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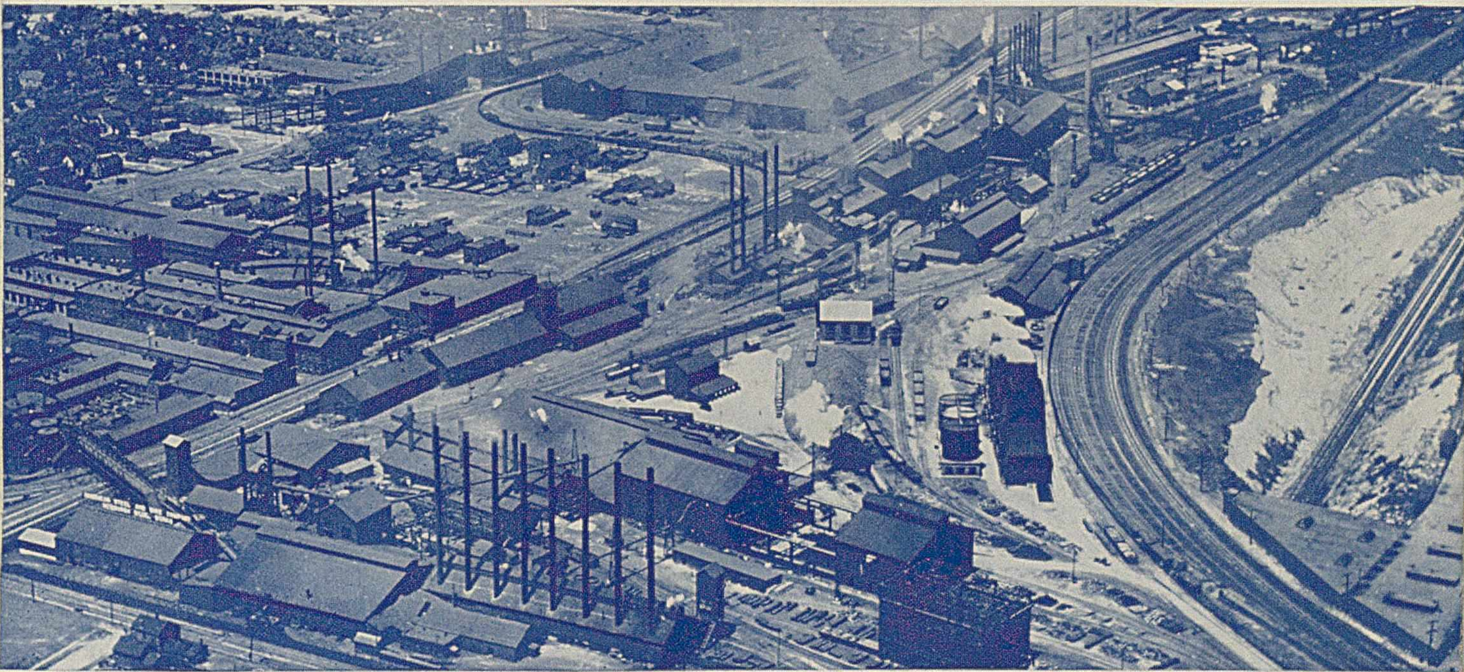
INDUSTRIAL AND ENGINEERING CHEMISTRY

P. 1611/40/I



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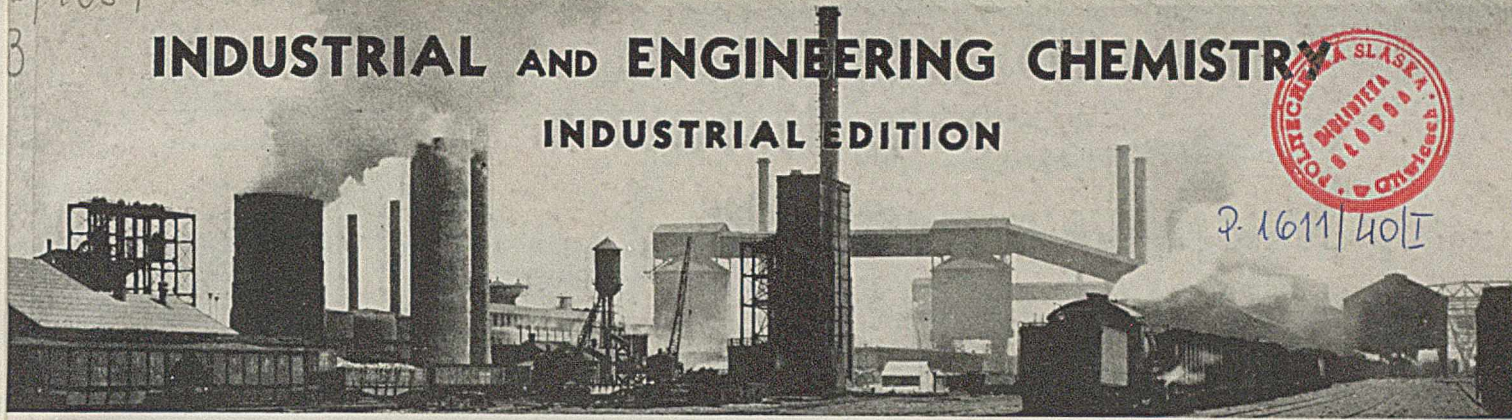

