, E. B. Hart, B. H. Roche, I. W. Rupel, and H. Steenbock.

The analytical work for 1937 was done by D. M. Hegsted. Credit is due G. M. Werner and C. E. Zehner for direct supervision of the feeding of the cows and collection of the milk samples.

We are indebted to George M. Rommel of the Tennessee Valley Authority, to the Monsanto Chemical Company, and to the Victor Chemical Works for the phosphoric acid used in these studies, and to Robert J. Evans for the fluorine analyses.

TABLE III. CAROTENE AND VITAMIN A CONTENTS OF THE BLOOD PLASMA OF COWS FED SILAGES

(In micrograms per cc. of plasma)

No.	Breed	Content	10/24/39[a]	11/14	11/28	12/12	1/16/40	2/14
		Cows Fed Phosphoric Acid Alfalfa Silage[b]						
93	Holstein	Carotene	17.7	11.9	11.6	10.0	6.4	8.6
		Vitamin A	0.65	0.31	0.28	0.34	0.23	0.34
445	Guernsey	Carotene	19.0	12.7	10.1	11.6	10.8	12.2
		Vitamin A	0.79	0.80	0.12	0.30	0.30	0.38
827	Brown Swiss	Carotene	13.0	8.5	7.5	6.8	5.7	5.7
		Vitamin A	0.29	0.32	0.32	0.30	0.31	0.34
		Cows Fed Molasses Alfalfa Silage[c]						
92	Holstein	Carotene	8.5	9.7	10.7	11.5	12.5	13.6
		Vitamin A	0.31	0.28	0.21	0.35	0.37	0.41
416	Guernsey	Carotene	19.3	30.3	25.5	29.7	25.2	25.3
		Vitamin A	1.05	0.74	0.24	0.37	0.60	0.57
472	Guernsey	Carotene	19.0	22.5	19.5	19.1	24.1	31.2
		Vitamin A	0.85	0.36	0.17	0.41	0.60	0.66

[a] Silage feeding was begun 11/1/39.

[b] Layer preserved with 20 lb. phosphoric acid per ton, fed from 11/1/39 to 11/21/39; with 14 lb. per ton fed from 11/21/39 to 1/3/40; and with 8 lb. per ton fed from 1/3/40 until conclusion of experiment.

[c] Preserved with 65 lb. of molasses per ton.

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Ketogluconic Acids from Glucose

BACTERIAL PRODUCTION

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The bacterial fermentation of glucose to 5-ketogluconic acid and to 2-ketogluconic acid has been studied in rotary drum fermenters and in vertical vat fermenters.

Approximately 90 per cent yields of 5-ketogluconic acid have been obtained from 10 per cent glucose solutions in 33 hours, using *Acetobacter suboxydans* as the bacterial agent. Approximately 82 per cent yields of 2-ketogluconic acid have been obtained from 10 per cent glucose solutions in 25 hours, using an unnamed bacterium as the fermentative agent.

THE formation of 5-ketogluconic acid from glucose by bacteria was reported more than fifty years ago by Boutroux (*9*). Since that time a number of investigators (*3*, *4*, *7*, *8*, *14*, *15*, *17*, *20*, *21*, *33*, *34*) have obtained this acid by the action of various species of acetic acid bacteria on glucose solutions in the presence of calcium carbonate, and on salts of gluconic acid.

In 1935 Bernhauer and Görlich (*3*) isolated small quantities of 2-ketogluconic acid from cultures of *Acetobacter gluconicum* grown on solutions of calcium gluconate, although 5-ketogluconic acid was the main oxidation product. In 1938 Bernhauer and Knobloch (*6*) reported relatively high yields (76 per cent of theory) of 2-ketogluconic acid, with only traces of 5-ketogluconic acid, by the action of *A. suboxydans* on salts of gluconic acid. However, they found that substantial amounts, up to 37 per cent of theory, of 5-ketogluconic acid were produced by the same organism from glucose in the presence of calcium carbonate. Recently Bernhauer and Knobloch (*5*) extended their studies to other organisms; they reported that, whereas their standard strain of *A. suboxydans* produced predominantly either 2-ketogluconic acid or 5-ketogluconic acid, according to whether the substrate contained gluconate salts or glucose, a subspecies, *A. suboxydans muciparum*, produced 5-ketogluconic acid under both conditions.

Previous studies of both 2-ketogluconic and 5-ketogluconic acid formation have been conducted in unagitated surface cultures, the time required for completion of the fermentation of dilute solutions of glucose or gluconates ranging from 20 to 90 days. The present paper is concerned with the bacterial production of these two acids from glucose solutions under submerged culture conditions, a procedure which has resulted in a rapid and efficient oxidation of glucose to the desired products.

Materials and Methods

The organism used in the study of 5-ketogluconic acid production was the strain of *Acetobacter suboxydans* which had been used previously in this division for the conversion of sorbitol to sorbose (*36*, *38*). The organism used in the study of 2-ketogluconic acid production was an unnamed bacterium isolated by the authors from aberrant 5-ketogluconic acid fermentation liquors. This organism appears to possess numerous properties similar to those of the acetic acid bacteria.

The media used in the experiments were prepared with commercial hydrated glucose, C. P. nutrient salts, and U. S. P. XI precipitated calcium carbonate. The concentrated corn steeping liquor used as a source of accessory nutrient factors was kindly supplied by the A. E. Staley Manufacturing Company, and according to analysis supplied by this firm, contained 55 to 60 per cent solids, of which approximately 45 per cent was protein, 38 per cent was carbohydrate, and 18 per cent was mineral matter.

Most of the experimental work reported in this paper was conducted in the aluminum rotary drum fermenters, previously described (*16*) and found to be excellent culture vessels for the production of gluconic acid (*23*, *37*), of sorbose (*38*), and of *d*-lactic acid (*35*). Unless otherwise stated, all fermentations in the drums were conducted under conditions which had previously been found most satisfactory for highly oxidative fermentations—namely, a gage pressure of 30 pounds per square inch (2.11 kg. per sq. cm.), an air flow of 1600 cc. per minute measured as exit gas at atmospheric pressure, and a rotation rate of 13 revolutions per minute. A charge of 3.3 liters was placed in each drum.

Toward the close of the work a few fermentations were conducted in vat-type fermenters, recently constructed by this division. These vats had a working capacity of 33 liters, were constructed of high-purity aluminum, and were equipped with propellers and means for aeration under superatmospheric pressures. Details of construction and operation of the vats will be presented in a future publication.

Analysis of the fermentation liquors for glucose and for the reducing ketogluconic acids was made by the copper-reduction method of Shaffer and Hartmann (*32*). Calcium in solution was determined by precipitation as the oxalate, which was subsequently titrated with standard potassium permanganate in the usual manner.

The bacterial population at selected times during the fermentation was determined by making cell counts according to the standard dilution plate technique. The plating medium contained 5 per cent glucose, 0.5 per cent yeast extract, and 5 drops of alcohol per 10 cc. of medium. It had been observed that the addition of alcohol resulted in higher and more consistent cell counts.

In order to prepare active inocula for the drum fermentations, the two bacterial strains were cultivated in the following media:

(1*a*) Ten cubic centimeters of 5 per cent sorbitol–0.5 per cent yeast extract liquid tube culture, in the case of *A. suboxydans*, or (1*b*) 10 cc. of 5 per cent glucose–0.5 per cent yeast extract liquid tube culture, in the case of the 2-ketogluconic acid-producing organism.

(2) Two hundred cubic centimeters of a medium containing 2 per cent glucose–0.5 per cent yeast extract, cultured in a Jena glass gas washing bottle, type 101*a*, and aerated with 200 cc. of air per minute.

(3) Three liters of 5 per cent glucose solution containing 0.5 per cent yeast extract and 37 grams of calcium carbonate, cultured in a 4-liter serological bottle and aerated with 5 liters of air per minute.

The organisms were allowed to grow for approximately 2 days at 30° C. on each of the above media before transfer *en masse* to the succeeding medium. Aliquots (300 cc.) of the solution from the final glucose medium were used to inoculate 3-liter charges of the main fermentation solutions, which differed slightly in composition in these two processes (Table I).

TABLE I. COMPOSITION OF NUTRIENT SOLUTIONS[a] FOR PRODUCTION OF KETOGLUCONIC ACIDS

Components	Grams for: 5-Ketogluconic acid	Grams for: 2-Ketogluconic acid
Commercial glucose	118[b]	118[b]
Corn steeping liquor	5	5
Octadecyl alcohol (antifoam agent)	0.3	0.3
Urea (sterilized separately)	...	2
$MgSO_4.7H_2O$	...	0.25
KH_2PO_4	...	0.60
$CaCO_3$ (sterilized separately)	27	27
Distilled water	To make 1000 cc., in both cases	

[a] The solutions were sterilized by autoclaving at 20 pounds pressure for 45 minutes.

[b] This quantity of commercial glucose gave a medium of 10% glucose concentration.

5-Ketogluconic Acid

CHEMICAL STUDIES. The product resulting from the submerged cultivation of *A. suboxydans* on glucose solutions was identified as calcium 5-ketogluconate. The solubility of the salt in water was approximately 0.2 gram per 100 cc., and the salt reduced the Shaffer-Hartmann alkaline copper reagent. A sample of the salt recrystallized from water and dried to constant weight at 100° C. showed a calcium content of 8.51 per cent, a value in excellent agreement with the work of Kiliani (*18*) who found 8.52 per cent calcium. Kiliani's assumption that the salt has the composition $Ca(C_6H_9O_7)_2.3H_2O$, which contains 8.34 per cent calcium, appears to be incorrect in view of the fact that his calcium determination, as well as ours, is almost exactly the correct value for the composition $Ca(C_6H_9O_7)_2.2^1/_2H_2O$, which yields 8.50 per cent calcium.

The specific rotation was determined by dissolving 2.4941 grams of the crystalline salt in 3 cc. of 5.9 *N* hydrochloric acid, diluting to 50 cc., and polarizing in a 1-dm. tube at 20° C. The observed rotation was −0.61°, which, calculated in terms of free acid, gives a specific rotation of −14.8°; this value is in substantial agreement with the figures reported by Cook and Major (*11*), by Barch (*2*), and by Boutroux (*9*).

The reducing power of calcium 5-ketogluconate toward the Shaffer-Hartmann alkaline copper solution was determined so that the proper reduction factors could be used in estimating this product in the fermentation liquors. A one-gram sample of the pure hydrated salt was dissolved in a small quantity of hydrochloric acid and made up to 100 cc. with water. Aliquots of this stock solution were used in the Shaffer-Hartmann procedure, the individual acid samples being neutralized to bromocresol green before addition of the alkaline copper reagent. The values in Table II are taken from the data thus obtained. For comparison, similar values for glucose are also presented; on a weight basis 5-ketogluconic acid has approximately 80 per cent of the reducing power of glucose toward this reagent.

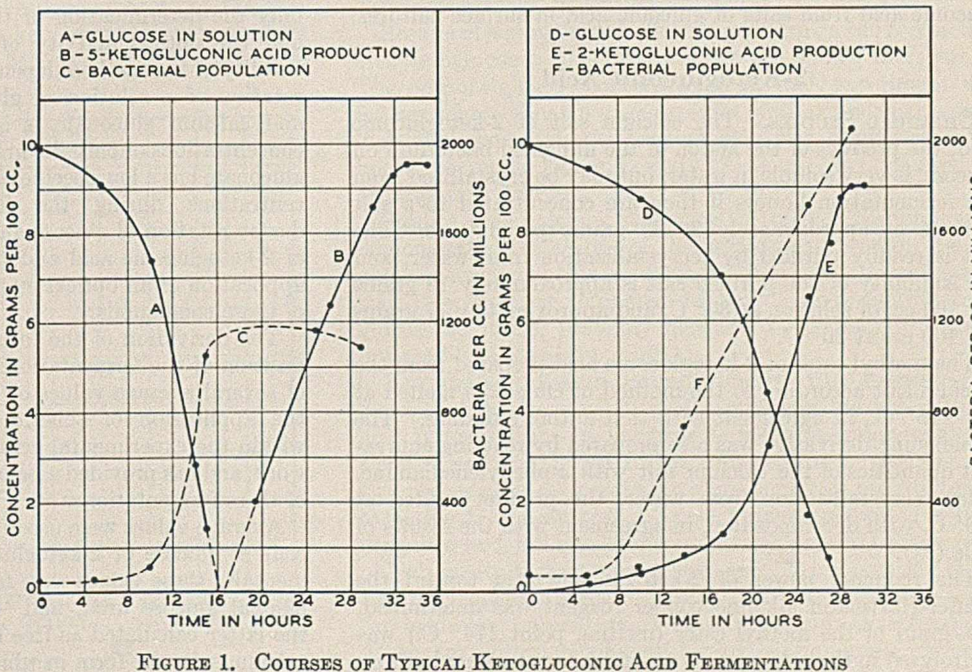

FIGURE 1. COURSES OF TYPICAL KETOGLUCONIC ACID FERMENTATIONS
Left, 5-ketogluconic acid fermentation; *right,* 2-ketogluconic acid fermentation

The limited solubility of calcium 5-ketogluconate in water permits the conclusion that no 5-ketogluconic acid is formed in the fermentation liquors until nearly all the glucose has been oxidized to gluconic acid, as will be explained later. Reducing values obtained during the first stage of the fermentation are therefore calculated to glucose, while those obtained during the second stage are calculated to 5-ketogluconic acid. The precipitation of calcium 5-ketogluconate in the form of fine granular crystals during the second stage of the fermentation requires the exercise of care in withdrawing samples for analysis, so that representative aliquots will be obtained; it has been found satisfactory to withdraw such samples while the rotary drums are in motion. To each measured sample (approximately 20 cc.) 2 cc. of concentrated hydrochloric acid were added, with stirring, to dissolve the calcium 5-ketogluconate. Aliquots of this homogeneous solution were then used for the determination of copper reduction values.

TABLE II. COPPER REDUCTION RATIOS OF GLUCOSE, 5-KETOGLUCONIC ACID, AND 2-KETOGLUCONIC ACID

Reduced Copper, Mg.	Ratios[a] Glucose	Ratios[a] 5-Ketogluconic acid	Ratios[a] 2-Ketogluconic acid	Reduced Copper, Mg.	Ratios[a] Glucose	Ratios[a] 5-Ketogluconic acid	Ratios[a] 2-Ketogluconic acid
20	1.94	1.645	1.70	160	2.08	1.65	1.80
40	2.045	1.685	1.80	180	2.07	1.65	1.79
60	2.085	1.695	1.825	200	2.06	1.64	1.775
80	2.10	1.685	1.835	220	2.05	1.635	...
100	2.10	1.68	1.83	240	2.04	1.63	...
120	2.095	1.67	1.825	260	2.03	1.625	...
140	2.09	1.66	1.815				

[a] Ratio of mg. reduced copper to mg. reducing substance.

Recovery yields of 5-ketogluconic acid at the conclusion of the fermentation period were determined by filtering off, on a sintered glass crucible, the insoluble calcium 5-ketogluconate contained in a measured volume of the suspension. The residue was washed with cold water, alcohol, and finally with ether, dried at 100° C., and weighed as $Ca(C_6H_9O_7)_2.2^1/_2H_2O$. Examination of the filtrates showed only traces of calcium 5-ketogluconate.

Fermentation Studies. The course of a typical 5-ketogluconic acid fermentation is shown in Figure 1 (left). It is evident that the conversion of glucose to 5-ketogluconic acid takes place in two definite stages—(*a*) the oxidation of glucose to gluconic acid and (*b*) the oxidation of gluconic acid to 5-ketogluconic acid. If the amount of calcium carbonate supplied to one of these submerged fermentations is slightly less than that required to neutralize the theoretical yield of gluconic acid, then at about the time nearly all the glucose is consumed, the medium is free of suspended particles of calcium carbonate or calcium 5-ketogluconate; as the fermentation continues, however, crystals of the latter salt appear in the medium in constantly increasing quantity.

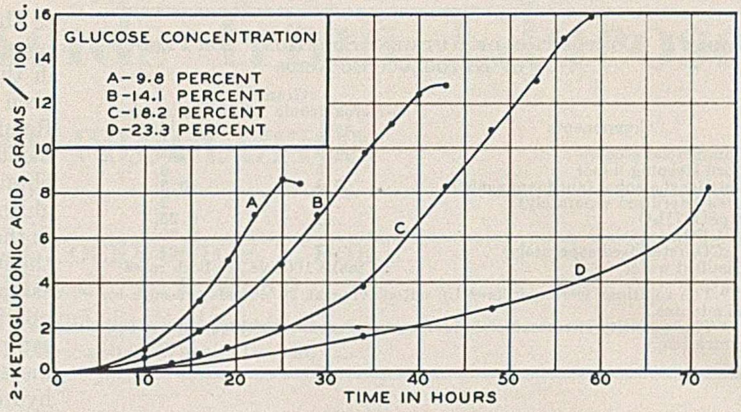

Figure 2. Effect of Concentration of Glucose on Production of 2-Ketogluconic Acid

The bacterial population increases only during the first stage and remains practically constant during the period when 5-ketogluconic acid is being formed. In the experiment represented by Figure 1 (left), 327 grams of glucose were oxidized to gluconic acid in 16 hours; during the next 17 hours 315 grams of 5-ketogluconic acid were produced. The yield of 5-ketogluconic acid was 89.5 per cent of theory, based on the glucose fermented.

Data were obtained on the effect of temperature and pressure on this fermentation process. A more rapid and more complete conversion to 5-ketogluconic acid was obtained at 25° than at 30° C. Comparison of the course of the fermentation at atmospheric pressure and at 30 pounds per square inch (2.11 kg. per sq. cm.) gage pressure indicated that little advantage was gained by employing the higher pressure.

A range of glucose concentrations was not studied because when glucose solutions containing more than about 12 grams of sugar per 100 cc. are fermented, the intermediate product, calcium gluconate, crystallizes from the medium as a "mushy" mass, which inhibits further fermentation.

When 5 per cent solutions of calcium gluconate were used as a substrate instead of glucose, the rate of production of 5-ketogluconic acid was slower, and no 2-ketogluconic acid was formed, although the production of the latter acid might have been expected in view of the report of Bernhauer and Knobloch (*6*) that *Acetobacter suboxydans* produced 2-ketogluconic acid from salts of gluconic acid in surface cultures.

2-Ketogluconic Acid

Chemical Studies. The calcium salt of 2-ketogluconic acid, the product of the action of the unnamed bacterium on glucose, is very soluble in water, but may be crystallized from the fermentation liquors if they are concentrated to a salt content of approximately 30–35 grams per 100 cc. The salt is readily purified by recrystallization from water, and the solubility of the purified salt is approximately 19 grams per 100 cc. of solution at 30° C. and approximately 17 grams per 100 cc. at 20° C.

The methyl ester of 2-ketogluconic acid prepared from the calcium salt according to the method of Ohle (*25*) melted at 174–175° C., in agreement with that author's finding. The quinoxaline derivative was also prepared by reacting equivalent quantities of the calcium salt with *o*-phenylenediamine. After recrystallization from water, the product melted at 199° C. with decomposition, in agreement with the results of Ohle (*24*).