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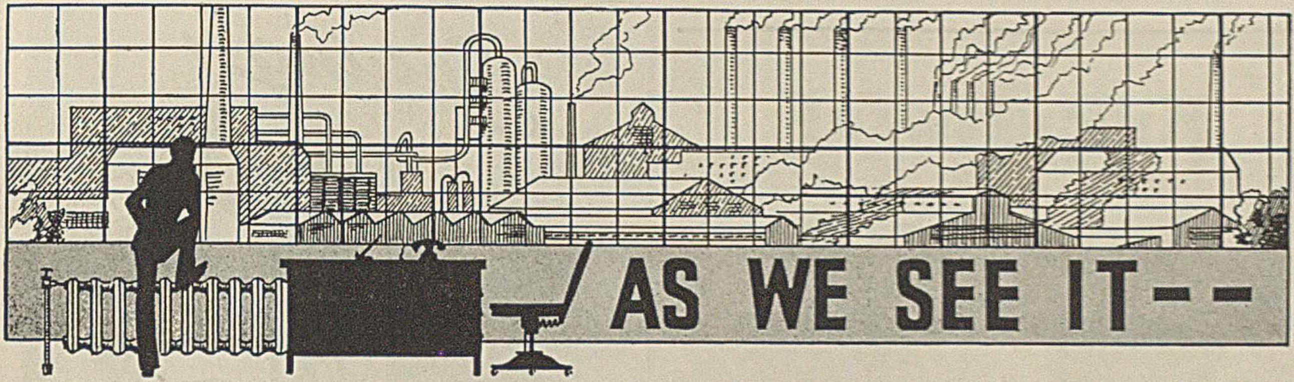


- 1939 and the rapid gains of the science and industry of chemistry during that year fittingly are first subjects for 1940. An editorial account (page 3) describes high lights of the recent past.

- **Vitreous Enamels** serve an increasing number of useful purposes to which they have been adapted by developments and improvements of recent years. Poste (page 9) reviews this field both as to applications and manufacturing processes.

- **Diketene**, newly available in commercial quantities, is seen by Boese (page 16) to possess important potentialities in synthetic processes. Its constitution and properties are described with special emphasis on its high reactivity. The appended bibliography contains fifty-one items.

- **Casein Plastics**, utilizing soybean meal or skimmed milk as the raw material, have been much in the limelight as industrial outlets for farm products. Brother (page 31) discusses these useful plastics and their applications.

- **Nitroparaffins**, now commercially available, form the basis of a huge family of derivatives of various chemical types. One of their promising reactions is condensation with aldehydes to form alcohols, details of which are given by Vanderbilt and Hass (page 34).

- **Coal Tar** and distillates from it have been found by Egloff and his co-workers (page 39) to lend themselves to cracking of somewhat the same type as that applied to petroleum. Gas, gasoline, coke, and tar acids of altered composition are produced.

- **Thermodynamic** properties can be calculated for substances from data on their behavior with respect to the gas laws by a method described by York (page 54).

- **Cellulose** from various sources has been studied by Bailey and Brown (page 57), who have sought to explain observed facts about this material. They find the basic cellulose units (fibrils) strikingly similar, regardless of source or treatment, and show that common tests of beating operations need revision.

- **Hydrocarbon** vapor-liquid equilibria in the range of critical pressures were investigated by Gilliland and Scheeline (page 48) with propylene-isobutane and propane–hydrogen sulfide as experimental systems. Their results have been put into an empirical correlation of general usefulness.

- **Lime-Base Greases**, useful for many lubricating purposes, derive their viscosity principally from the lime soap around their yield values and from their oil content in other ranges, according to Blott and Samuel (page 68). Mathematical expressions of flow have been found which agree with experimental values except near the yield point.

- **Solvents** used in nitrocellulose lacquers must be mixtures to give satisfactory results. Ware and Bruner (page 78) compare hydrocarbon diluents of several types by the constant viscosity method with interesting and useful results.

- **Coal**, classified into bright and splint varieties, from a number of sources has been subjected to tests to determine its usefulness for hydrogenation by Eisner and others (page 73). They conclude from their experiments on splint coals that these are less well adapted than bright coals for the production of liquid fuels by this method.

- **Resins** formed by the copolymerization of different resinifying materials are coming into increasing prominence. Rust (page 64) describes the reactions, conditions, and products of the copolymerization of glycol maleates with vinyl derivatives and limits of compatibility found by varying proportions in the mixture.

- **Fluorine** in fertilizer phosphates is shown by MacIntire and Hardin (page 88) to be responsible for their reversion to insoluble forms. The mixtures studied contained superphosphate and calcined rock phosphate, and the availability of their phosphorus content was not affected by mixing so long as both constituents were free from fluorine.

- **High Pressure Methods**, now so widely employed, frequently require physical data hitherto unavailable. Wan and Dodge (page 95) have determined the solubility of carbon dioxide in benzene at pressures up to the critical pressure of the gas at various temperatures.

- **Isopropyl Ether**–isopropanol mixtures have been investigated by Miller and Bliss (page 123). Specific gravities, boiling points, and vapor compositions over the entire range of mixtures are given.

- **Gum Formation** is used as a test of quality of cracked gasoline. Yabroff and Walters (page 83) have looked into the effects of varying conditions of the test and report their findings.

- **Resins** of several types have been modified by Ralston and co-workers (page 99) with fatty acid derivatives to produce highly flexible products. Base resins of the dicyclopentadiene, coumarone, and indene types when so modified showed promise of usefulness in the coating industry.

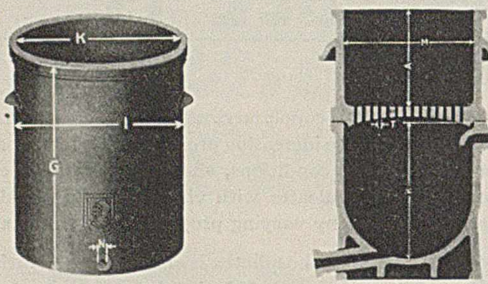
- **Silica** of high adsorptive power has been prepared from vermiculite by Hansen, Samuel, and Forni (page 116), and its properties have been studied. Data are given on preparation and use.

- **Separation Processes**—specifically, fractional distillation—operate most efficiently when designed on the principle of minimum dilution, according to Randall and Longtin (page 125). The principle and typical applications are discussed.

- **Water** can be softened by the lime-soda process to certain limits only. The limits of the process and methods of improvement by other additions are described by Larson and Buswell (page 130). Colloidal effects and the electrical charges on different colloidal particles in water softening are also discussed by these two writers (page 132).

- **Chemical Engineering** translates chemical processes from the laboratory to the industrial scale, according to Chilton (page 23), who in his Chandler Lecture describes in some detail and with numerous examples the functions of chemical engineers in industry.

DHKilleffer



TO BEGIN a new year properly, one must look backward and establish base lines to plot his course ahead. Like the mariner, each of us will more surely reach objectives in the uncharted future by starting his journey or his search after careful study of known landmarks of experience. This month a few of our points of departure are reviewed. In February we shall have a more penetrating analysis of one group of landmarks by a recognized expert in their applications.

Stine, acclaimed by the award of the Perkin Medal, will tell us, as only one intimate with the whole subject can, of the rise of our organic chemical industry. The importance of the subject and the vital role of the writer in the dramatic events he describes lend his words an interest and an authority seldom equaled.

Not to abandon so interesting a subject too quickly, we shall look into some of its future phases as well. This we shall do by considering the unit chemical processes, again distinguishing them from the unit physical operations. On these we shall learn of new developments in hydrolysis, methylation, amination, and fluorination. Some important new data on calculating the effects of high pressures on reactions, and on some new methods of producing more or less familiar compounds will be disclosed, all with an eye trained on the chemical aspects of the processes. On the whole, this group of papers supplies a substantial grist for the process development mill.