The reducing power of 2-ketogluconic acid toward the Shaffer-Hartmann alkaline copper reagent was determined. One gram of the methyl ester (melting point 174° C.) was hydrolyzed in the cold with 48 cc. of 0.1 *N* potassium hydroxide, neutralized to phenolphthalein, and made up to 100 cc. with water. Aliquots of this stock solution were used to determine the reducing power of 2-ketogluconic acid over the range 10 to 110 mg. of acid. The results in Table II are taken from these data. On a weight basis, 2-ketogluconic acid has about 87 per cent of the reducing power of glucose toward the Shaffer-Hartmann reagent. The values reported in Table II were also checked with calcium 2-ketogluconate as the standard; complete agreement was found.

Simultaneous Analysis for Glucose and 2-Ketogluconic Acid. The course of the 2-ketogluconic acid fermentation cannot be determined by analysis for reducing sugar alone because both 2-ketogluconic acid and glucose possess reducing properties, and the acid is formed during almost the entire course of glucose utilization, as will be shown later in this paper. Similarly, a determination of soluble calcium is not indicative of keto acid formation since at times both calcium gluconate and calcium 2-ketogluconate are present in the liquors. Although glucose can be determined satisfactorily in the presence of 2-ketogluconic acid by the alkaline iodine titration method of Kline and Acree (*19*), the procedure is slow and tedious.

Consideration of this problem led to the development of a simple and rapid method for the estimation of glucose and 2-ketogluconic acid in fermentation solutions which required only the determination of the gross copper-reduction value and the optical activity of aliquots of the liquors. The validity of the method depends on the fact that the observed rotation of a solution of glucose, calcium 2-ketogluconate, and calcium gluconate is substantially dependent on the concentrations of only the first two components, since calcium gluconate has a low specific rotation and is present in low concentrations during the fermentation. The appreciable dextro rotation of glucose and the even greater levo rotation of 2-ketogluconic acid and its salts are factors favoring the application of an optical method for the analysis of mixtures of these compounds.

The derivation of the formula used to ascertain the composition of the fermentation liquor is given below. The use of several average values or approximations is involved, but the application of this formula yields results which are within the experimental error of other factors related to the work, and has provided a helpful means of following the course of these fermentations.

Average values were used for the rotation due to each 1 per cent of glucose or 2-ketogluconic acid in solution. Experimentally these values were found to be +0.55° for the commercial glucose used, and −0.88° for 2-ketogluconic acid, the latter calculated as free acid but actually determined as calcium salt, the form in which it is present in the fermentation solution:

$$\alpha = 0.55\,G - 0.88\,K \qquad (1)$$

$$CU = Cu_G + Cu_K \qquad (2)$$

Using 1 cc. sample for reducing sugar determinations:

$$G = \frac{Cu_G}{2.07 \times 10} = \frac{CU - Cu_K}{20.7} \qquad (3)$$

$$K = \frac{Cu_K}{1.80 \times 10} \qquad (4)$$

where G = glucose concentration, grams/100 cc.
K = 2-ketogluconic acid concentration, grams/100 cc.
α = observed rotation in a 1-dm. tube at approx. 23° C., angular degrees
CU = total copper reduction, as obtained in Shaffer-Hartmann determinations, mg.
Cu_G = reduced copper due to glucose, mg.
Cu_K = reduced copper due to 2-ketogluconic acid, mg.

The values 2.07 and 1.80 are average ratios of copper to glucose and of copper to 2-ketogluconic acid, respectively, over the portions of the copper-reduction curves involved—i. e., 150 to 200 mg. of copper.

Substituting Equations 3 and 4 in Equation 1,

$$\alpha = \frac{0.55(CU - Cu_K)}{20.7} - \frac{0.88\,Cu_K}{18} \qquad (5)$$

Equation 5 simplifies to

$$Cu_K = 0.353\,CU - 13.28\,\alpha \qquad (6)$$

which is the convenient form for use.

Sample Calculation. A test solution was made up to contain 5.83 per cent glucose and 3.53 per cent 2-ketogluconic acid (as its calcium salt). The experimentally found values were:

$$CU = 185.5 \text{ mg. of copper}$$

$$\alpha = +0.06°$$

Applying Equation 6,

$$Cu_K = 0.353\,(185.5) - 13.28\,(0.06) = 64.7$$

$$Cu_G = 185.5 - 64.7 = 120.8$$

$$\therefore K = \frac{64.7}{1.83 \times 10} = 3.54\% \text{ (present 3.53\%)}$$

$$G = \frac{120.8}{2.096 \times 10} = 5.76\% \text{ (present 5.83\%)}$$

The values 1.83 and 2.095 in the denominators of the two preceding equations are ratios taken from the copper-reduction curves at copper values of 64.7 and 120.8, respectively, and are considered preferable to those of 1.80 and 2.07 (average values only) used in the derivation of general Equation 6.

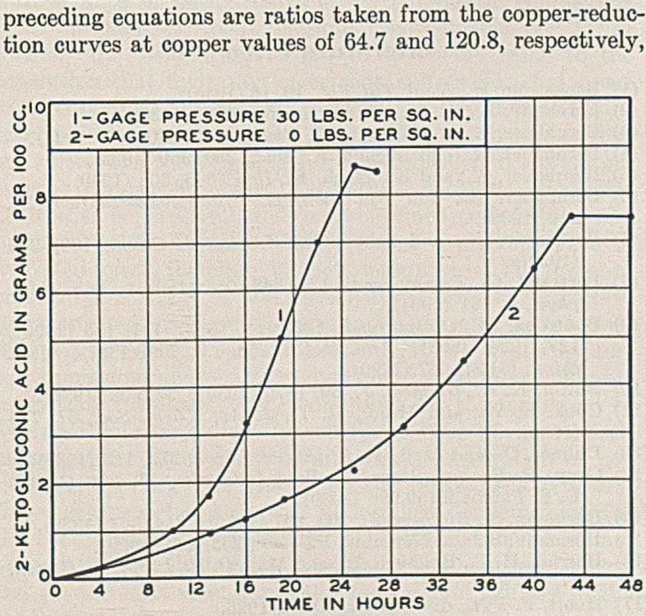

Figure 3. Effect of Air Pressure on Fermentation of Glucose to 2-Ketogluconic Acid

Fermentation Studies. The course of a typical 2-ketogluconic acid fermentation is shown in Figure 1 (right). In contrast to the 5-ketogluconic acid fermentation, where practically all of the glucose is converted to gluconic acid before 5-ketogluconic acid production begins, the formation of 2-ketogluconic acid starts early in the process, so that only a small amount of calcium gluconate accumulates in the fermentation solution. This fact makes it possible to ferment higher concentrations of glucose without precipitation of calcium gluconate before the fermentation is completed, as was the case with 5-ketogluconic acid production. Also, calcium 2-ketogluconate exerts a stabilizing influence on supersaturated solutions of calcium gluconate.

Preliminary studies in which the solutions were maintained at 25° and at 30° C. showed that, although the fermentation proceeds rapidly at either temperature, slightly higher yields are obtained at 25° C. Accordingly, subsequent experiments were conducted at this temperature.

The production of 2-ketogluconic acid when the organism was grown on glucose solutions of various concentrations was studied with the results shown in Figure 2 and Table III. A rapid conversion was obtained in all cases except where a 23 per cent glucose solution was used. The highest yield of keto acid, 87.2 per cent, was obtained in 71 hours with an initial glucose concentration of 18.2 grams per 100 cc. The initial lag periods were progressively longer as the glucose concentrations were increased, and the average rate of production of acid was much greater when less concentrated solutions of glucose were used.

Table III. Effect of Concentration of Glucose on Production of 2-Ketogluconic Acid

(Air flow, 1600 cc. per minute; pressure, 30 pounds per square inch; r. p. m., 13; temperature, 30° C.; volume of fermentation solution, 3.3 liters)

Glucose Concentration	Fermentation Period	Total Glucose Available	2-Ketogluconic Acid Produced	Yield (Based on Glucose Available)
%	*Hours*	*Grams*	*Grams*	%
9.8	25	323	284	81.7
14.1	43	465	422	84.2
18.2	71	600	564	87.2
23.3	72	769	271	32.7[a]

[a] Fermentation not completed at 72 hours.

Results of a study of the effect of pressure on the production of 2-ketogluconic acid from glucose are shown in Figure 3. The original glucose concentration in each experiment was 9.8 per cent. When a gage pressure of 30 pounds per square inch was employed, the fermentation was completed in 25 hours; a much longer period, 43 hours, was required at atmospheric pressure.

Studies with calcium gluconate as the sole carbon source demonstrated the ability of the organism to produce 2-ketogluconic acid from this compound. However, the conversion was very slow as compared to keto acid formation from glucose solutions, probably because the gluconate alone is not readily utilized for growth.

Ketogluconic Acid Production in Vat Fermenters. To determine the feasibility of conducting the ketogluconic acid fermentations in vat-type fermenters which might in some cases be preferred to the rotary drum fermenters, the two processes were operated in aluminum vats recently made available to the authors. These fermenters, which will be described in detail in a later communication, were constructed of high-purity aluminum and were capable of operation at the superatmospheric pressures which had been shown desirable for oxidative fermentations in rotary drum investigations. Means for agitating and aerating the solution under increased pressure were also provided.

In a representative 5-ketogluconic acid fermentation conducted in a vat fermenter at 25° C. and 30 pounds gage pressure, with an aeration rate of 500 cc. per minute per liter of medium, 33 liters of a 10.2 per cent glucose solution were fermented to 5-ketogluconic acid in 48 hours, with a yield of 95.4 per cent. A 2-ketogluconic acid fermentation conducted in a vat fermenter under similar conditions showed an 84.4 per cent yield of 2-ketogluconic acid from 33 liters of a 9.9 per cent glucose solution in 29 hours. The possibility of using vat fermenters for conducting these fermentations is thus apparent.

Discussion

It is significant that the culture conditions (i. e., aeration, agitation, and pressure) previously found desirable for conducting oxidative fermentations such as the oxidation of glucose to gluconic acid and that of sorbitol to sorbose, have likewise proved effective in the production of ketogluconic acids from glucose. The extension of these principles to other oxidative reactions will undoubtedly be possible in the future.

The marked difference in the sequence of keto acid production in the 2-ketogluconic acid fermentation as compared to the 5-ketogluconic acid fermentation is probably of fundamental significance. In the former case the enzyme system required to catalyze the oxidation of gluconate to 2-ketogluconate is active at the same time as is the enzyme system effecting the primary oxidation of the glucose; in the latter case, a sharp separation of these reactions is apparent. This circumstance, which exists in our submerged fermentation studies, recalls the work of Butlin (*10*) and of Kluyver and Boezaardt (*20*) on the existence of two distinct types of oxidizing systems in *Acetobacter suboxydans*. Butlin reported that either a mild or a strong oxidative activity could be called forth in the organism according to the mode of culture; the presence or absence of chalk in the medium and the age of the culture were determining factors. Kluyver and Boezaardt used a manometric technique to follow the oxygen uptake of *A. suboxydans* in a glucose medium; they found that the first half of the oxygen was consumed at a rapid rate while the second half was consumed at a much slower rate. Since the total oxygen uptake corresponded to the quantity of this gas needed to convert the available glucose to 5-ketogluconic acid, it was concluded that the oxidation proceded in two stages—(*a*) the oxidation of glucose to gluconic acid and (*b*) the oxidation of gluconic acid to ketogluconic acid. The reducing action of the system was almost nil when half the total quantity of oxygen had been absorbed. The results obtained in our submerged fermentations are in complete accord with these findings. The cessation of bacterial growth (Figure 1, left) would appear to indicate that the enzymic activity involved in 5-ketogluconic acid production from gluconic acid is derived from nonproliferating cells. Portion *B* of Figure 1 represents one of the most rapid secondary oxidation phases encountered in our studies; usually this second phase proceeds at a rate considerably slower than the first phase.

Under the conditions used in our work, specificity of the organism is the factor deciding whether 2-ketogluconic or 5-ketogluconic acid will be produced, rather than the initial substrate, as claimed by Bernhauer and Knobloch. A more definite characterization of our 2-ketogluconic acid-producing organism is now being undertaken, with the hope that its identification will provide an explanation of such results.

Several uses have been suggested for 2-ketogluconic and 5-ketogluconic acids. Recent patents (*28*) describe a process for the catalytic hydrogenation of calcium 5-ketogluconate to a mixture of calcium *l*-idonate and calcium *d*-gluconate. The use of this mixture in calcium therapy is suggested, since the mixture is more soluble than calcium gluconate. 5-Ketogluconic acid was oxidized by Barch (*2*) to a mixture of tartaric, trihydroxy glutaric, and oxalic acids, using nitric acid in the presence of vanadium. A refinement in the oxidation of 5-ketogluconic acid, leading to a practical method for obtaining *d*-tartaric acid, was patented recently by Pasternack and Brown (*29*).

Calcium 2-ketogluconate gives promise of industrial utilization, since it may be converted readily and in good yield to *d*-araboascorbic acid (isovitamin C) (*22*, *27*), which is reported to possess approximately one twentieth to one fortieth as much antiscorbutic activity as *l*-ascorbic acid (*12*, *22*). The use of this analog of ascorbic acid has been suggested as an antioxidant in foods and other products (*13*) and as a developing agent in photography (*1*, *26*, *30*, *31*).

Summary

The oxidation of glucose to 5-ketogluconic acid by *Acetobacter suboxydans* and to 2-ketogluconic acid by an unnamed bacterium were studied in rotary drum fermenters. Desirable operating conditions are vigorous agitation and aeration under pressure.

The 5-ketogluconic acid fermentation takes place in two distinct stages: the first, in which glucose is oxidized to gluconic acid, and the second, in which gluconic acid is further oxidized to 5-ketogluconic acid. The second stage does not begin until the first stage is substantially complete. The bacterial population increases during the first stage but not during the second. Approximately 90 per cent yields of 5-ketogluconic acid were obtained from 10 per cent solutions in 33 hours.

In the 2-ketogluconic acid fermentation, keto acid formation occurs simultaneously with glucose utilization, and bacterial growth occurs during the entire fermentation period. Approximately 82 per cent yields of 2-ketogluconic acid were obtained from 10 per cent glucose solutions in 25 hours.

Both ketogluconic acid fermentation processes were successfully conducted in vat fermenters.

A method based on polarimetric data and copper-reduction values was developed for the rapid analysis of fermentation liquors for glucose and 2-ketogluconic acid.

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Composition and Properties of Superphosphate

Conditions Affecting the Distribution of Water, with Special Reference to the Calcium Sulfate Constituent[1]

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Calcium sulfate is the principal potential carrier of water of crystallization in ordinary superphosphate. The form (anhydrous or hydrated) in which this compound occurs in superphosphate is governed largely by the concentration and temperature of the sulfuric acid used in the mix. Anhydrite predominates in commercial superphosphate; usually only meager quantities of hydrated forms are present. Underacidulation favors the occurrence of hydrated forms; drying subsequent to granulation has the opposite effect and may be carried to the point of dehydration of the monocalcium phosphate. Ammoniation is conducive to the hydration of calcium sulfate in superphosphate, and very marked hydration occurs when aqueous ammonia is used.

IN A PREVIOUS paper from this laboratory (*11*) anhydrite was shown by chemical analysis and x-ray diffraction pattern examinations to be the predominant form of calcium sulfate in both fresh and aged domestic commercial superphosphates. About the same time Lehrecke (*14, 15*) in Sweden and Belopol'skiĭ *et al.* (*2*) in Russia came to the conclusion that hydration of calcium sulfate does not occur in superphosphate. Several years earlier Pratolongo (*20*) in Italy found by chemical and microscopic examinations that anhydrite was the principal form of the calcium sulfate occurrent in superphosphate. All of the fore-mentioned studies dealt with superphosphates that contained anhydrite as the principal calcium sulfate; the effect of a predominance of hydrated forms, therefore, was not determined. The presence of small quantities of the hemihydrate and the dihydrate (gypsum) in some commercial materials indicates that at some time, either during the manufacturing process or during storage, these superphosphates existed under conditions favorable to hydrate formation. The conditions for the formation of hydrated calcium sulfate in superphosphate have not been investigated. Since either hydration or dehydration of calcium sulfate may give rise to setting phenomena (*18, 21*), the study reported here was undertaken to determine (*a*) the conditions under which the hydrates of calcium sulfate may be formed during the manufacture of superphosphate and (*b*) the relative stabilities of the calcium sulfates in the products.

General Considerations

When ground phosphate rock and sulfuric acid are mixed and stirred for a brief period, the temperature rises rapidly. Initially the liquid phase is aqueous sulfuric acid. Shortly, however, the small amount of liquid relative to the total bulk consists principally of aqueous phosphoric acid saturated (or supersaturated) with monocalcium phosphate. The rapid formation of calcium sulfate that accompanies this stage of the process, therefore, takes place under rapidly changing

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[1] For previous papers in this series see literature citations *9-12, 16, 17.*

TABLE I. ANALYSIS OF INGREDIENT PHOSPHATE MATERIALS (AIR-DRY BASIS)

Sample No.	Type or Source of Phosphate	P_2O_5, %	CaO, %	MgO, %	Fe_2O_3[a], %	Al_2O_3, %	Na_2O, %	K_2O, %	SO_3[b], %	CO_2, %	F, %	H_2O at 105° C., %	H_2SO_4 Required for 100% Imposed Acidulation (v), Parts/100 Parts Phosphate
1225	Bone ash	40.46	54.18	1.10	....	....	0.93	c	0.36	0.70	0.05	0.18	70.4
912	Fla. land pebble	35.19	48.80	0.08	0.70	1.05	0.15	0.11	0.20	1.47	3.71	0.53	62.8
908[d]	Tenn. brown rock	34.30	49.00	0.02	2.51	1.16	0.19	0.26	0.70	1.95	3.79	0.43	64.6
1253	Idaho	32.95	46.06	0.31	0.86	1.15	0.71	c	1.59	1.70	3.25	0.95	59.4

[a] Total Fe. [b] Sulfate soluble in 1:4 hydrochloric acid. Included in figure for Na_2O. [d] Contained 0.13 per cent MnO.

TABLE II. EFFECT OF CONCENTRATION OF SULFURIC ACID AND TYPE OF PHOSPHATE ON THE FORM OF CALCIUM SULFATE IN DAY-OLD SUPERPHOSPHATE[a]

H_2SO_4 Concn. Per cent	° Bé. at 15.56° C.	Bone Ash: Maximal Temp., ° C.	Bone Ash: Identified Ca Sulfates[b]	Land Pebble: Maximal Temp., ° C.	Land Pebble: Identified Ca Sulfates[b]	Brown Rock: Maximal Temp., ° C.	Brown Rock: Identified Ca Sulfates[b]	Idaho Rock: Maximal Temp., ° C.	Idaho Rock: Identified Ca Sulfates[b]
53.66	44	77.5	H, G	60	H, tr. G.	..	...	52	H, G
56.48	46	83	H	..	...	..	...	52	H, tr. G
59.32	48	86	H	64	H	58	H	54	H
62.18	50	89	A, H[c]	68	H	59	H	54	A, H[b]
63.66	51	92	A, tr. H	72	H, A[c]	61	A, H[c]	..	...
65.13	52	94	A	78	A, H[c]	66	A, H[c]	64	A, H[b]
66.63	53	98	A	86	A, tr. H	83	A., tr. H	..	...
69.65	55	105	A	86	A	84	A, tr. H	80	A, tr. H

[a] Temperature of ingredients, 20° to 30° C.; imposed acidulation, about 100 per cent.