Hardly off this subject is the dehydrogenation of gaseous paraffins, a process widely practiced in making more and better superfuels out of gas from wells and from the cracking stills of the oil industry.

Which leads rather naturally to the question of refining oil products by the removal of sulfur. Since sulfur commonly occurs as mercaptans, their extraction with alkali solutions is to the point.

Fuel, of course, brings up coal, which lustily carries on in spite of internal combustion, oils, and water power. About it and the old problem of its deterioration and spontaneous combustion in storage piles, we shall learn more.

Resins will not be neglected and new data will be provided on some of the synthetic members of this prolific family which include rosin in their make-up.

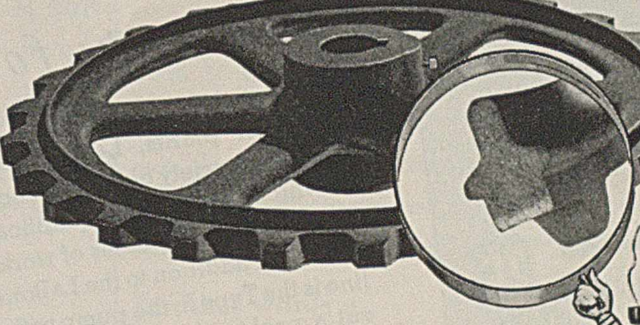
From resins it is scarcely any jump at all today to the many aspects of the paint, varnish, and lacquer industry now using them in such rapidly increasing quantity and variety. New information on formulation of solvent mixtures and the effects of different constituents on their characteristics can be expected. Behavior of titanium pigments in exterior paints will also be discussed.

Agricultural wastes have been submitted to destructive distillation with interesting results of which we shall learn.

And that suggests insecticides. Nicotine is the one this time and some of its properties in spray mixtures will be the specific topic.

And there are more, but if these should be described there would be no room for a cheery Happy New Year from

Your humble spy



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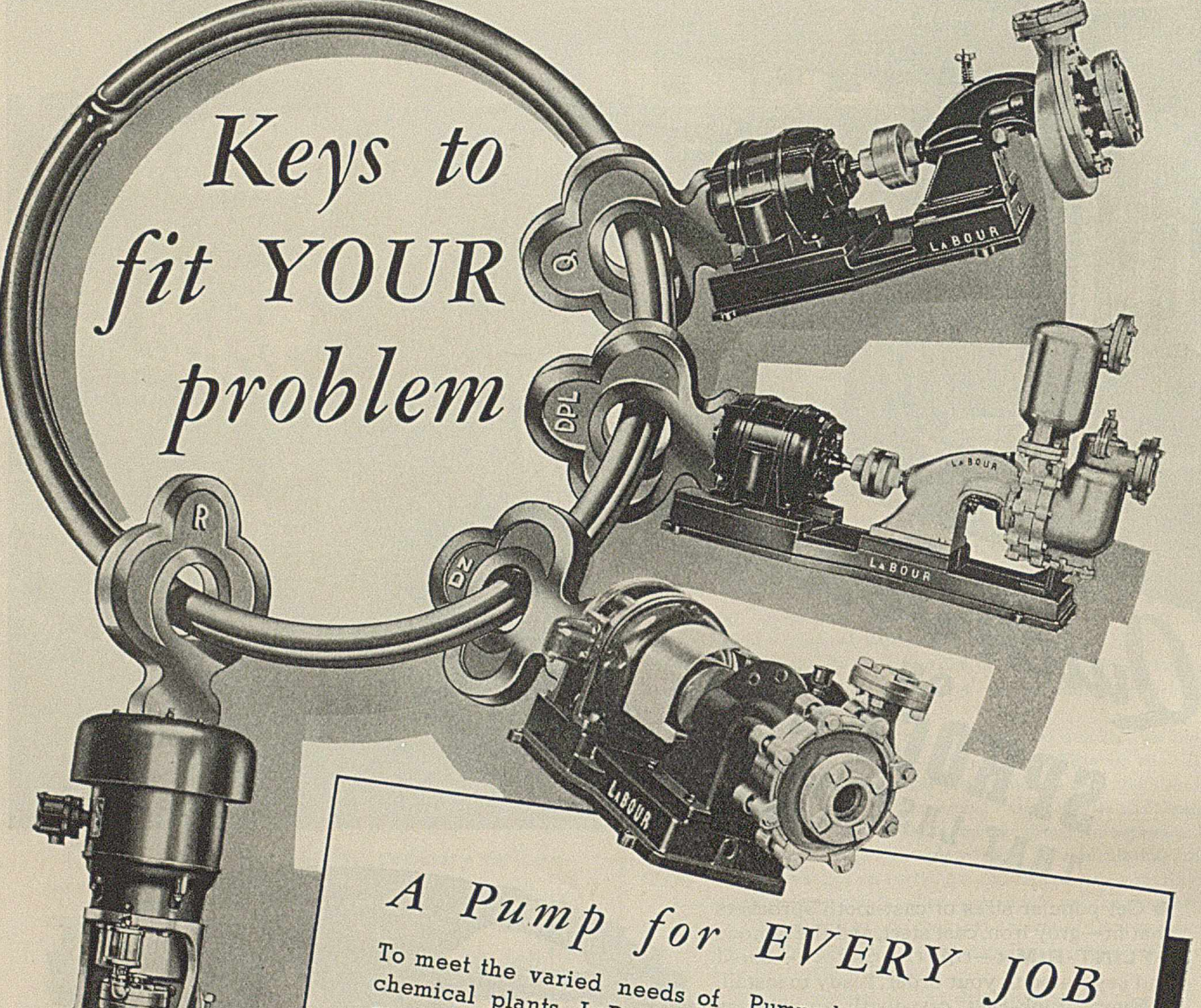
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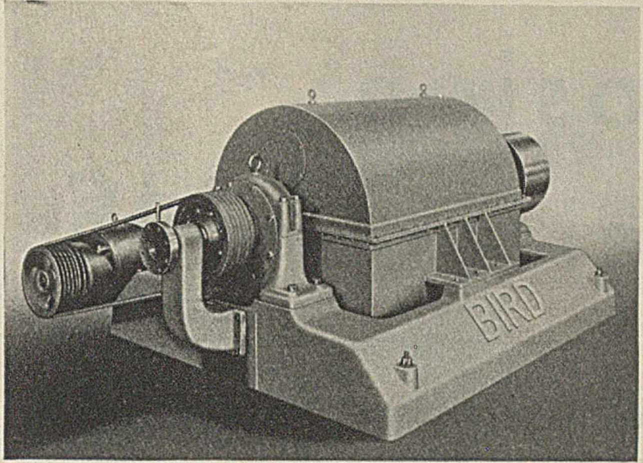

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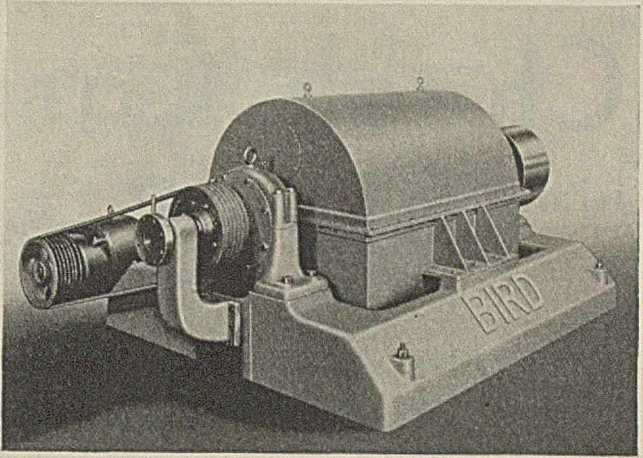

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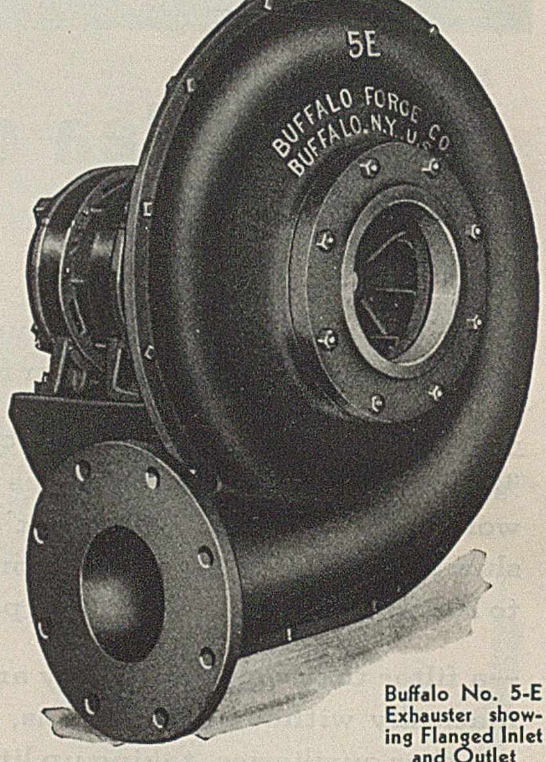