[b] Anhydrite, $CaSO_4.{}^1/_2H_2O$, and $CaSO_4.2H_2O$ are indicated by A, H, and G, in the descending order of the amounts present. Wherever a compound was barely detectable, its symbol is preceded by tr.

[c] In other runs with sulfuric acid at 60° C. or above, where the maximal temperature was 95° to 98° C., the products contained anhydrite with very little or no hemihydrate.

conditions of temperature and solution composition, and for this reason data (*1*, *23*, *24*) relating to the solubility of calcium sulfate in phosphoric acid do not forecast the forms of calcium sulfate that appear in superphosphate. Surface coatings of stable compounds may result in the prolonged existence of unstable forms. Furthermore, soluble salts are known to have a marked effect on the rate of hydration of $CaSO_4.{}^1/_2H_2O$ (*25*). Phosphates delay the change, whereas sulfates in concentrated solution promote it. Helpful general conclusions as to the probable appearance and stability of the different forms of calcium sulfate in superphosphate can be drawn from the phase data for the systems $CaSO_4$–H_2O (*8*, *19*) and CaO–P_2O_5–SO_3–H_2O (*3*, *4*).

Superphosphate simulating closely the commercial product can be prepared in small batches in the laboratory. During the mixing of the ingredients the temperature of the mixture rises rapidly to a maximum and then drops slowly. Obviously, under otherwise uniform conditions the maximal temperature, which is observable within 2° to 3° C., depends upon (*a*) the initial temperature of the ingredients, (*b*) their relative proportions or the degree of acidulation, (*c*) the concentration of the ingredient acid, and (*d*) the character of the ingredient phosphate. The terms "ingredient acid" and "ingredient phosphate" refer to the acid and phosphate rock in the condition in which they are delivered to the mixer. The degree of imposed acidulation (*v*) is expressed in per cent of the difference between the sum of the acid equivalents of the total CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, Na_2O, and MnO regarded as monobasic phosphates, and that of the P_2O_5 in the ingredient phosphate (*16*, *17*).

The first three factors can be varied at will. The fourth, character of the ingredient phosphate, includes several variables, none of which has been studied to any extent, if at all. They are: proportion of substances other than calcium phosphate in the phosphate rock—for example, compounds of silicon, aluminum, and iron, which affect the total heat liberated; possible differences, structural or chemical, in the apatitelike phosphate compound itself; and rate of reaction. The present study does not permit the differentiation of their separate effects.

Materials and Methods

The superphosphates were prepared in 100-gram lots in the laboratory from 100-mesh samples of bone ash, Florida land pebble, Tennessee brown rock, and Idaho rock, respectively, and C. P. sulfuric acid brought to the desired concentration with distilled water. The analyses of the raw phosphates and the amounts of sulfuric acid required for complete acidulation are given in Table I. The preparations were made by the procedure outlined in a previous article (*17*). The raw phosphate (always at room temperature) was added to a 150-cc. beaker (tall form without lip) containing the acid at the chosen temperature, and the mixture was stirred with a thermometer until the maximal temperature was reached (about 3 minutes). The beaker was then closed with a stopper carrying an open glass tube (25 cm. long) and placed in an electrically heated oven set to operate at the observed maximal temperature. At the end of 5 hours the superphosphate was removed from the oven and exposed in a thin layer (0.5 inch or 1.27 cm.) to the air overnight. The product was then put through a 20-mesh sieve and stored in a tightly stoppered bottle at room temperature (20° to 30° C.).

The water, exclusive of water of constitution in sulfuric acid, in the ingredients amounted to 33 to 37 parts per 100 parts of rock for acidulations close to 100 per cent. Of this water, 34 to 46 per cent was volatilized during the preparation of the superphosphate. In the series of preparations (Table V) at different degrees of acidulation, the water in the ingredients ranged from 28 to 36 parts per 100 parts of rock, and 37 to 76 per cent was volatilized. The loss of water increased with a decrease in the acidulation and occurred for the most part during the exposure of the product in a thin layer.

In the study of the effect of the initial temperature of the sulfuric acid, the maximal temperature of some of the runs was below 30° C. Thus, when the acid was cooled to 0° C., the maximal temperature of the mixture was 20° to 25° C. The resultant preparations were allowed to stand at room temperature for a 5-hour period before they were spread out to dry overnight. By cooling the acid to 0° C. and keeping the container immersed in an ice bath, the maximal temperature was only 10° C., in which case the mixture was aged 5 hours at this temperature.

The free acid (*10*), free water (*12*), and crystal water were determined in the day-old superphosphates and also after 30 and 90 days.

Water of crystallization was determined on the sample from which the free water and acid had been removed by ether extraction (*10*, *12*). The extracted sample was weighed to determine the loss of weight on extraction and then transferred to a platinum dish, reweighed, and heated overnight in an oven at 120° C. The loss in weight at 120° C. represents water of crystallization plus a few tenths per cent of fluorine. Fluorine was determined

TABLE III. EFFECT OF TEMPERATURE AND CONCENTRATION OF SULFURIC ACID ON THE FORM OF CALCIUM SULFATE AND THE DISTRIBUTION OF WATER IN DAY-OLD SUPERPHOSPHATE[a]

H_2SO_4		Maxima Temp. of Mixt., ° C.	Identified Ca Sulfates[b]	Water of Crystallization[c], %	Compn. of Liquid Phase			Atmospheric Condition
Temp., ° C.	Concn., % (° Bé.)				Free water[c], %	Free H_3PO_4[c], %	Concn. of aqueous H_3PO_4, %	
0	53.66 (44)	10[d]	G	12.2	13.9	10.8	44	Humid
	62.18 (50)	10[d]	G, H	9.4	13.0	10.6	45	Humid
	69.65 (55)	10[d]	A, H	1.9	11.4	12.8	53	Dry
0	53.66 (44)	23	G, tr. H	14.7	16.6	12.6	43	Humid
	62.18 (50)	23	G, H	9.3	10.2	12.1	54	Dry
	69.65 (55)	25	A, H	2.2	9.2	13.0	59	Dry
25–30	53.66 (44)	60	H, G	5.4	19.5	12.5	39	Very humid
	62.18 (50)	68	H	4.4	15.2	10.7	41	Humid
	66.63 (53)	95	A, tr. H	1.4	10.5	11.1	51	Dry
	69.65 (55)	95	A, tr. H	1.4	16.8	11.1	40	Very humid
60	53.66 (44)	95	H	4.1	8.3	10.6	56	Dry
	62.18 (50)	95	A, H	3.1	6.2	9.8	61	Humid
	69.65 (55)	95	...	1.4	7.9	10.5	57	Very humid

[a] Florida land-pebble rock was used; imposed acidulation was 103 per cent.
[b] Table II gives meaning of symbols.
[c] Result expressed in per cent of water-free superphosphate.
[d] The reaction vessel was kept in an ice bath while the ingredients were mixed.

in the oven-dry sample, the ether extract, and the original superphosphate to ascertain the amount volatilized in the oven. The volatilized fluorine was obtained by difference. The difference between the loss in weight in the oven in per cent of the superphosphate and the amount of volatilized fluorine is taken as a measure of water of crystallization.

The foregoing procedure gives the water of crystallization held by calcium sulfate, by monocalcium phosphate, and by complex monobasic phosphates of the type, $CaO.R_2O_3.2P_2O_5.8H_2O$, discussed in a previous article (*17*). It is therefore applicable to the classes of ordinary superphosphate prepared in this study. The procedure is not applicable to the determination of water of crystallization of products that contain hydrated dicalcium phosphate, because only a fraction of the water in this salt is expelled by drying in an oven at 120° C. (*11*). The same would be true of products that contain ardealite, $CaSO_4.CaHPO_4.4H_2O$*. Halla (*5*) suggested that this double salt may play the role of an intermediate compound in the decomposition of phosphate rock by means of sulfuric acid. The authors are aware of no evidence indicating its presence in ordinary superphosphate. Conditions far more favorable to its formation prevail in ammoniated superphosphate.

The forms of calcium sulfate in the superphosphates were identified by x-ray diffraction methods. The details and limitations of this technique as applied to superphosphate are contained in the report of a previous study (*11*), which showed close correlation between the results by x-ray diffraction examination and the determined values for water of crystallization.

Effects of Acid Concentration and of Phosphate Type

An increase in the concentration of the sulfuric acid resulted in a higher temperature in the mixing vessel (Table II). Furthermore, the temperature attained by the mixtures varied with the type of phosphate, decreasing in the order bone ash, land pebble, brown rock, and Idaho rock. Hemihydrate was the predominant calcium sulfate in products prepared by the use of dilute acids, but anhydrite appeared with smaller amounts of the hemihydrate in products obtained with acid in the concentration range 62 to 65 per cent, corresponding to 50° to 52° Bé. The first appearances of anhydrite were at the respective maximal temperatures of 89°, 72°, 61°, and 54° C. for products prepared from bone ash, land pebble, brown rock, and Idaho rock. With higher concentrations of sulfuric acid the hemihydrate tended to disappear.

Effect of Acid Temperature

The experiments of the preceding section were supplemented by a few that were made under threshold conditions for anhydrite formation. The results (footnote [e], Table II) show that when the initial temperature of the acid was 60° C., the hemihydrate content of the product was nil or only a trace. Furthermore, when the more dilute acid was cooled to 0° C., the product contained the dihydrate as the predominant form (Table III).

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* A specimen of the natural ardealite used in previous work (*11*) was supplied by E. P. Henderson of the National Museum. This sample, dried overnight at 120° C., lost only 1.64 per cent of water, whereas the loss on ignition at 600° C. was 23.76 per cent.

TABLE IV. CONDITIONS PREVAILING IN COMMERCIAL MANUFACTURE OF ORDINARY SUPERPHOSPHATE IN THE UNITED STATES[a]

Manufacturer No.	Ingredient H_2SO_4		Mixing-Pan Conditions				Maximal Temp.[b], in Den[e], ° C.
	Temp.[b], ° C.	Concn.[c], % (° Bé.)	% P_2O_5 in rock	Parts acid/100 parts rock	Imposed acidulation (*v*)[d], %	Maximal temp.[b], ° C.	
			Florida Land-Pebble Superphosphate				
9	33.9	71.17 (56.0)	33.3	82.7	94–98	85.6	109.4
10	44.0	69.65 (55.0)	35.0	84.8	93–95	110.0	106.7
3	54.4	69.95 (55.2)	32.0	83.5	93–100	110.0	110.0
2	54.4	69.65 (55.0)	32.8	86.0	95–101	116.7	107.2[f]
1	43.3–54.4	70.87 (55.8)	33.0	95.0	105–112	[g]	104.4
4	48.9–54.4	71.17 (56.0)	33.0–33.5	84.4	95–100	115.6	[g]
5	48.9–60.0[h]	69.65–71.17 (55–56)	33.7	83.2	93–97	[g]	[g]
6	54.4–60.0	69.65 (55.0)	33.5–34.0	93.8	103–108	112.8	107.2–110.0
			Tennessee Brown-Rock Superphosphate				
5	48.9–60.0	69.65–71.17 (55–56)	[g]	89.3	...	[g]	[g]
8	54.4	68.13 (54.0)	34.3	90.8	96–99	82.2	110.0
7	54.4–60.0	68.89 (54.5)	33.5	90.2	98–101	121.1–126.7	96.1–98.9
10	71.1	70.11 (55.3)	33.5	89.1	99–102	112.8	104.4[i]

[a] The data were obtained in June, 1938, by K. D. Jacob of this bureau in correspondence with a number of large producers of superphosphate.
[b] Reported in ° F.
[c] Reported in ° Bé. at 15.56° C., corrected to represent true acidity.
[d] Figures given by Marshall and Hill (*16*).
[e] Unless indicated otherwise, a nonmechanical den was used.
[f] Sturtevant den. [g] Not reported.
[h] Desired temperature is 48.9° C., but in zero weather it may be as low as 27° C.
[i] Svenska den.

TABLE V. EFFECT OF DEGREE OF ACIDULATION AND AGE ON THE FORM OF CALCIUM SULFATE AND THE DISTRIBUTION OF WATER IN SUPERPHOSPHATE[a]

					Water of Crystallization, %		Compn. of Liquid Phase, %		
Superphosphate No.	Imposed Acidulation (v), %	Maximal Temp. of Mixt., ° C.	Age of Superphosphate, Days	Identified Ca Sulfates[b]	In excess of $Ca(H_2PO_4)_2 \cdot H_2O$[c,d]	Total[c]	Free water[c]	Free H_3PO_4[c]	Concn. of aqueous H_3PO_4
M-5	107	86	1	A, tr. H	−0.25	1.40	10.45	11.11	52
			90	A, H	0.44	2.23	8.88	10.20	54
M-4	102	84	1	A, tr. H	0.04	1.83	10.37	9.87	49
			100	A, H	1.27	3.17	9.50	7.88	45
M-3	96	80	1	A	−0.92	1.06	7.63	6.35	45
			90	A, H	1.48	3.87	6.70	3.50	34
M-2	91	80	1	A, H	−0.36	1.78	4.12	4.65	53
			90	A, H	1.92	4.50	2.14	0.84	28
M-1	86	80	1	A, H	0.36	2.51	1.51	3.61	71
			90	A, H	0.68	3.08	1.20	1.44	55

[a] Land-pebble rock was acidulated with 66.63% (53° Bé.) acid; temperature of ingredients, 20° to 30° C.

[b] Table II gives meaning of symbols.

[c] Result expressed in per cent of water-free superphosphate.

[d] Content of $Ca(H_2PO_4)_2.H_2O$ calculated from difference between water-soluble and free-acid P_2O_5.

The results by x-ray diffraction methods are in essential agreement with the determined percentages of water of crystallization. The concentration of the ingredient acid governed the appearances of the dihydrate and anhydrite; the greater the acid concentration, the greater was the quantity of anhydrite in the product. In the case of products obtained with sulfuric acid at 0° C. (Table III), the maximal temperatures are about the same and are well below the gypsum-anhydrite transition point (42° C.) in the system $CaSO_4$-H_2O (*8*, *13*, *19*). These results, therefore, demonstrate the effect of sulfuric acid concentration of the form of calcium sulfate that occurs in the product. A similar relation involving the hemihydrate and anhydrite is manifested at the higher temperatures.

In many instances (Tables II and III) two forms of calcium sulfate were observed, even when the imposed conditions as to initial acid concentration and maximal temperature would be expected to preclude the presence of the minor phase. This behavior is attributable to the fact that calcium sulfate precipitation occurs under varying conditions and takes place over a wide range of temperature. It is therefore probable that the small amount of hemihydrate frequently found associated with anhydrite separates first and then persists in the superphosphate as a consequence of a sluggish change from hemihydrate to anhydrite or to the dihydrate. The traces of the dihydrates sometimes observed in very old commercial superphosphates probably owe their presence to the slow hydration of meager quantities of the hemihydrate formed during acidulation.

According to the available data (Table IV) the temperatures that obtain in batch operations in industry are usually considerably higher (15° to 30°) than the highest of those noted in the laboratory experiments reported here. The higher temperature favors anhydrite formation and practically precludes the occurrence of hydrated forms of calcium sulfate in most commercial superphosphates produced in this country.

Effect of Degree of Acidulation

A series of superphosphates was prepared with the use of land-pebble rock and 66.63 per cent (53° Bé.) sulfuric acid to determine the effect of the degree of acidulation (acid-rock ratio) on the form in which the calcium sulfate precipitates. The results (Table V) show a small decrease in the maximal temperature with lowering of the degree of acidulation. The results of x-ray diffraction analysis and the analytically determined amounts of water of crystallization indicate the occurrence of hemihydrated calcium sulfate in underacidulated (less than 100 per cent) superphosphate after one day; this is in agreement with Pratolongo's observation (*20*) of the effect of decreasing the proportion of ingredient sulfuric acid.

Persistence of Several Forms of Calcium Sulfate in Superphosphate

Since gypsum in contact with 45.35 per cent H_3PO_4 is transformed into anhydrite at 25° C. (*1*), it may be assumed that anhydrite is the stable form of calcium sulfate in a superphosphate that contains free H_3PO_4 of that concentration. The anhydrite in such a superphosphate would not be expected to undergo hydration at 25° C. or above. The foregoing condition is met by many of the superphosphates given in Tables III and V and also by some commercially prepared materials (*9*). Nevertheless, the actual persistence of the hydrated forms can be determined only by experiment. To this end a study was made of the changes that occur when superphosphates are aged, granulated, and ammoniated.

Although the results of Table V as to the influence of aging are not conclusive as to temperature effects because of the wide variation in storage temperatures (20° to 30° C.), they do show a definite tendency toward hemihydrate formation. This is especially true of the products in which the proportion of free acid to free water became less than that in 45 per cent phosphoric acid. Some of the day-old superphosphates contained an insufficient quantity of water of crystallization to account for complete hydration of the monocalcium phosphate. This condition, previously observed in double superphosphate (*11*), is indicated by negative signs in the sixth column of Table V.

Hardesty and Ross (*7*, *22*) granulated superphosphate several years old by adding sufficient water to increase the free water to about 15 per cent, then granulating, and drying the

TABLE VI. EFFECT OF GRANULATION ON THE FORM OF CALCIUM SULFATE AND THE DISTRIBUTION OF WATER IN COMMERCIALLY PREPARED SUPERPHOSPHATE

			Water of Crystallization, %		Compn. of Liquid Phase, %		
Superphosphate No.	Nature of Superphosphate	Identified Ca Sulfates[a]	In excess of $Ca(H_2PO_4)_2 \cdot H_2O$[b,c]	Total[b]	Free water[b]	Free H_3PO_4[b]	Concn. of aqueous H_3PO_4
1[d]	Not granulated	A, tr. G	3.28	5.34	0.48	0.41	46
	Granulated[e]	A	0.99	2.96	1.66	1.04	38
2[f]	Directly from den	A	−0.47	1.64	9.10	5.05	36
	Before granulation	A	−0.31	1.68	8.55	4.15	33
	After granulation[g]	A	−1.01	0.91	3.10	5.16	62

[a] Table II gives meaning of symbols.

[b] Result is in per cent of water-free superphosphate.

[c] Content of $Ca(H_2PO_4)_2.H_2O$ calculated from the difference between the water-soluble and free-acid P_2O_5.

[d] This superphosphate was several years old.

[e] The granulated material was prepared by J. O. Hardesty of this bureau. Before granulation the free water was increased to about 15 per cent by sprinkling (*7*, *22*).

[f] Florida land-pebble superphosphate. The samples were kindly furnished by a prominent superphosphate producer.