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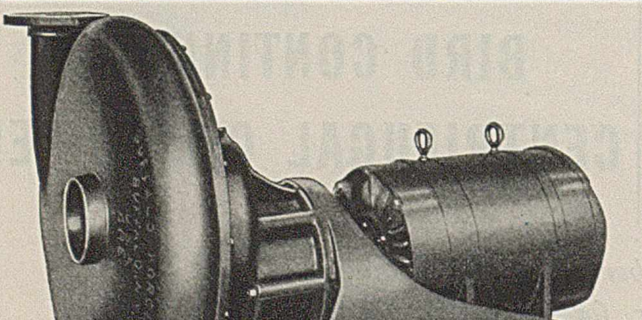

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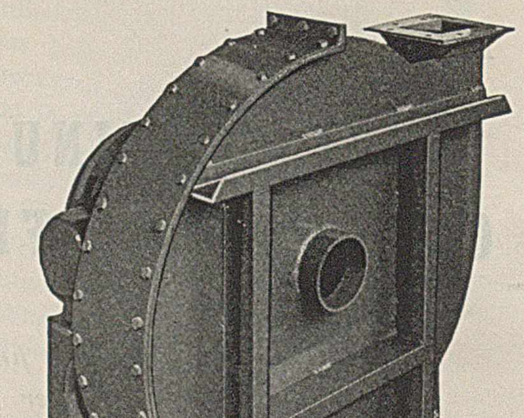

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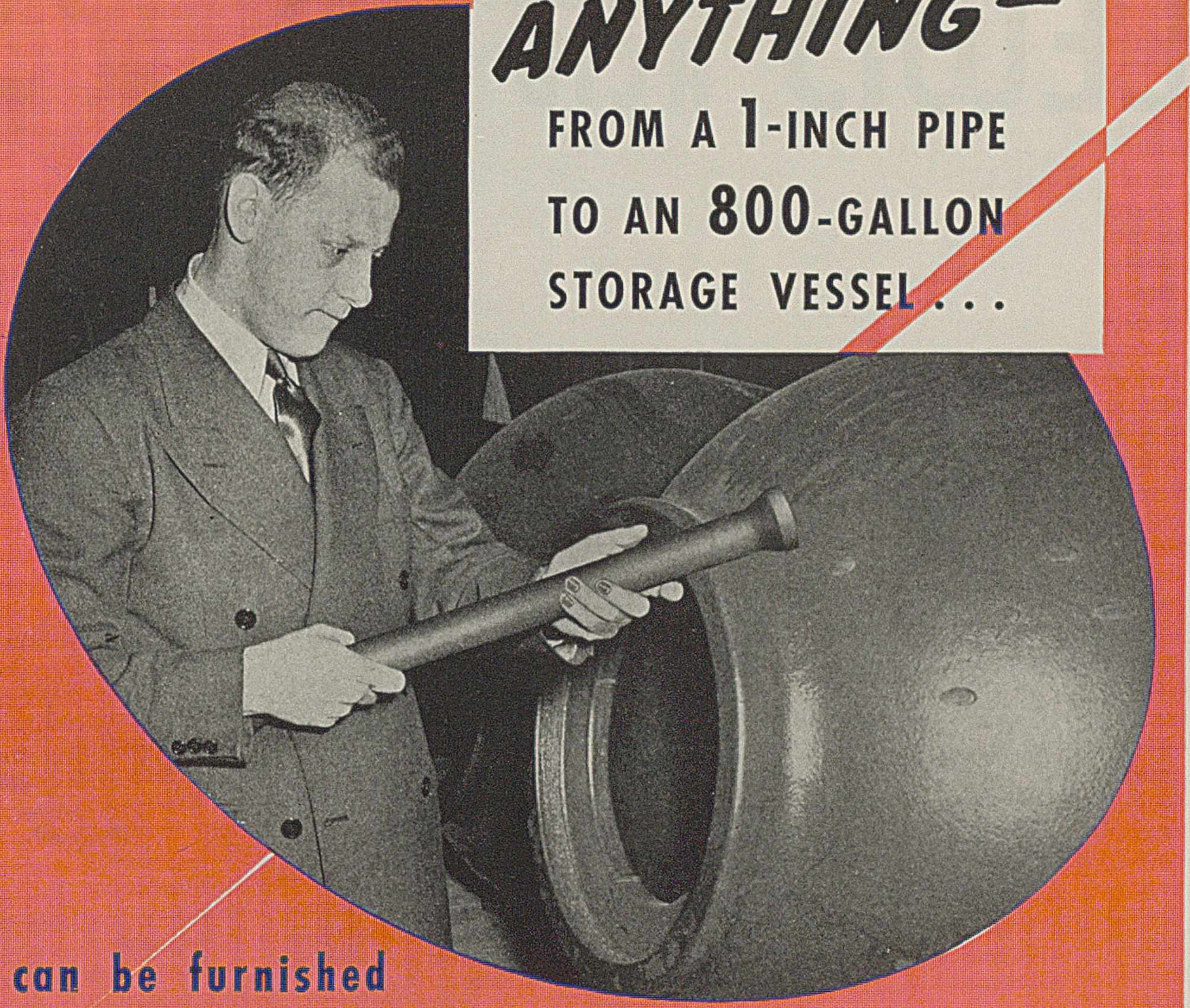