[g] Granulated on a commercial scale.

product at 75° C. This treatment (Table VI, superphosphate 1) converted the small amount of hydrated calcium sulfate into anhydrite, decreased the water of crystallization by nearly one half, and yielded a product that contained more free water and free acid than the ungranulated superphosphate. A similar change in the water of crystallization (superphosphate 2) accompanied granulation in a fresh commercial superphosphate (96 to 99 per cent acidulation). In this case, however, the decrease in water of crystallization was attributable to the dehydration of monocalcium phosphate. Prior to granulation the total water of crystallization was insufficient for the complete hydration of this constituent. Furthermore, in the granulation of the commercial product the relatively large decrease in free water by volatilization was accompanied by an appreciable increase in the free acid.

Table VII. Effect of Ammoniation on the Form of Calcium Sulfate in Flordia Land-Pebble Superphosphate

Superphosphate No.	Water-Sol. P_2O_5, %	Ammonia Source[a]	Decrease in Water-Sol. P_2O_5 with Ammoniation[b], %	% Water of Crystallization after: 1 day	90 days	180 days	Identified Ca Sulfate[c] after: 1 day	90 days
		Superphosphate Prepared in the Laboratory[d]						
3[e]	18.97	Not ammoniated	...	3.70	....	4.95	H	..
	13.12	Anhydrous NH_3	5.3	3.70	3.70	3.92	H	H
	13.82	Aqueous NH_3	3.3	4.28	8.08	8.18	H, tr. A	H, G
4[f]	19.95	Not ammoniated	...	1.57	....	3.10	A, tr. H	A, H
	14.01	Anhydrous NH_3	5.4	2.27	2.61	2.91	A, H	A, H
	15.17	Aqueous NH_3	2.8	1.68	5.50	5.67	A, H	A, G
		Superphosphate Prepared and Ammoniated Commercially						
5[g]	...	Not ammoniated	...	1.57	2.67	....	A	A
	...	Anhydrous NH_3	...	1.68	1.98	....	A	A

[a] NH_3 absorbed, 2.2 to 3.3 per cent.
[b] Result is in per cent of ammoniated material.
[c] Table II gives meaning of symbols.
[d] Ammoniation of these materials was by J. O. Hardesty and L. F. Rader, Jr., of this bureau.
[e] Acidulation, 90% with 62.18% (50° Bé.) acid; temperature of acid, 20° to 30° C.
[f] Acidulation, 90% with 66.63% (53° Bé.) acid; temperature of acid, 20° to 30° C.
[g] Superphosphate was several weeks old at the time of ammoniation.

The introduction of 2 to 3 per cent of ammonia into a superphosphate (*6*) affords conditions that are more favorable to changes in the state of hydration of the calcium sulfate constituents, especially when aqueous solutions of ammonia are used. The occasional hardening of superphosphate after ammoniation with ammonia liquors has been attributed to hydration of calcium sulfate hemihydrate, which was assumed to be the predominant calcium sulfate phase in the superphosphate. (At least two such instances of hardening have been reported to this laboratory during the past few years.) Accordingly, laboratory-prepared superphosphates containing the hemihydrate or anhydrite as the predominant calcium sulfate were studied after ammoniations with anhydrous and aqueous forms of ammonia. The results and also data obtained on commercial superphosphate are given in Table VII.

The superphosphates ammoniated with anhydrous ammonia did not show marked changes in water of crystallization, either immediately or after aging. There was a tendency toward an increase, but the differences were too small to be detected by x-ray diffraction methods. On the other hand, when aqueous ammonia was used, the observed water of crystallization increased slightly upon ammoniation and markedly upon aging. Alteration of the amount of water of crystallization during ammoniation arises principally from the decomposition of monocalcium phosphate, which is at least partially hydrated, and from other reactions—namely, (*a*) either hydration or dehydration of calcium sulfate, (*b*) formation of hydrated dicalcium phosphate, and possibly (*c*) formation of ardealite, $CaHPO_4.CaSO_4.4H_2O$. The immediate problem is to determine which of these possibilities is the most probable.

The change in water-soluble phosphorus upon ammoniation gives a measure of the maximal amount of dicalcium phosphate or of ardealite that can be present in the ammoniated product. For example, the change in the water-soluble P_2O_5 content of superphosphate 3 (Table VII) was 3.3 per cent of the ammoniated material, and the water-soluble phosphorus in the sample did not change appreciably with age. The increase in water of crystallization would amount to 1.7 per cent if it were caused by the formation of $CaHPO_4.2H_2O$, and 3.4 per cent if it were caused by the formation of $CaHPO_4.CaSO_4.4H_2O$, against an observed increase of 3.8 per cent with age. This comparison shows that neither hydration of dicalcium phosphate nor formation of ardealite can account for the observed change in crystal water. This finding is supported by the fact that the analytical method gives only a fraction of the water of crystallization held in those compounds. It is therefore concluded that hydration of calcium sulfate is mainly responsible for the increase in the crystal water content of ammoniated superphosphate prepared with aqueous ammonia. This conclusion is also supported by the results of x-ray diffraction analysis, although that examination is not conclusive as to the presence of calcium sulfate dihydrate because of the close similarity of its pattern and those of hydrated dicalcium phosphate and ardealite. The results by x-ray diffraction pattern analysis do, however, demonstrate that anhydrite participated in the transition of water of crystallization to the extent of hemihydrate formation (Table VII, superphosphate 4).

The fact that the hydration of calcium sulfate was far more pronounced in the superphosphates treated with aqueous ammonia than in nonammoniated superphosphate (Table V) is to be attributed to the difference in composition of the solution phases. The radical alteration of the solution phase by ammoniation was conducive to hydration, whereas the water added with the ammonia made possible the extensive hydration observed.

Afterhardening of Superphosphate

Previous work has shown that anhydrite is the predominant calcium sulfate in commercial ordinary superphosphate. This form is the one which is stable in many superphosphates above 25° C. It follows that hydration of calcium sulfate is not a general cause of afterhardening of superphosphate at temperatures above 25° C. Disregarding the qualification as to temperature, this conclusion is identical with that of Lehrecke (*15*). Monocalcium phosphate is therefore to be regarded as the principal participant in the hardening of ordinary superphosphate. This view is also supported by the fact that considerable hardening frequently occurs in double superphosphate of meager sulfate content.

The manner in which monocalcium phosphate may bring about hardening cannot be determined without further study. Lehrecke (*15*) attributed afterhardening to the progressive crystallization of a monocalcium phosphate gel formed in the early stages of the manufacturing process. Gel formation in superphosphate has, however, not been demonstrated. In some cases, hardening can be attributed to hydration of monocalcium phosphate, either that separated initially in the anhydrous condition or that formed by a subsequent drying operation. According to observation thus far made, however, the occurrence of this anhydrous salt in fresh ordinary superphosphate is not sufficiently widespread to justify the conclusion that its hydration is a common cause of superphosphate hardening.

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Active Carbon from Cottonseed Hull Bran

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Laboratory experiments have demonstrated that carbons with high adsorptive capacities can be prepared from carbonized cottonseed hull bran by activation with superheated steam. The adsorption of iodine and methylene blue increases as the weight loss during activation increases. The phenol adsorption power is improved by treatment of the carbons with dilute mineral acids. The acid-extracted carbons conform to the specifications of purity and activity required for water purification and for medicinal use.

COTTONSEED hull bran is a by-product obtained in the manufacture of hull fibers. About two million tons of cottonseed hulls are produced annually in the United States, only a fraction of which is now reduced to hull bran. Although many uses have been proposed (*5*) for hulls and hull bran, none except the sweeping compound (*6*) developed recently has shown much promise of success. At present these products are utilized principally as diluents for cottonseed meal in stock feeds.

Basore and Schweickhardt (*3*) in 1931 examined a hull bran residue, remaining after extraction of xylose, as a raw material for the manufacture of activated carbon and reported promising results on the basis of iodine adsorption alone. They did not, however, employ the untreated hull bran. So far as we are aware, this possibility has never been investigated.

There are various opinions concerning the relative merits of steam, air, and other gases as activating agents. Dense, granular forms of carbon, such as coconut shell carbon, are generally produced by steam activation; but for the preparation of some powdered carbons, such as water purification grades, air is also utilized. In Europe flue gases are widely used.

The experimental work described here establishes the fact that activated carbon of excellent quality for water purification and medicinal use can readily be produced from cottonseed hull bran by steam activation.

Carbonization and Activation

Divers methods have been developed for the production of active carbons. The most generally used and perhaps the most successful of these processes consists of a preliminary heating operation for the deposition of primary carbon, followed by treatment with an oxidizing gas, such as steam, air, or carbon dioxide. The first step is referred to as carbonization, the second, as activation.

CARBONIZATION. An alloy steel retort fitted with a tight screw top was used for the carbonization experiments. The evolved gases escaped through a tar line attached to the top of the retort. Reasonably constant temperatures were obtained with an electrically controlled heating unit.

The optimum conditions of processing were determined in a series of preliminary trials. Judged from the results of the phenol and iodine adsorption tests, the best carbons, irrespective of yield, were produced at 600° to 650° C.; heat treatments at higher or lower temperatures resulted in inferior carbons. Best results were obtained when the rise from 25° to 600° C. required about 2 hours. The optimum time of heating at the maximum carbonization temperature was 4 hours.

Activation. The carbonized hull bran was activated with steam in a cylindrical alloy steel retort incased in an electric furnace and provided with a steam inlet and a gas outlet (Figure 1). The retort was mounted on bearings by means of outside shafts. At intervals it was turned to provide agitation during the activation process. The volume of gas evolved was measured by a wet gas meter; the data afforded an estimate of the weight loss. The temperature in all activation experiments was about 950° C.

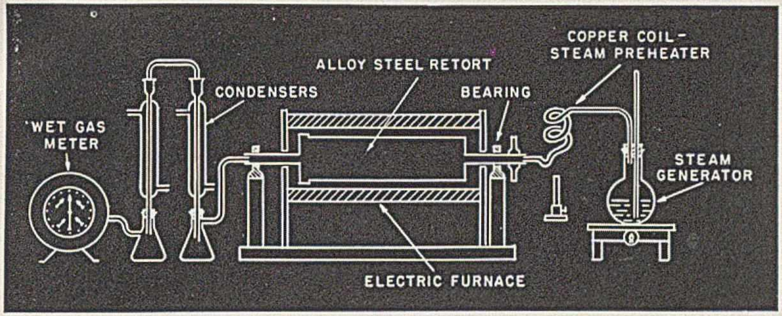

Figure 1. Steam Activation Apparatus

A typical run will be described to illustrate the procedure used in this work: The retort was charged with 30 grams of carbonized hull bran, and the furnace brought to 950° C. in about one hour. Superheated steam was then passed slowly over the carbon at a rate such that the temperature of the furnace and the evolution of gas remained almost constant. The steam treatment was continued until 1.09 cubic feet (3.087×10^4 cc.) of gas at 23° C. had been evolved. This required about an hour and corresponded to a 64.7 per cent yield of activated carbon.

An electrically heated stationary glazed porcelain tube (*4*) which was used in preliminary experiments yielded a carbon with a variable activity, probably because the product near the steam entrance was oxidized more completely than the carbon at the outlet of the tube.

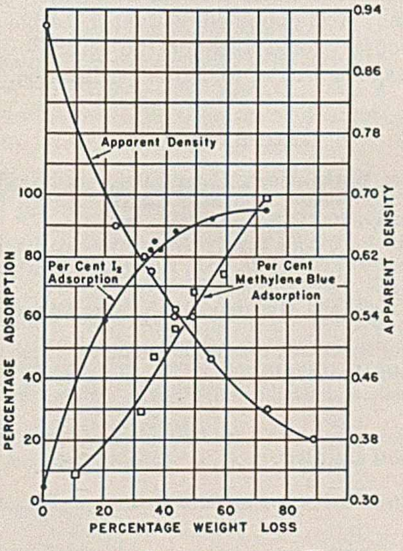

Figure 2. Relation of Various Properties of Hull Carbons

Tests. The adsorption values for phenol, iodine, and methylene blue were used to indicate the effect of increasing degrees of oxidation and of subsidiary activating processes, such as acid leaching, on the sorptive capacity of the carbon for different types of adsorbates.

The phenol adsorption was estimated by the colorimetric procedure (*1*) recommended by the American Water Works Association. Dibromoquinonechlorimide was employed as the indicator in a solution of pH 9.2.

The iodine adsorption was obtained by adding 1 gram of carbon to 100 ml. of 0.1 *N* iodine solution, shaking mechanically for one hour, filtering, and titrating an aliquot portion of the filtrate with 0.05 *N* thiosulfate solution. Blank determinations were run and corrections made for the iodine which had disappeared.

In the methylene blue test, 0.1 gram of carbon was added to 100 ml. of a solution containing 0.03 gram of the dye. The suspension was agitated for one hour and then filtered. The amount of methylene blue remaining was determined by a Duboscq colorimeter. The reliability of data obtained by this test has been questioned, for it has been shown that in some cases (*2*) completely decolorized solutions give positive tests for methylene blue, as estimated by the iodine titration procedure of Rosin, Beal, and Szalkowski (*7*).

A more precise determination of methylene blue adsorption is described in the official U. S. P. tests. Data given in Table IV were obtained by applying this procedure to cottonseed hull carbons.

The apparent density of the carbon which was ground to pass 200 mesh was found by placing it in a 25-ml. graduated cylinder, tamping until no further volume decrease resulted, and weighing the known volume of carbon.

Evaluation of Hull Carbons

In order to evaluate the carbons produced from cottonseed hull bran, parallel determinations were run on six of the best grades of commercial activated carbons. Carbons A, B, C, E, and F are vegetable carbons produced by four leading manufacturers; D is a powdered coconut carbon.

Figure 2 shows the interrelation of iodine adsorption, methylene blue adsorption, apparent density, and weight loss during activation as observed for the hull carbons. The percentage weight loss is based on the weight of carbonized material. Table I gives the data on these properties as found for the commercial carbons; values interpolated from Figure 2 are included for comparison.

For each preparation it is apparent that iodine adsorption and methylene blue adsorption vary directly with the weight reduction in activation. With increased time of activation, the yield becomes lower and the hull carbon steadily shows a greater sorptive capacity for iodine and methylene blue. The highest activity is exhibited by the carbon that has been oxidized to the greatest extent in the activation process for the range of yields studied. The apparent density is also a function of activation and gradually decreases with the total weight lost by the carbon during activation.

Table I. Comparison of Hull Carbons with Commercial Carbons

Carbon	% Weight Loss in Activation	Apparent Density	% I_2 Adsorption	% Methylene Blue Adsorption
A	..	0.61	58.3	35.0
B	..	0.31	43.6	29.0
C	..	0.29	55.0	33.0
D	..	0.48	96.9	99.8
Hull	10	0.78	38.0	9.0
	20	0.70	59.0	18.0
	30	0.62	74.0	32.0
	40	0.56	84.0	47.0
	50	0.51	90.0	64.0
	60	0.46	93.0	80.0
	70	0.42	94.0	95.0

Hull carbons which readily adsorbed iodine and methylene blue were found to be comparatively inactive as phenol adsorbents. Phenol values determined at several different weight losses of the preparations were in each case greater than 50.

Preliminary experiments indicated that an acid treatment of the carbon subsequent to activation enhanced the adsorbing power for phenol. The procedure consisted in boiling the hull carbon in 4 per cent hydrochloric acid for 10 minutes, washing in water, oven drying, and finally grinding in a mortar and pestle (power-driven) until it passed a 200-mesh screen. Typical results are given in Table II.

Table II. Hull Carbons Acid-Washed after Activation

Hull Carbon No.	% Weight Loss in Activation	Apparent Density	Phenol Value
17	20	0.73	66.7
16	35	0.71	37.5
13	39	0.70	36.7
15	44	0.68	36.0
12	58	0.59	27.3
18	62	0.61	41.0

Further experimentation revealed that a significant increase in the phenol adsorbing capacity can be effected by a double acid extraction of the carbon—that is, before and after activation. Data on representative hull carbons prepared by this procedure are recorded in Table III; the improvement in phenol adsorption effected by the double washing is clearly seen by comparing the samples in this series with the approximately corresponding carbons in Table II. The values for the commercial grades of active carbons, which were analyzed as received, are included for comparison.

Table III. Hull Carbons Acid-Washed before and after Activation

Carbon No.	% Weight Loss in Activation	Apparent Density	Phenol Value
19	23	0.66	25.7
20	33	0.64	17.9
22	33.4	0.62	20.0
23	49	0.55	23.0
24	54	0.46	21.4
28	89	0.38	26.0
A	..	0.61	37.5
C	..	0.31	30.0
F	..	0.52	19.0
E	..	0.41	20.9
D	..	0.48	22.5

The increased phenol adsorption brought about by treatment of the hull carbon with dilute acids is probably the result of several factors. The acid wash removes the sulfur-containing compounds, ash, and alkaline mineral components present in the activated carbons. The removal of these ingredients effects a loss of about 6 per cent, based on the weight of the activated carbon. The purified materials would therefore be expected to exhibit greater adsorptive capacity.

The treatment with acids effects, in addition to the increase in carbon content, a change in the polarity of the active carbon. The boiling acid neutralizes the alkaline ash components of the activated carbon; accordingly it shifts the pH value and tends to make it more electropositive. This change would therefore favor the increased adsorption of the negatively charged substances.

The acid-treated carbons were washed repeatedly in hot water and then oven-dried at 105° C. The pH of aqueous extracts of the dried carbons was determined (portable glass electrode) with the following results: unwashed carbon, 9.9; active carbon produced from carbonized hulls which were washed in 4 per cent hydrochloric acid, 9.8; and carbon washed in 4 per cent hydrochloric acid after activation, 7.0. The ash content of the latter carbon was equal to 2.8 per cent. The apparent density of the carbonized hulls was 0.92 while that of the acid-washed material corresponded to 0.85.

The primary carbon produced in the carbonization of the air-dried starting material amounts to about 30 per cent of the hull bran. The yield obtained in the activation process depends upon the type of carbon desired. A product with strong phenol-adsorbing properties may be produced from carbonized hull bran in 65–70 per cent yields. A carbon which readily adsorbs iodine and methylene blue requires further oxidation and may be obtained in about 40 per cent yield. The over-all recovery of active carbon, on the basis of the air-dried hull bran, therefore varies from 12 to 20 per cent.

Preliminary examination seemed to indicate that the acid-washed activated carbons would be suitable for pharmaceutical use. Therefore, samples 12, 13, and 17 (Table II) were evaluated according to the specifications set forth in the U. S. Pharmacopœia (*8*) in respect to the following criteria: ash content, acid-soluble substances, volatile substances, completeness of carbonization, chlorides, sulfates, sulfides, cyanogen compounds, heavy metals, strychnine sulfate adsorption, and methylthionine chloride adsorption. Typical results are recorded in Table IV.

Table IV. Conformance to U. S. P. Requirements

	Hull Carbon	U. S. P. Limit
Volatile substances, %	5.0	15
Ash, %	2.8	4
Acid-soluble substances, gram	0.005	0.035
Completeness of carbonization (NaOH extn.)	Filtrate colorless	Filtrate colorless
Chlorides (AgCl), gram	0.0084	0.0258
Sulfates ($BaSO_4$), gram	0.0000	0.0279
Sulfides (PbS)	Negative	Negative
Cyanogen compounds (Turnbull's blue)	Negative	Negative
Heavy metals (precipitable as sulfides), gram	0.0000	0.0006
Adsorptive power (strychnine sulfate)	Complete	Complete
Adsorptive power, g. methyl thionine chloride adsorbed/g. carbon	0.1066	0.0750

It is evident that activated carbon can be prepared from cottonseed hull bran which will fall well within the U. S. P. requirements. Acid-extracted activated carbons obtained from this source would therefore be entirely suitable for medicinal usage as well as for water purification.

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Contribution from the Cotton Research Foundation Fellowship at Mellon Institute.

Correction—Spirit Varnishes

Through an unfortunate error the footnote at the bottom of page 1539, of the November, 1940, issue, states that one of the authors, I. W. Hutchison, Jr., is the Dow Chemical Company Fellow at the University of Kentucky. This, of course, should have read the "University of Louisville", where the work was carried out.

Thermal Stability of Furfural

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The data presented show that, under the specific conditions of these experiments, refined furfural is quite stable. The rate of decomposition at 230° C. is so slow that from an industrial standpoint furfural is thermally stable. No commercial process is known wherein furfural is subjected to temperatures of the magnitude of 230–275° C. for more than a few minutes, and the data presented show that it is a matter of hours before a change in the properties of furfural can be detected.

THE scarcity of information pertaining to the physical and chemical changes involved when furfural is exposed to elevated temperatures has led to considerable speculation regarding the thermal stability of this solvent. There are numerous processes involving the use of large quantities of furfural, sometimes at comparatively high temperatures; hence it seems desirable to have quantitative data relating to this subject. The data presented in this paper were obtained about five or six years ago but are now being offered because of the increasing industrial interest in the stability of furfural.

The experiments carried out in this study were designed to show the rate of decomposition of furfural. They may be divided into two main classes on the basis of the conditions adhered to for the purpose of obtaining: a comparison of the stability of furfural at 140°, 180°, and 230° C.; and a measure of the effect of various metals on the stability of furfural at 230° C.

Materials and Preparation of Samples

The furfural used in this work was the refined grade which has been sold in this country for a number of years. This grade was chosen because in industrial practice the recovery of furfural results in its refinement. For instance, in solvent refining processes, furfural is recovered in a highly purified state after having been once circulated through the plant. The following table shows the properties of the refined furfural under discussion:

Furfural by Hughes-Acree method (*4*), %	99.6
Specific gravity, d_{20}^{20}	1.161
Acidity, moles/liter as acetic acid	0.025
Ash, %	0.0017
Moisture (*1*), %	0.24
Distillation of 100 cc.	
Temp. at end of 1st drop, ° C.	147
Temp. at end of 1st cc., ° C.	153
Max. temp. at dry point, ° C.	162
Recovery, %	99.0
Loss, %	0.57
Residue, %	0.43

The furfural supply was stored in sealed bottles in a cool dark room. A fresh bottle was opened and analyzed at the beginning of each series of experiments, which accounts for the slight discrepancy between the values for the initial densities and acidities of each series.

In each case approximately 40 cc. of furfural were added to a Pyrex glass tube and sealed under a vacuum of 45–50 mm. of mercury. The gas space above the liquid in the tube was only slightly larger than that necessary to allow for liquid expansion on heating. The sealed glass tube was enclosed in a bomb of iron pipe (Figure 1) and then immersed in a vertical position in an oil bath maintained at the desired temperature. To keep a uniform temperature throughout the bath, the bombs were supported on a rack which was rotated continuously through the oil.

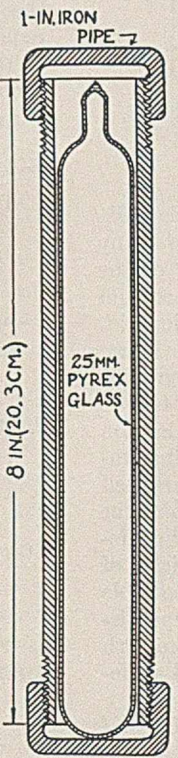

FIGURE 1. CROSS SECTION OF BOMB AND SEALED TUBE USED IN EXPERIMENTS

For the study of the effect of metals, a constant ratio of 0.76 sq. cm. of metal per cc. of furfural (ratio available in 2-inch pipe) was obtained by adding the calculated length of 18-gage wire to the furfural in the glass tube.

Preliminary experiments showed that changes in the furfural were so slight after heating for a few hours as to be immeasurable by the ordinary methods of analysis. It was found necessary to heat the samples for extended periods in order to produce changes of measurable magnitude. The data were then plotted and extrapolated to zero time for the purpose of estimating the changes occurring in furfural during short intervals of heating.

Analytical Methods

Samples were cooled immediately on withdrawal from the oil bath and were analyzed as soon as possible. In some instances, however, analysis was delayed, and some variation may have been introduced into the data as a result of this circumstance.

DECOMPOSITION. The difference in furfural content of the initial furfural and of a sample after heating is reported as the amount of furfural which decomposed. Analyses were made by the Hughes-Acree method (*4*) and checked by the bisulfite-iodine method (*3*). The results were in close agreement, and indicated that any furan compounds which might have been formed by the decomposition of furfural did not interfere with the analysis. In the event that furan or any other highly volatile compound was formed, it was undoubtedly lost since the heated tubes (especially after prolonged heating) were invariably found to be under superatmospheric pressure which was released on opening the tube.

RESIN FORMATION. The resin formed on heating furfural was insoluble in hydrocarbons such as toluene and xylene. The amount of resin in the heated samples was determined in the following manner: The treated furfural was shaken vigorously, and an aliquot was taken and weighed. The aliquot was filtered through a Gooch crucible packed with asbestos fiber which had been previously heated at 105° C. to constant weight. The residue left in the crucible was washed with hot xylene until the filtrate ran colorless; then the crucible was heated to constant weight at 105° C. Blanks were run using resin-free furfural, and from the values obtained the amount of resin formed was determined.

The samples found to contain 8–12 per cent resin appeared quite solid. This confirms the finding of Berthelot and Rivals (*2*) when working with old, solidified samples of furfural. These workers found that only about one tenth of such samples of furfural were nonvolatile, and from a carbon-hydrogen analysis of the resin they assumed it to be formed by the condensation of three molecules of furfural with the elimination of one molecule of water.

ACIDITY. Ten cubic centimeters of the heated furfural were pipetted into 200 cc. of neutral distilled water, and the mixture was shaken vigor-

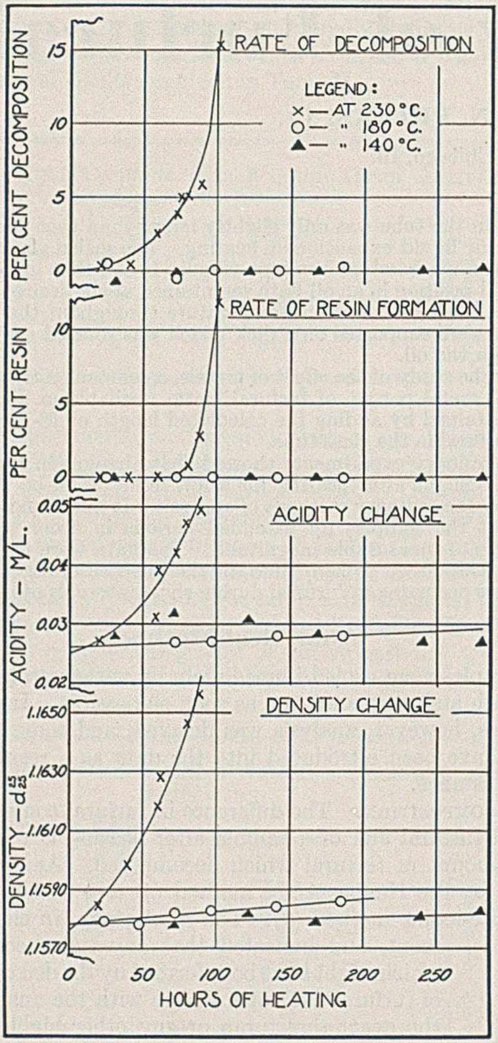

Figure 2. Effect of Heat on Furfural in Contact with Glass

ously. Phenolphthalein (10 drops) was added, and the mixture was titrated with 0.1 *N* sodium hydroxide. In many cases the end point was obscured by the dark color of the samples, and it was found advisable to add an excess of sodium hydroxide and then back-titrate with 0.1 *N* sulfuric acid. The results were calculated as moles of acetic acid per liter.

Density. The density was obtained with 25-ml. gravity bulbs in a constant-temperature bath regulated at 25° C.

Other Determinations. We planned to include data on color, refractive index, and viscosity, but it was found impractical to make these determinations. The color darkened rapidly on heating and soon became practically the same for all samples. This color also precluded the possibility of determining refractive indices accurately. Small particles of resin, in suspension in the heated furfural, were responsible for erratic viscosity determinations in an Ostwald type viscometer. The small quantity of furfural available from each sample made it difficult to attempt any other method of determining viscosity.

An attempt was made to ascertain the amount of metal corrosion, if any. This was done by weighing the metal before and after treatment, but the difference was very low. A gain or loss in weight of less than 0.015 per cent was observed. A sulfated ash determination on the furfural in a number of cases gave a maximum of 0.02 per cent, of which an estimated one half to two thirds was metal.

Discussion

Figure 2 shows the data presented in Table I. It is of the utmost significance that refined furfural shows a decomposition of only 0.28 per cent after 280 hours of heating at 140° C., and of 0.32 per cent after 185 hours at 180° C.

Table I. Effect of Heat on Furfural in Contact with Glass

Temp., ° C.	Time, Hours	Decomposition, %	Resin Formed, %	Acidity as Acetic, Mole/Liter	Density, d_{25}^{25}
140	0.00	0.00	0.00	0.026	1.1578
	30.00	−0.87	0.00	0.028	1.1573
	70.50	−0.12	0.00	0.032	1.1578
	121.50	0.03	0.01	0.031	1.1582
	167.00	−0.04	..	0.028	1.1579
	239.00	0.08	0.01	0.027	1.1581
	280.00	0.28	0.01	0.027	1.1583
180	0.00	0.00	0.00	0.026	1.1578
	24.00	0.53	0.01	...	1.1579
	48.00	..	..	...	1.1578
	72.00	−0.57	0.01	0.027	1.1582
	97.00	0.09	0.01	0.027	1.1583
	141.00	−0.02	0.02	0.028	1.1584
	185.50	0.32	0.01	0.028	1.1586
230	0.00	0.00	0.00	0.025	1.1576
	20.00	0.39	0.01	0.027	1.1584
	40.00	0.40	0.03	0.041	1.1598
	58.50	2.54	..	0.031	....
	59.67	..	0.05	0.039	1.1618
	72.00	3.96	0.09	0.042	1.1628
	75.00	5.00	..	...	....
	79.25	5.12	0.71	0.047	1.1646
	88.25	5.84	2.78	0.049	1.1656
	101.00	15.36	11.93	...	....

The demand for greatest stability is in solvent extraction processes where residual furfural is sometimes flashed off at 275° C., although a maximum of 230° C. is usually recommended. The curves shown for 230° C. are decidedly steeper than those at 140° and 180° C., and indicate less stability. It will be seen, however, that even at 230° C. any change in the physical properties of furfural during the short interval required for flashing off is so small as to be undetectable.

Any change in the rate of decomposition of furfural due to contact with metals would be expected to be greater at higher temperatures. For this reason the effect of metals was

Table II. Effect of Metals on Furfural at 230° C.

Metal	Time, Hours	Decomposition, %	Resin Formed, %	Acidity as Acetic, Mole/Liter	Density, d_{25}^{25}
None	0.00	0.00	0.00	0.025	1.1576
Black iron	20.00	0.70	0.01	0.027	1.1588
	58.50	2.54	0.10	0.045	1.1612
	72.00	3.29	0.11	0.043	1.1626
	79.25	5.46	0.18	0.048	1.1649
	88.25	...	2.24	...	....
	101.00	14.74	10.35	...	....
Polished iron	20.00	0.14	0.02	0.029	1.1585
	40.00	0.74	0.03	0.035	1.1598
	58.50	3.04	0.10	0.045	1.1615
	72.00	3.31	0.12	0.042	1.1629
	79.25	5.38	...	0.048	....
	88.25	7.22	4.31	0.052	1.1642
	101.00	17.29	12.39	...	....
Copper	20.00	0.34	0.02	0.027	1.1585
	40.00	0.54	0.03	0.035	1.1603
	58.50	3.04	0.09	0.041	1.1607
	72.00	3.61	0.09	0.042	1.1621
	79.25	5.20	0.21	0.046	....
	88.25	5.20	0.16	0.044	1.1635
	101.00	13.59	9.09	...	....
Nickel	20.00	0.01	0.01	0.028	1.1584
	58.50	2.43	0.06	0.042	....
	72.00	4.22	0.11	0.045	1.1622
	79.25	...	...	0.039	1.1633
	88.25	7.87	3.94	0.042	....
	101.00	17.42	12.44	...	....
Aluminum	20.00	0.01	0.02	0.028	1.1585
	58.50	2.67	0.10	0.041	1.1620
	72.00	3.28	0.11	0.044	1.1626
	79.25	5.90	...	0.046	....
	88.25	6.44	3.94	0.049	1.1653
	101.00	16.19	12.57	...	....

studied only at the highest temperature employed—namely, 230° C. The results of this study are shown in Table II; it is interesting to note that the curves for furfural in contact with glass at 230° C. (Figure 2) are the approximate mean of the data on the effect of metals. However, with the possible exception of black iron and copper, the decomposition of furfural at 230° C. appears to be slightly accelerated after approximately 80 hours owing to the presence of the various metals employed. If there is any initial effect due to the metals, the present analytical methods are not sufficiently refined to show it.

Additional work which has not been completed indicates that, when the moisture content of refined furfural is increased, the rate of decomposition at 230° C. is increased. At 180° C., however, this acceleration is not noticeable, even after prolonged treatment.

Acknowledgment

The collaboration of J. Pokorny of G. S. Blakeslee and Company, Chicago, is gratefully acknowledged.

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Cellulose Derivatives as Basic Materials for Plastics

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Cellulose derivatives are adaptable for use in plastics because of their inherent properties. Cellulose is a long-chain molecule whose chemical and physical nature may be changed by different degrees and kinds of substitution. By proper adjustment of the composition of its derivatives, moldability and compatibility with solvents and plasticizers may be altered to conform to diversified plastic specifications. The chainlike structure of cellulose and cellulose derivatives, the high molecular weight of these chains, and the relatively uniform distribution of the size of such chains contribute to its outstanding strength, toughness, flexibility, and other important physical characteristics.

Because of these inherent properties, cellulose products have enjoyed and will continue to enjoy an important place in the plastics industry and related fields.

At a time when plastics which claim synthesis from basic raw materials such as coal, air, water, coke, limestone, and other similar basic materials have been so widely publicized, it may appear old-fashioned to review chemical products such as cellulose derivatives which cannot claim similar creation in the laboratory and chemical plant. However, in nature's own laboratory, cellulose and hence its derivatives are synthesized similarly from the combustion product of carbon (carbon dioxide) and water, aided by the energy of sunlight and the catalyst chlorophyll in the living plant. Thus, a yearly recurring crop is produced in the form of cotton, linters, or wood cellulose in abundant quantities. Through this genesis these polymers possess certain inherent properties, only difficultly reproduced by chemical manufacture alone, which make them eminently suitable for use in plastics.

The story of the discovery of nitrocellulose about a hundred years ago and of other cellulose derivatives has been adequately told by Sproxton (*49*), Conaway (*3*), and others (*59*, *60*, *62*). The industrial utilization of the first cellulose derivative, nitrocellulose (*19*, *20*, *36*, *47*, *61*), in plastics matured only after the development, during fifty years, of suitable solvents and plasticizers (*30*, *31*, *41*, *48*, *56*). The springboard for the present-day industrial success of cellulose acetate was the discovery, forty years after the first successful acetylation of cellulose (*11*, *44*, *45*, *64*), that partial hydrolysis of the triacetate produced a secondary acetate with profoundly altered properties (*34*). Commercial production of cellulose acetate began with the demand for airplane dopes during the World War and was further increased by its introduction into plastics in 1926 (*15*). Recently the production has been accelerated because of its utility in injection molding. The stories of the mixed cellulose esters and of the ethers (*6*, *8*, *27*, *63*) are newer but similar, all illustrating the necessity of exact, expensive, and long-time research and plant development work.

Economics and Trends

A graphic picture of the growth of the nitrocellulose and cellulose acetate plastics industry is shown in Figure 1. No official figures are available on the newest cellulose ester, cellulose acetate butyrate (*37*), to be adopted by the plastics industry. The introduction of cellulose ethers, particularly ethylcellulose, into plastics is a still more recent development (*58*). Steadily declining trends in prices of nitrocellulose, cellulose acetate, and ethylcellulose are shown in Figure 2. The abundance and continuous formation of cellulosic raw materials and the ready availability of other important ingredients, such as nitric acid, acetic anhydride, and ethyl chloride, make it obvious that the raw materials for the cellulose-derivative plastics industry are of satisfactory supply and relatively low cost.

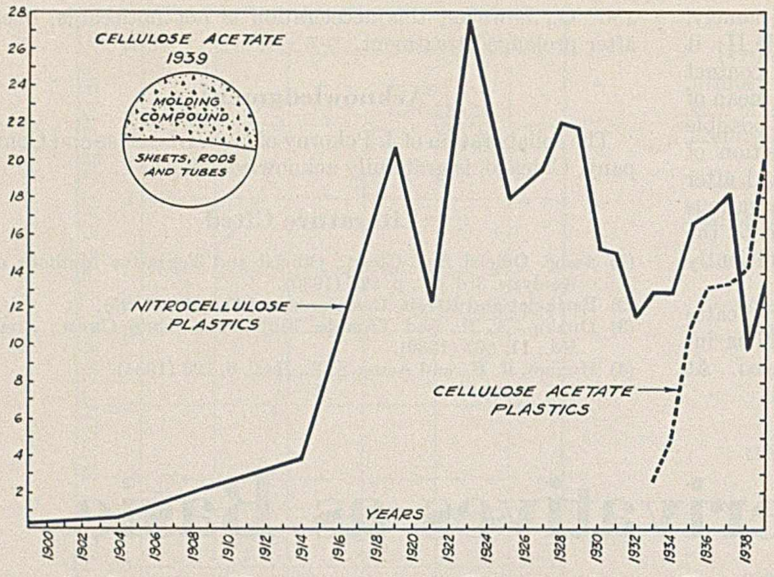

FIGURE 1. GROWTH OF NITROCELLULOSE AND CELLULOSE ACETATE PLASTICS INDUSTRY

(Based on United States Bureau of Census Data.)

While cellulose derivatives are the materials from which the original foundations of the plastics industry were fashioned, their importance today cannot rest alone on historic performance. Their value to the present and future plastics industry must be justified by their intrinsic properties, to be discussed in the following paragraphs.

Constitution and Structure of Cellulose

The elucidation of the constitution and structure of cellulose on the basis of both physical and chemical evidence has been investigated by many during the past forty years (*4*, *18*). Of various structures proposed for the cellulose molecule, the concept that it is made up of a large number of β-glucose anhydride units linked together through oxygen bridges in the manner shown in Figure 3 has now won almost universal acceptance because it accounts most satisfactorily for the properties and reactions of cellulose. The glucose anhydride units in the cellulose chain are relatively rigid rings coupled together by primary valence forces. Besides, there is so much steric hindrance around the oxygen bridges that only a limited amount of rotation of the building units relative to one another is possible. As a result, the molecules of cellulose and its derivatives form extended chains with low internal flexibility (*13*, *29*).

Influence of Substitution

In the glucose anhydride long-chain picture of the cellulose molecule (Figure 3) it is characteristic that each glucose anhydride building unit contains three replaceable hydroxyl groups. By varying the amount and nature of the groups introduced into the molecule in place of these hydroxyl groups, a series of esters, ethers, or ether-esters varying widely in physical and chemical properties can be obtained. The degree of substitution is customarily designated by the average number of hydroxyl groups replaced. For example, if analysis of a cellulose derivative shows that, on an average, 2.5 of these hydroxyl groups have been reacted, then the product is said to have a substitution of 2.5. A cellulose derivative with all hydroxyls esterified or etherified would have the maximum substitution of 3.0.

An appreciable amount of information has been accumulated on the effect on properties of the nature and amount of substituent groups, but only a few examples will be given to indicate the trend of the results obtained.

One of the most frequently quoted papers dealing with the effect of substituent groups is that of Hagedorn and Möller (*14*) who demonstrated the variation in film strength and solubility of a series of cellulose esters, mixed esters, and ethers. (These results would be of even greater value if the products used had been characterized more accurately by viscosity data and, for the mixed esters, by the relative proportions of the different substituents.) In the case of the cellulose triester films the tensile strength decreases (Figure 4, left) and the elongation increases (right) as the size of the substituent increases.

Sheppard and Newsome (*46*) measured the variation in some of the properties of cellulose triesters containing ester groups ranging from the acetate to the myristate. The effect of this variation on melting point and moisture absorption is shown in Figure 5.

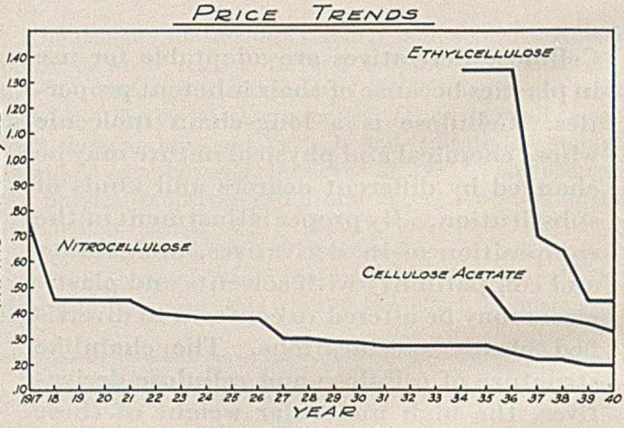

FIGURE 2. PRICE TRENDS

In regard to the effect due to the degree of substitution, some interesting results have been reported by Lorand (*28*) on the variation in the properties of ethylcellulose with variation in ethoxyl content. This investigator found, as Figure 6 shows, that the softening point of ethylcellulose is at a minimum at an ethoxyl content of about 47 per cent and rises sharply as the ethoxyl content is varied in either direction from this value. Figure 6 shows a similar curve for benzylcellulose. This work illustrates, therefore, the effect on softening point of a change in the nature of the substituent ethyl group. Moisture absorption was found to decrease linearly with increase in ethoxyl content (Figure 6). The solubility

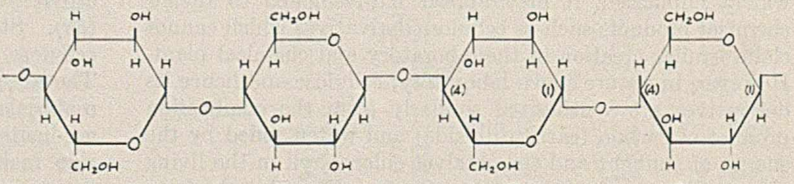

FIGURE 3. THEORETICAL CONFIGURATION OF A PORTION OF A CELLULOSE MOLECULE

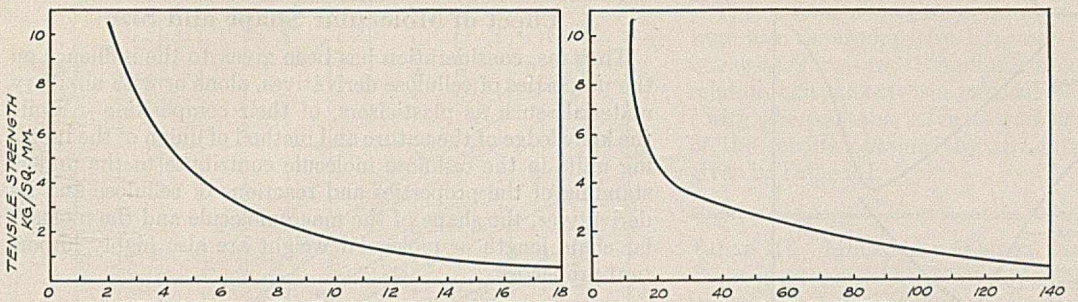

FIGURE 4. TENSILE STRENGTH (*left*) AND ELONGATION (*right*) OF CELLULOSE TRIESTER FILMS (*14*)
Curves by Sheppard and Newsome (*46*)

of ethylcellulose passes through a number of different stages as the ethoxyl content is increased (Table I). These data are sufficient to demonstrate adequately the wide variations in properties that can be obtained by varying either the nature or amount of the substituent group introduced into the cellulose molecule. The large number of possible cellulose derivatives indicates the technical feasibility of obtaining tailor-made materials conforming to diversified specifications.

TABLE I. VARIATION OF ETHYLCELLULOSE SOLUBILITY WITH SUBSTITUTION (*46*)

Substitution Range	Solubility
About 0.5	Alkali (4–8% NaOH)
1.0 (0.8–1.3)	Water
1.4–1.8	Increasing swelling in (organic) polar-nonpolar solvent mixtures
1.8–2.2	Increasing soly. in above type of mixtures
2.2–2.4	Increasing soly. in alcohol and less polar solvents
2.4–2.5	Maximum soly.
2.5–3.0	Rapid drop in alcohol soly.; sol. only in nonpolar solvents

The variation of physical properties of cellulose derivatives with degree of substitution may be explained by taking into consideration the attractive forces between molecules. By replacing a small hydroxyl group with a larger substituent, the original high degree of hydrogen bonding between adjoining cellulose chains is largely destroyed as a result of the greater separation of the chains. Hence, when the degree of substitution is high enough, the derivatives become more soluble. The increase in solubility with substitution does not continue up to the substitution of 3.0, but goes through a maximum at a degree of substitution between 2.0 and 2.5 for most cellulose derivatives. This can be correlated with the increased area of contact between adjoining chains as substitution becomes more uniform through completion.

Functions of Plasticizers

In considering the use of cellulose derivatives for plastics, the interest is in the behavior of the solid substance rather than solutions. The solid, however, usually contains plasticizer, and it is desirable that the possible functions of the plasticizer be examined.

As one mode of action, the plasticizer solvates the cellulose chain, increases the average distance between chains, and reduces the force holding a given chain to its neighbors. The theory of elasticity of rubberlike materials proposed by Mark (*13*, *29*), Meyer (*32*), and Kuhn (*25*) shows that this increases flexibility by increasing the amplitude of internal movement of the chains and permitting kinking of the molecules within the limits imposed by the steric relations within the molecule. There is another action of the plasticizer, first emphasized by Kratky (*24*). This lies in the formation of a network of membranes and filaments of solvated cellulose derivatives surrounding and penetrating areas of much higher concentration of plasticizer. This system may be pictured as consisting of two phases with incomplete miscibility, in which the more fluid phase (plasticizer-rich) is held by surface tension in the pores of the other phase and thereby prevents the collapse of the structure.

Celluloid is an excellent example of the first type of structure in which the plasticizer is firmly bound to the nitrocellulose molecule. The attractive forces between unsolvated nitrocellulose chains appear to be high on account of the relative smallness of nitrate groups and the strong forces surrounding them. In order to dissolve or plasticize nitrocellulose, it is necessary to choose a substance which has powerful solvating action on the chains. Such substances will naturally be highly compatible and uniformly distributed throughout the mass, and hence will not lead to the gel type of structure. Camphor, which is an excellent plasticizer for nitrocellulose, forms a relatively stable complex with the nitrate groups of the compound. Such a system, then, is composed of chainlike molecules containing nitrate groups, hydroxyl groups, and camphor solvate groups. The amount of camphor used is sufficient to hold the cellulose chains apart except at rare intervals where the chains cross or touch and are strongly held to one another. A system results which resembles vulcanized rubber, with long stretches of the chains loosely attracted to their neighbors and free to move under the influence of thermal agitation, while the occasional linking to neighboring chains prevents cold flow. Such a cellulose de-

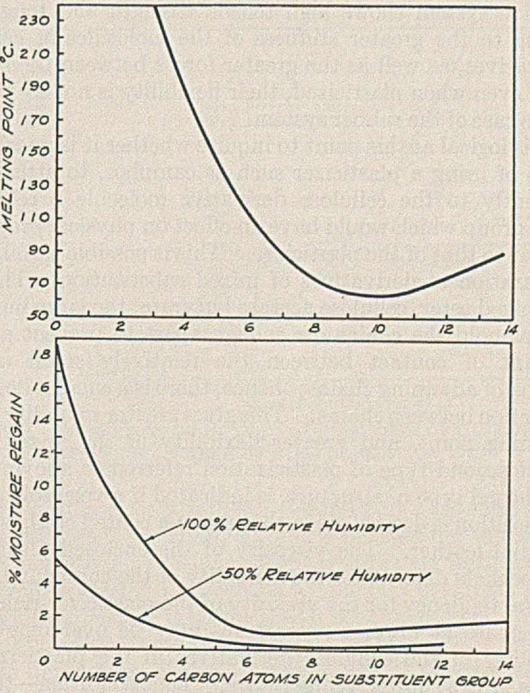

FIGURE 5. MELTING POINT AND MOISTURE REGAIN AT 25° C. OF CELLULOSE TRIESTERS (*46*)

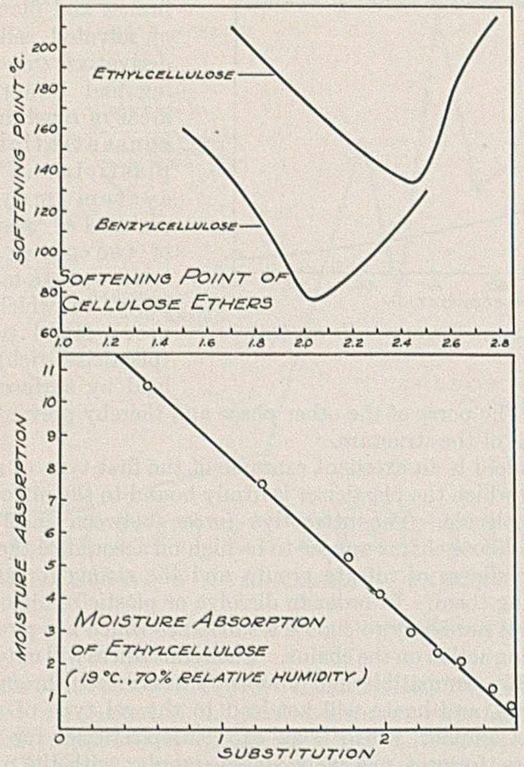

Figure 6. Effect of Substitution on Softening Point and Moisture Absorption (*28*)

rivative system shows high tensile strength and toughness. Owing to the greater stiffness of the molecules of cellulose derivatives, as well as the greater forces between their molecules even when plasticized, their flexibility is not so high as in the case of the rubber system.

It is logical at this point to inquire whether it is possible, in place of using a plasticizer such as camphor, to attach permanently to the cellulose derivative molecule a relatively large group which would have an effect on physical properties similar to that of the plasticizer. This is possible through the preparation of derivatives of mixed substitution. Thus, in the mixed ester, cellulose acetate butyrate, the large butyrate groups hold the chains far enough apart to prevent a great amount of contact between the relatively small acetate groups of adjoining chains; hence, there is a smaller degree of attraction between chains. This gives greater solubility, lower softening point, and greater flexibility of the mixed ester.

The second type of plasticization referred to above, yielding the gel type of structure, is indicated if a very soft pliable composition is desired, as in the case of a coated cloth, such as artificial leather. The viscosity of the enclosed plasticizer-rich pockets determines the flexibility of the compound. The natural tendency for the viscosity of the plasticizer-rich phase to increase at lower temperatures may be overcome if the solubility of the cellulose derivatives in the plasticizer becomes less at lower temperature. This condition—that is, increase of solubility with temperature—is easier to obtain with ethylcellulose than with nitrocellulose, the commonly used base for artificial leather. It is possible, therefore, to formulate ethylcellulose compositions with the same flexibility as nitrocellulose at room temperature, but with much better flexibility at low temperatures. It is clear that exactly the right degree of solvent power is necessary for the gel type of composition to be successful. Too low solvent power leads to exudation of plasticizer; too high solvent power gives soft, weak compositions at high temperature and brittle compositions at low temperature.

Effect of Molecular Shape and Size

Thus far, consideration has been given to the influence on the properties of cellulose derivatives, alone or with auxiliary materials such as plasticizers, of their composition. While the knowledge of the nature and method of union of the building units in the cellulose molecule contribute to the understanding of the properties and reactions of cellulose and its derivatives, the shape of the macromolecule and the molecular chain length or molecular weight are also highly important properties.

Shape of Molecule

In considering briefly the influence of the shape of the high-molecular-weight substances, such as are used in plastics, on their physical properties, Staudinger's classification of these materials into two general groups (*53*) is helpful. Members of the first group of macromolecular substances, such as cellulose and its derivatives, have long threadlike molecules which impart toughness, elasticity, and ability to form fibers. Members of the second group, such as starch, differ from cellulose in that they possess a highly branched molecule. This clarifies a situation that long puzzled the cellulose industry. It was early found that starch derivatives do not give flexible films, even if their solutions are high in viscosity. Starch derivatives show other peculiarities; for example, a solution of starch nitrate is not miscible with one of nitrocellulose of the same degree of substitution.

It is now apparent that the lack of film strength of starch derivatives and their peculiarities in solution are both due to the branched structure and the compactness of the molecule. It is further apparent that any other substances possessing this type of structure will suffer from the same disadvantages. The work of Staudinger's school (*53*) has demonstrated that certain synthetic polymers such as polystyrene have a branched-chain structure. On the other hand, cellulose, at least in the form of derivatives that are at present technically important, does not have branched chains. This is one of the significant factors responsible for the excellent physical properties of cellulose derivatives.

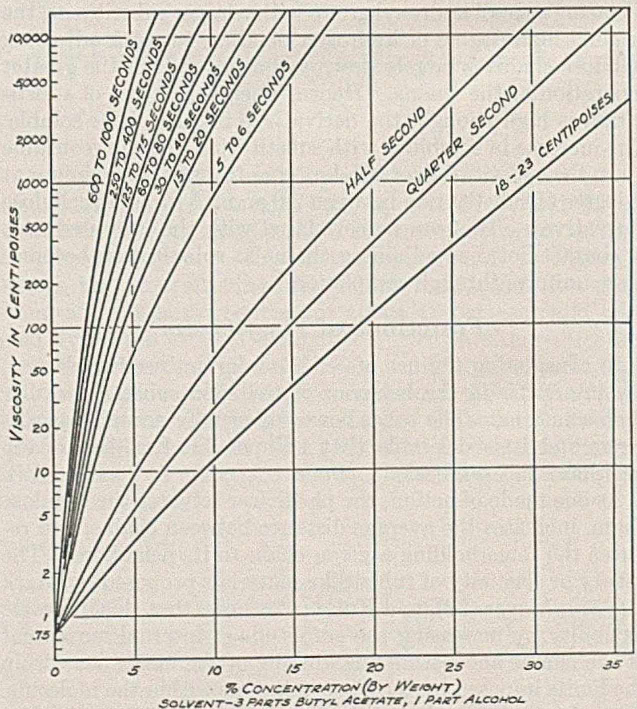

Figure 7. Viscosity-Concentration Curves (*17*) for Hercules Nitrocellulose (11.8–12.2 Per Cent Nitrogen)

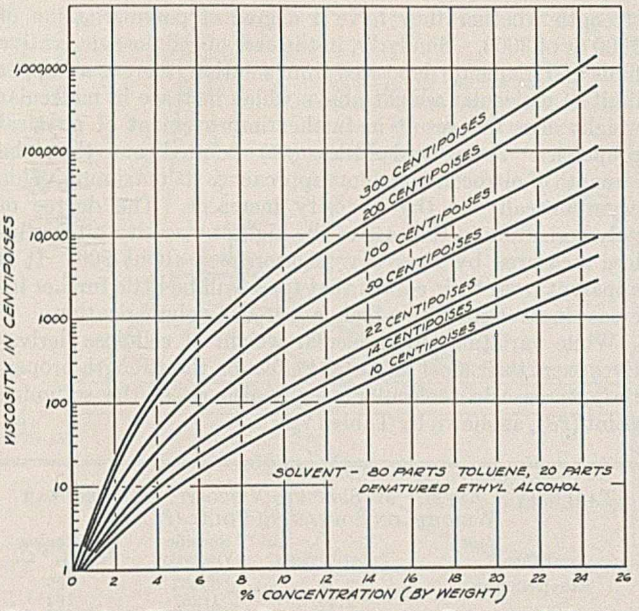

FIGURE 8. VISCOSITY-CONCENTRATION CURVES (*16*) FOR HERCULES ETHYLCELLULOSE (46.8–48.5 PER CENT ETHOXYL)

Size of Molecule

A discussion of the influence on physical properties of the length of the cellulose derivative molecules falls naturally into two phases—the variation of properties with average chain length and the effect on properties of chain length distribution.

One of the many interesting observations made early in the work on cellulosic materials was their ability to yield solutions of extremely high viscosity. It was found that, unlike simple organic substances, the viscosities of solutions of cellulose derivatives increase enormously with moderate increase in the concentration of the solute. This behavior is illustrated in the typical series of viscosity-concentration curves for nitrocellulose (*17*) and ethylcellulose (*16*) shown in Figures 7 and 8.

TABLE II. DEGREE OF POLYMERIZATION BY VISCOSITY AND OSMOTIC PRESSURE MEASUREMENTS (*55*)

Cellulose or Derivative	Degree of Polymerization
Native cellulose (cotton, ramie, flax)	2000–3000
Commercial wood pulp	800–1000
Purified wood pulp	900–1500
Commercial regenerated celluloses	250–500
Nitrocellulose (from native cellulose)	2000–3000
Nitrocellulose (lacquer type)	300–600
Commercial cellulose acetate	200–350
Commercial ethylcellulose	200–500

It had also been known for some time that the strength properties of cellulose and its derivatives increase with their viscosities. Thus, Clibbens and Ridge (*2*) found that, as the viscosity of cotton cellulose fibers in cuprammonium hydroxide is decreased as the result of degradation treatments, a corresponding decrease in tensile strength also occurs. A similar relation was found between the viscosity and film strength of cellulose acetate by Werner and Engelmann (*57*) and nitrocellulose by Jones and Miles (*21*). As a result largely of the investigations of Staudinger and co-workers (*52*), it was established that the viscosity of cellulose and its derivatives is a function of their molecular weight or chain length. Some of the values for the degree of polymerization (that is, the number of glucose anhydride units in the molecule) determined by viscosity and osmotic pressure measurements and reported by Staudinger (*55*) are shown in Table II.

The molecular weights of cellulose and cellulose derivatives were also determined by Kraemer (*22*), using the Svedberg ultracentrifuge, and Staudinger's contention that a simple relation existed between molecular weight and intrinsic viscosity when suitable solvents were used was confirmed. Some of the results obtained by the ultracentrifuge method are given in Table III.

TABLE III. MOLECULAR WEIGHT DETERMINATIONS BY ULTRACENTRIFUGE METHOD (*22*)

Cellulose or Derivative	Mol. Weight	Degree of Polymerization
Native cellulose	>570,000	>3500
Purified cotton linters	150,000–500,000	1000–3000
Wood pulps	90,000–150,000	600–1000
Commercial regenerated celluloses	30,000– 90,000	200–600
Nitrocellulose (dynamite)	750,000–875,000	3000–3500
Nitrocellulose (plastics)	125,000–150,000	500–600
Nitrocellulose ($^1/_2$-sec.)	45,000	175
Commercial cellulose acetate	45,000–100,000	175–360

With the development of methods of estimating molecular weight, it became possible to correlate directly the physical properties of cellulose and its derivatives with their molecular weight. Two interesting points were brought out. First, it was shown by Gloor (*12*), Jones and Miles (*21*), Kumichel (*26*), Ohl (*35*), Rocha (*38*), Spurlin (*50*), and Staudinger (*53*) that there is a low limit of molecular weight below which cellulose and its derivatives possess poor physical properties. Practically, this means that they yield plastics with poor strength or lose their ability to form films or fibers. It is of interest to point out Meyer's hypothesis (*33*) that the molecular weight below which there is no film-forming ability seems to be associated with the chance that a number of molecule ends are located close together. Secondly, it was found that, going in the other direction, a point is reached beyond which further increase in molecular weight results only in slight improvement in strength properties. This fact has great practical significance since it means that it is not necessary, for the preparation of products with satisfactory strength, to utilize cellulose derivatives of the highest degree of polymerization whose extremely high viscosity would cause considerable difficulty in the handling of these products either in solution or in the form of a plastic.

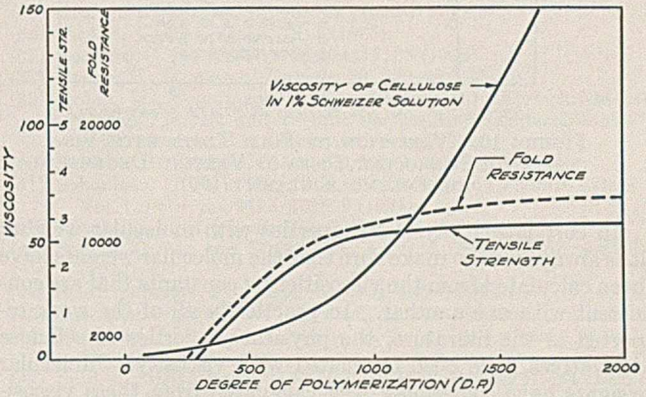

FIGURE 9. VARIATION OF PHYSICAL PROPERTIES OF CELLULOSE FIBERS WITH DEGREE OF POLYMERIZATION (*53*)

The range referred to above is illustrated in Figure 9, which shows that the strength of cotton, ramie, or flax cellulose fibers increases rapidly as the degree of polymerization (D. P.) rises from 200 to 600. Contrasted with this behavior, cellulose-derivative films or filaments deposited from solution show measurable strength and flexibility with a degree of polymerization less than 200. On the basis of molecular weights of polymers other than cellulose, such as the polyesters of

Carothers and Hill (*1*) and the vinyl esters of Douglas and Stoops (*5*), it would appear that the lower limit of degree of polymerization would be nearer 50. If, however, this limit is calculated (for instance, for the vinyl compounds) by using a viscosity–molecular weight constant consistent with that used by Staudinger in the above work on cellulose fibers, it becomes somewhat higher.

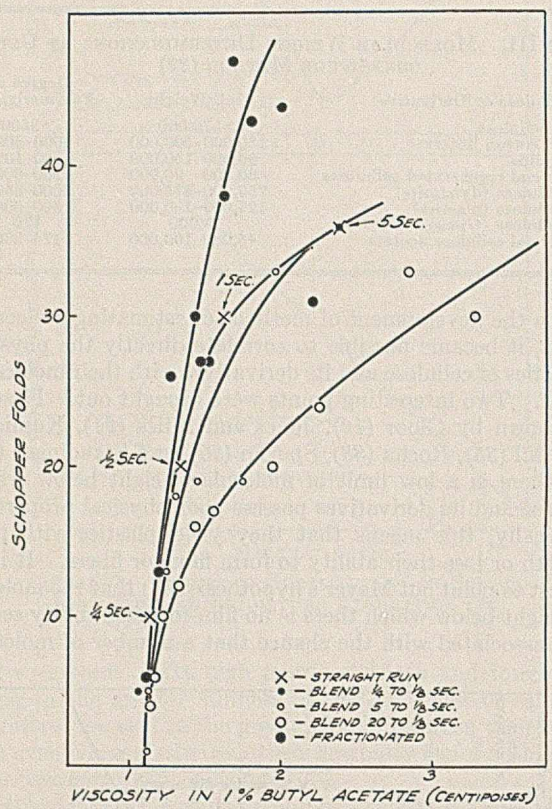

FIGURE 10. VARIATION OF FOLD TESTS WITH VISCOSITY FOR NITROCELLULOSES OF VARYING DEGREES OF POLYMOLECULARITY (*50*)

In correlating physical properties with molecular weights it is always well to make sure that the molecular weights have been calculated from the viscosities by constants that are consistent with one another. In practically all of the work reported in the literature, the physical properties of cellulose derivatives have been correlated with viscosity. Molecular weights have sometimes been calculated from these viscosities, using constants derived directly from osmotic methods of determining molecular weights. This leads, of course, to number-average molecular weights, as pointed out by Kraemer and Lansing (*23*). The viscosity and the important physical properties of cellulose derivatives are, however, functions of the weight-average molecular weight. Flory (*10*) showed that, for the type of molecular weight distribution likely to be encountered in cellulose derivatives, the weight-average molecular weight is about double the number-average value. In the present paper the constants of Kraemer (*22*) were adopted. These constants are approached by Staudinger's latest values (*39*) but lead to molecular weights two or three times as high as those given by Staudinger's original constants. In the absence of data on the molecular weight distribution of the product, the weight-average molecular weight is the only one of significance. With Kraemer's constants and the viscosity values found by Gloor (*12*), Jones and Miles (*21*), and Spurlin (*50*) as the limit below which film-forming properties vanish, the corresponding degree of polymerization is found to be about 100.

Native cellulose fibers have approximately the same strength whether they have a degree of polymerization of 1000 or of 3000. Similarly, in the case of cellulose-derivative films and filaments deposited from solution, there is an upper limit of molecular weight above which increase in molecular weight does not result in further improvement of physical properties. Jones and Miles (*21*) pointed out that the strength of nitrocellulose films approaches its maximum value asymptotically as the viscosity increases. The degree of polymerization in the case of the highest viscosity nitrocellulose measured by these investigators was about 900. It is apparent from their curves that there will be little further increase in strength with a higher degree of polymerization.

While variations in molecular weight of cellulose derivatives exert their most important effect on the strength properties, increase in molecular weight also raises the softening point (*28*), as shown by Table IV.

TABLE IV. EFFECT OF SPECIFIC VISCOSITY (MOLECULAR WEIGHT) ON SOFTENING POINT (*28*)

Ether	Substitution	Specific Viscosity	Softening Point, ° C.
Ethylcellulose	2.16	0.132	99
	2.14	1.267	162
	2.52	0.229	112
	2.50	2.847	144
Benzylcellulose	2.2	0.362	68
	2.2	1.183	104

Molecular Weight Distribution

It should be emphasized that the molecular weight values ordinarily determined for high-molecular-weight substances are, as a rule, only an average value. For, as discussed by Kraemer and Lansing (*23*), in a given material the molecules are not uniform but vary in size. As a consequence, the physical properties of cellulose derivatives are affected not only by their average molecular weight but also by their molecular weight distribution; that is, the relative number and size of the molecules make up the average value.

During the early course of the study of cellulose derivatives, it was realized that the addition of extremely low-viscosity material to one of high viscosity caused a decrease in the flexibility of the latter product. Thus, Spurlin (*50*) found that addition of 15-centipoise nitrocellulose (which is too low in molecular weight to have film-forming properties of its own) to nitrocellulose of higher viscosity resulted in a mixture with much poorer flexibility than a uniform nitrocellulose having the same viscosity as that of the mixture (Figure 10).

Schieber (*40*) and Eisenhut (*7*) investigated the effect on the strength properties of viscose rayon of variations in the chemical and physical properties of the cellulose constituting the rayon fibers. Molecular weight distribution was found to have an important effect on the strength properties, and these authors stressed the harmful effect on strength properties caused by the presence of low-molecular-weight cellulose.

Schulz (*42*, *43*) showed, on the basis of fractionation experiments (Figure 11), that the molecular weight distribution of a cellulose derivative such as nitrocellulose is more uniform than that of synthetic polymers such as polystyrene and polyisobutylene. Staudinger (*54*) ascribed these differences to differences in their method of preparation. Nitrocellulose is prepared by the degradation of a relatively uniform high-molecular-weight substance, and in the process low-molecular-weight portions are formed only in small amount. Flory (*9*) and Schulz (*42*, *43*) gave expressions for calculating molecular weight distribution for polymers, which agree substantially with one another and with Schulz's data for fractionated polystyrene and polyisobutylene.

The points brought out above apply even to cellulose derivatives of relatively low molecular weight. Flory (*9*)

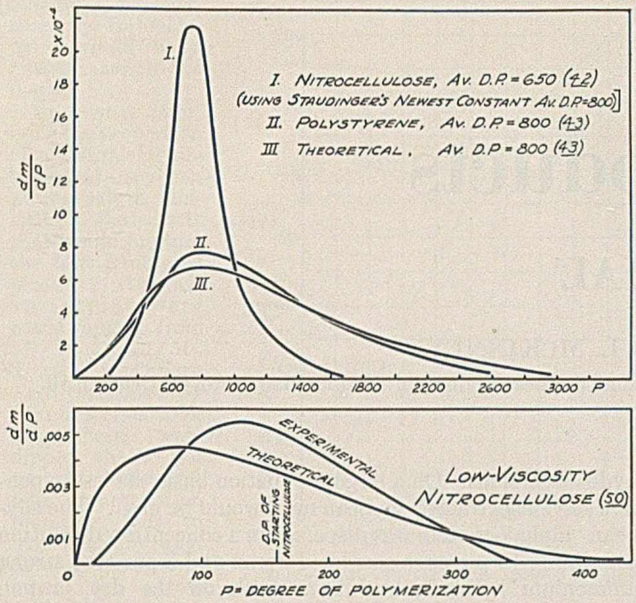

FIGURE 11. MOLECULAR WEIGHT DISTRIBUTIONS
dm/dp = rate of increase of amount of material with degree of polymerization.

showed that the molecular weight distribution of cellulose products will approach that of the synthetic polymers, the more cellulose is degraded; in spite of that fact, Spurlin's fractionation data (*50, 51*) on relatively low-molecular-weight nitrocellulose show less molecular weight dispersity than is calculated for a condensation polymer of the same average degree of polymerization (Figure 11). Inasmuch as it has been shown previously that experimental facts and calculation of molecular weight distribution of synthetic polymers agree, the above difference appears to be significant.

In view of these results, it is believed that a cellulose derivative will always show a greater uniformity in molecular weight distribution than a synthetic polymer, and as a result the cellulose derivatives when properly prepared will be expected to suffer less from the disadvantages associated with the presence of low-molecular-weight fractions.

Summary

An effort has been made to present in this review an adequate picture of the role and significance of cellulose derivatives for the plastics industry. They possess an enviable versatility in regard to adaptability to various requirements of tailormade plastic raw materials. The chainlike structure of the cellulose molecule contributes to its inherent properties of strength, toughness, and flexibility, in contrast to some other natural and synthetic materials. Cellulose products have a more uniform distribution of molecular weight when compared to synthetic polymers, which gives them additional favorable properties. While the discussion has been primarily concerned with cellulose derivatives in plastics, most of the arguments apply as well to their use in other applications.

Acknowledgment

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Protein Plastics from Soybean Products

LAMINATED MATERIAL[1]

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A protein laminated plastic material prepared from unsized kraft paper impregnated with formaldehyde-hardened thermoplastic soybean protein salt compared favorably with similar commercial materials as regards impact and flexural strength and modulus of elasticity, but not as regards water resistance. By placing a single sheet of phenolic- or urea-impregnated paper on each exposed face before pressing, a product resulted with the water resistance and other desirable properties of present commercial products, except for the edges, in materially reduced time of pressing. It is proposed to extend this investigation to cellulose fibers before sheeting and to the preparation of fabric laminated material.

When it was found that formaldehyde-hardened soybean protein was thermoplastic (*2*), the possibility of developing an aqueous dispersion of formaldehyde-hardened soybean protein was considered. With such a dispersion it would be possible to impregnate fibrous materials such as sheets of saturating kraft paper, textiles, and similar materials. Upon drying, these could be united by the thermoplastic hardened protein into laminated plastic material under the action of heat and pressure. This material should have good strength and be considerably less expensive in materials and in process of manufacture than the phenolic and urea laminated plastic materials now in use.

Soybean Protein–Formaldehyde Dispersion

Accordingly, a dispersion of soybean protein in aqueous formaldehyde solution was developed, which, in concentrations up to 10 per cent protein, remained stable for long periods. This development is described in detail elsewhere (*9*), so it is sufficient merely to outline here the method for its preparation. For this investigation, conducted as it was on a small laboratory scale, the commercial soybean "alpha"-protein was used in preparing the soybean protein–formaldehyde dispersions. On a large production basis the less expensive solvent-extracted soybean meal would be used. The soybean "alpha"-protein was dispersed in a concentrated solution containing 10 per cent powdered borax and 8 per cent strong ammonium hydroxide solution (both on the dry protein weight). This was heated to about 65° C. to obtain a clear dispersion, cooled, and diluted to 10 per cent protein with water to which had been added formaldehyde in amount to give 4 to 5 per cent in the final solution. The protein will not be hardened by formaldehyde in this solution at a pH within the isoelectric range of the protein, as was found most advantageous for protein plastic material (*2*). This was shown to be impractical (*8*). However, the protein is hardened at as low a pH as possible. The resultant product will be designated "formaldehyde-hardened soybean protein salts" to differentiate it from the formaldehyde-hardened soybean protein which is properly hardened within the isoelectric range of the protein. The dispersion would be made in an analogous manner from the solvent-extracted soybean meal, except that it would be necessary to hydrolyze the protein by preliminary treatment with caustic solution or by other means before proceeding to disperse it. It is doubtful whether it would be necessary to remove the insolubles, as they would cause no difficulty in making the laminated material. In this way difficult filtration would be avoided.

Several types of unsized or saturating paper used in the production of present commercial laminated plastics were investigated. Included were samples of saturating rag, alpha-cellulose, and bleached and unbleached kraft papers, in thicknesses ranging from 0.003 to 0.022 inch. It was found that a regular saturating kraft paper, 0.011 inch in thickness (eleven-point), gave satisfactory results. Since this was also the least expensive paper investigated, it was adopted.

Experimental Procedure

The size of the panels of laminated soybean plastic prepared was limited by the equipment available. A 25-ton press with 12 × 12 inch platens was used. This restricted the work to a laboratory basis, and the results obtained must be so construed.

The method used for impregnating the paper with the soybean protein–formaldehyde salt was on a laboratory scale. The sheets were dipped in the dispersion and hung up in a well-ventilated hood to drain and dry at room temperature. The paper absorbed about one third of its weight of formaldehyde-hardened soybean protein salt in the first dip and about one fifth more in each succeeding dip. From 3 to 5 hours were required to dry the paper between treatments. On a commercial scale the paper would be run directly from rolls through the soybean protein–formaldehyde salt dispersion, stripped, and then run through heated forced-draft dryers. It could be treated in this way as many times as necessary, and was cut into sheets when finally ready to be loaded into presses. Since the dispersing medium was water, there are no valuable solvents to be recovered; the amount of formaldehyde that might be recovered is too small to have economic significance. Air from the dryers would have to be exhausted

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[1] Previous papers in this series appeared in 1938 (pages 437 and 1236), in 1939 (page 84), and in 1940 (page 1002).

[2] A cooperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and of Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

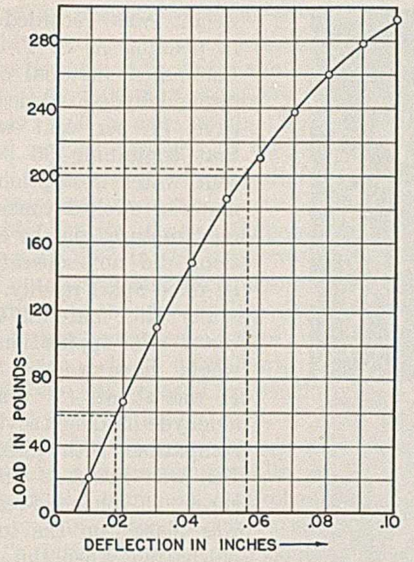

FIGURE 1. LOAD-DEFLECTION CURVE

outside, however, since the formaldehyde would be a health hazard in the factory.

In order to determine the proportion of formaldehyde-hardened soybean protein salt to cellulose in the sheets that would produce the best laminated plastic material, variations were made ranging from 30/70 to 50/50. These variations were controlled by the number of times the sheets were dipped, the 50 per cent hardened protein impregnation requiring four to five treatments. After the final treatment, the sheets were dried to a moisture content of 9 to 10 per cent, which required from 16 to 20 hours at room temperature. This amount of moisture was found to be adequate to plasticize the hardened soybean protein salt satisfactorily in the hot press.

The final stage in the process consisted in pressing the sheets between the heated platens of a hydraulic press so that they united to form the laminated panel. A temperature of 250° to 280° F. gave satisfactory results. The time of the cycle depends upon the thickness of the panel, but since the formaldehyde-hardened soybean protein salt is thermoplastic, no curing time is necessary. The time, therefore, is merely that necessary to heat the material uniformly. This is a marked improvement in efficiency over laminated materials as now produced, the curing time of some requiring as much as a 2-hour cycle. The soybean laminated material, as is the case with phenolic and urea laminated, should be cooled while under pressure to prevent subsequent warping. The surface will be that of the plates between which it is pressed; in order to produce material with highly polished faces, highly polished steel plates should be used in the press.

Impact and Flexural Strength Tests

In order to obtain data on the most practical pressure to employ in the preparation of soybean laminated plastic material, a series of test pieces were made with twenty sheets of paper impregnated with 30 to 50 per cent formaldehyde-hardened soybean protein salt. This gave sheet material averaging 0.17 inch thick, and requiring 3 to 4 minutes of hot pressing to laminate properly. Pressures of 500, 1000, and 2000 pounds per square inch were used, and all were pressed at 280° F. Test pieces were prepared from this material, and tests were run according to A. S. T. M. standards as described below. The results are given in Table I. Less than 1 per cent moisture was lost during the pressing operation, leaving 8 to 9 per cent in the material. At the end of 3 months the moisture content was found to be about 8 per cent, showing that this was the equilibrium moisture content of the material. The test pieces were conditioned 24 hours at 50° C. This conditioned material was found to have about 10 per cent less strength, both impact and flexural, than the nonconditioned.

TABLE I. STRENGTH OF LAMINATED MATERIAL AS DETERMINED BY FLEXURAL AND IMPACT TESTS[a]

	Percentage of Formaldehyde-Hardened Soybean Protein Salt:							
	29	31	36		44		47	
Molding Pressure	Flexural	Flexural	Flexural	Impact	Flexural	Impact	Flexural	Impact
Lb./sq. in.	*Lb./sq. in.*	*Lb./sq. in.*	*Lb./sq. in.*	*Ft.-lb./in. notch*	*Lb./sq. in.*	*Ft.-lb./in. notch*	*Lb./sq. in.*	*Ft.-lb./in. notch*
500	[b]	21,850	22,400	0.45	13,530	0.39	17,030	0.41
1000	23,500	21,930	23,300	0.49	20,730	0.44	18,250	0.41
2000	24,400	24,220	25,510	0.57	21,230	0.47	20,170	0.42

[a] The average flexural strength of paper-base Bakelite laminated is 20,000 pounds per square inch (*1*).

[b] Test piece did not laminate at this pressure.

Test pieces were sawed from sheet material and milled to the proper dimensions. Care was taken not to burn the material by friction while preparing the samples. Impact tests were made according to the A. S. T. M. standard method, D-256-38, for sheet material. The cantilever beam method (Izod) was used. A standard notch was milled in the specimen, and two pieces were used as a composite sample, making a total thickness of about 0.35 inch along the notch. The test pieces were broken edgewise, and the averages are reported as foot-pounds per inch of notch. Each figure recorded in Table I for impact strength is the average of five determinations.

Flexural strength, correctly called "modulus of rupture" (*7*), was determined by A. S. T. M. standard method D-229-38T, using a machine designed in the Soybean Laboratory (*4*) and built to A. S. T. M. specifications. A composite of two specimens was used, the pieces being fastened together by small bolts at each end. This gave a test piece about 0.34 inch thick, and uniform results were obtained by breaking the samples edgewise. The average maximum fiber stress (modulus of rupture) is recorded in Table I in pounds per square inch; each figure represents the average of three determinations.

The data in Table I show that the strength of the material, both flexural and impact, is a direct function of the molding pressure. This is in accord with expectation, as the higher the molding pressure, the tighter the lamination and the thinner the panel produced. Panels produced at pressures of less than 1000 pounds per square inch are inclined to warp too readily. Also, both the flexural and impact strengths of the material vary inversely with the percentage of protein in the sample. This again is in accord with expectation, since the cellulose fiber (paper) is less brittle than the hardened protein salt. Apparently the strongest material is that prepared with just enough protein to bind the paper into a unified whole, which from these data is about 35 per cent. The strength of this material compares favorably with present commercial laminated material, Bakelite (*1*).

Modulus of Elasticity

Load-deflection curves were plotted for the samples tested, and Figure 1 is typical. The curve approximates Hooke's law, the deflection being approximately proportional to the load. Above the 200-pound load the curve deviates much more sharply; this indicates that shearing stresses within the material exceed the cohesive strength of the protein binder, the failure progressing until the piece ruptures.

Modulus of elasticity was calculated from the load-deflection curves by the formula and method suggested by Hopkins (*5*):

$$E = \frac{L^3 (W_{70} - W_{20})}{4BH^3 (D_{70} - D_{20})}$$

where E = modulus of elasticity
W = load, pounds
L = length of test bar, inches
D = deflection of bar, inches
B = width of test bar, inches
H = height of test bar, inches

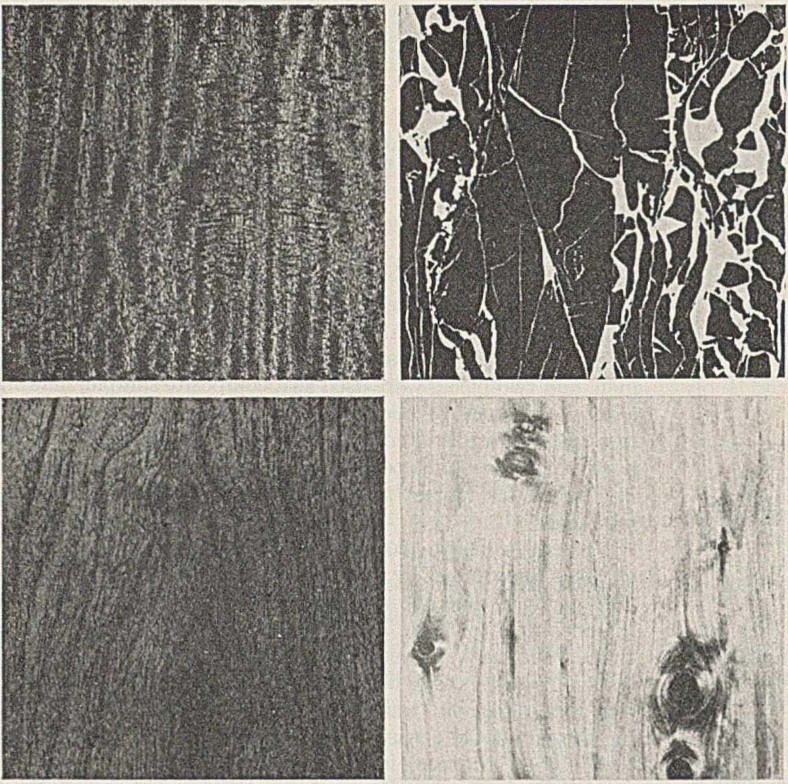

FIGURE 2. WOOD-GRAIN AND BLACK-ONYX EFFECTS

W and D represent the loads and deflections corresponding to 20 and 70 per cent of the maximum load. Modulus of elasticity computed in this manner for twenty-one samples gave a range of 900,000 to 1,600,000 pounds per square inch. For Bakelite laminated, the modulus of elasticity averages 1,500,000 pounds per square inch (*1*).

It is appreciated that this method of determining the modulus of elasticity is not so rigorous as that employing tensile and compression strength data. Since the above formula is derived from the well-known flexure formula (*6*), it involves the same assumptions as does the formula used to calculate the modulus of rupture or flexural strength. However, the error will be very small. The largest error comes from the assumption that the modulus of elasticity in tension equals that in compression for this material, but by the use of flexural data the mean of the two is obtained; these results are adequate for the purpose as applied here.

Water Resistance

Resistance to water was not very good as compared to that of phenolic laminated material, and water absorption was quite high as would be expected. Test pieces measuring 1 × 3 inches were sawed from sheets, conditioned for 24 hours at 50° C., immersed in distilled water for 24 hours, superficially dried, and weighed. The gain in weight was recorded as water absorption (a pending A. S. T. M. tentative method). Laminated material containing 47 per cent formaldehyde-hardened soybean protein salt gave 77 per cent water absorption, and that containing 36 per cent gave 57 per cent water absorption. In both cases the material swelled considerably, and, on drying, fractured on the edges, but the laminations did not separate; neither could they be pried apart readily.

For this material to have any extended commercial application, the water resistance would have to be materially improved. It was shown (*3*) that thermoplastic formaldehyde-hardened soybean protein is perfectly compatible with phenolic and urea resins. Use was made of this fact, and a single sheet of phenolic-resin-impregnated paper was placed on the top and on the bottom of the pile when the sheets were introduced into the press for lamination. The result was a panel with exposed faces of phenolic and center of soybean-protein binder. The water absorption of this material fell to 24 per cent, with swelling only around the edges for a distance of $^3/_{16}$ inch. For areas larger than the test pieces this percentage would be reduced, and with the protection of the edges (a simple and economical matter) the water resistance is the same as that of the phenolic.

Practical Possibilities

The greatest difficulty encountered in developing the soybean laminated plastic with phenolic faces was in obtaining a phenolic-impregnated paper which would cure rapidly enough. In the manufacture of straight phenolic laminated material, the curing time is a matter of 15 to 30 minutes; so all available phenolic-impregnated paper was found to cure slowly. Protein cannot be held at 300° to 350° F. for many minutes without decomposing. Phenolic paper was finally secured which, with a preliminary heating to 212° F. for 5 minutes, cured in 2 to 5 minutes when pressed with the soybean protein sheets. This is a satisfactory arrangement from all angles, especially the economic, since this material can be advantageously produced on a short cycle, and production

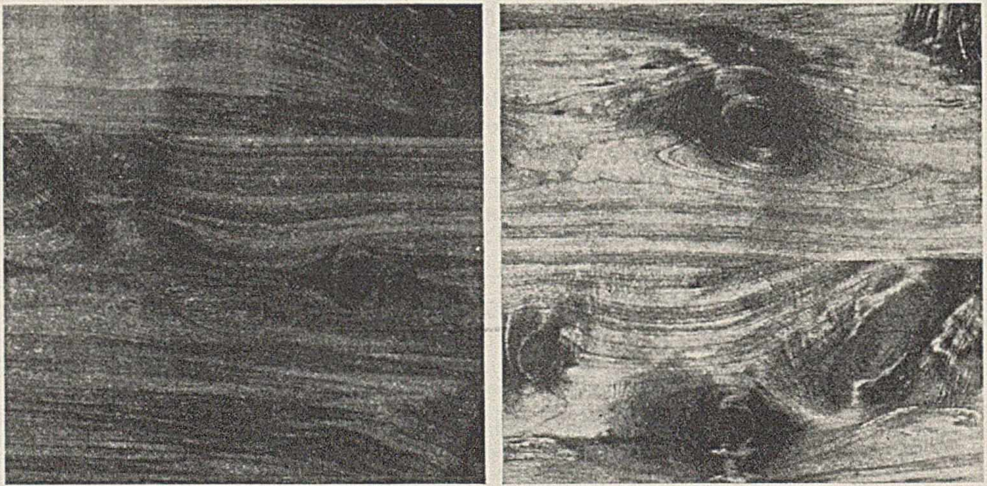

FIGURE 3. COMPARISON BETWEEN COMMERCIAL ALL-PHENOLIC MATERIAL (*left*) AND SOYBEAN PROTEIN MATERIAL FACED WITH PHENOLIC (*right*)

is thereby increased. The phenolic-impregnated sheets on the top and bottom are in direct contact with the heated platens; hence they are in position to cure in minimum time. This shortest period at the temperature necessary for proper curing of the phenolic is ample to activate the thermoplastic formaldehyde-hardened soybean protein salt throughout the rest of the pile so that a well-sealed product results.

Sheets of urea-resin-impregnated material may be used for the faces in place of the phenolic. Lower temperatures and usually a somewhat longer time in the press would be required. Any color or practically any effect desired may be produced, the only limit being the reproducing ability of the printing press. Figure 2 shows some wood grains and a black onyx, all produced by placing sheets printed with these designs on the top and bottom of the piles of hardened soybean-protein-salt-impregnated paper when introduced into the press. These particular effects are given by phenolic resin sheets, but urea resin would give analogous results. An interesting difference between the commercial all-phenolic material and the soybean-protein-center phenolic-faced material is shown in Figure 3. The latter has much more depth of color because of the translucency of the soybean interior, which gives the material a more natural wood appearance than the all-phenolic.

This development has been confined to laminated paper plastics and to the impregnation of paper in sheets. There remains the investigation of impregnating cellulose fibers with the formaldehyde-hardened soybean protein salt before sheeting. A more thorough, and possibly a more economical, impregnation may result. The investigation of fabric laminated material offers other fields of possible application. The strength of the soybean-protein-paper laminated material compares favorably with that of present analogous commercial products. The strength of hardened soybean-protein-fabric laminated plastics may be greater than the present resin-fabric laminated material, because the protein binder will not have so much tendency to cut the fabric on bending as has the vitreous resin binder. This type of material is used generally for silent mesh gears. These are subjected to more or less oil, protein resistance to which, except at excessive temperatures, should prove excellent. Further work is contemplated along both suggested lines of future development.

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Thermal-Value Nomograph for Anthracite Coal

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IN CONNECTION with their study of the effect of oxidation on the thermal value of anthracites, Scott, Jones, and Cooper (*2*) correlated data on volatile matter, ash content, and heating value in the equation:

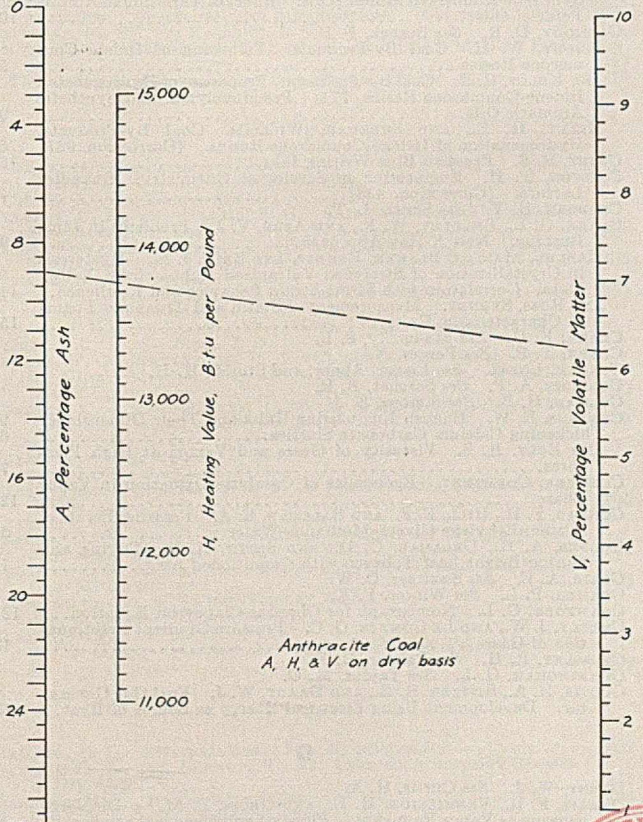
$$H = 14{,}803 + 75.8\,V - 167.4\,A$$

where H = heating value, B. t. u./lb.
V = volatile matter, per cent by weight
A = ash, per cent by weight

H, V, and A are all on a dry basis.

This relation was based on 1008 anthracite samples; 76 per cent of them deviated by less than 100 B. t. u. and 96 per cent deviated by less than 200 B. t. u. from the calculated value. The equation represents the average run of anthracites and warrants construction of a nomograph for rapid and convenient solution.

On the chart the broken line shows that an anthracite containing 9 per cent ash and 6.2 per cent volatile matter will average 13,750 B. t. u. per pound. A somewhat similar nomograph covering bituminous coals was given previously (*1*).



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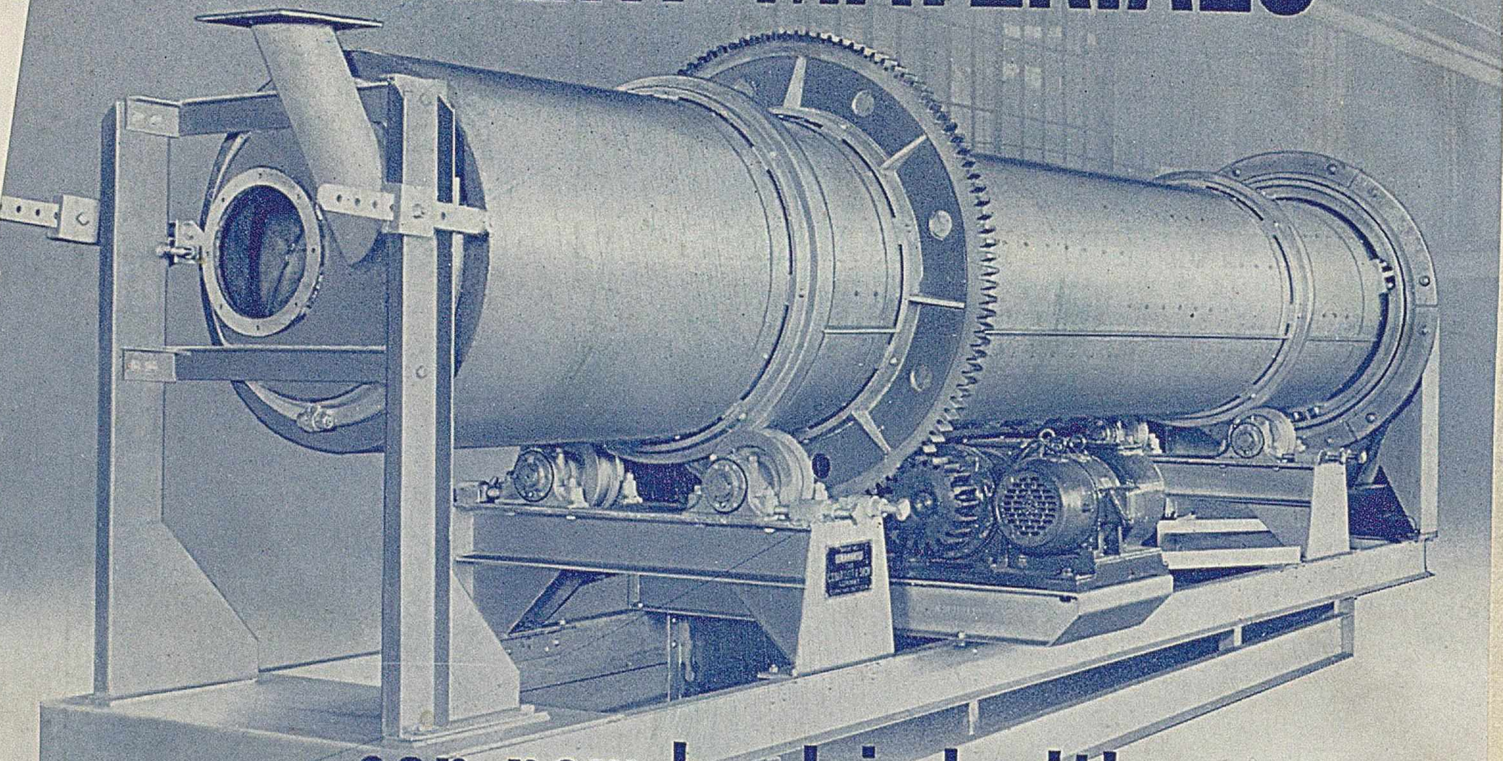
POWDERY MATERIALS



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