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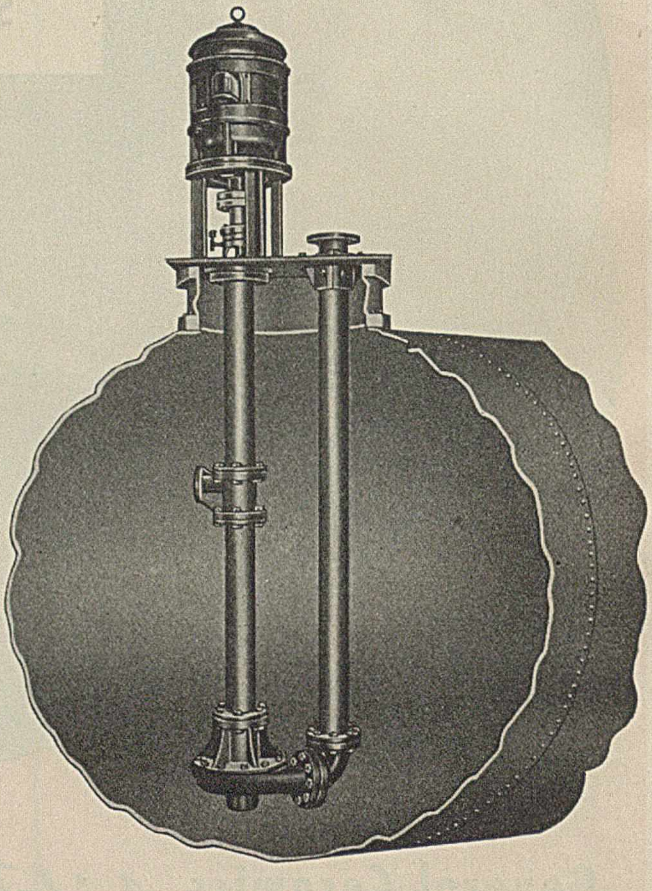

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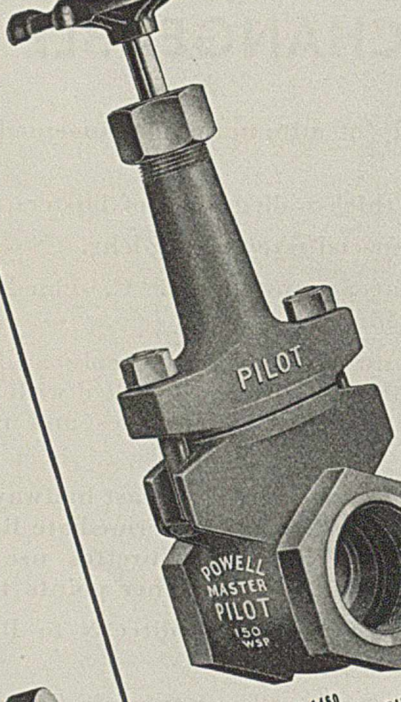

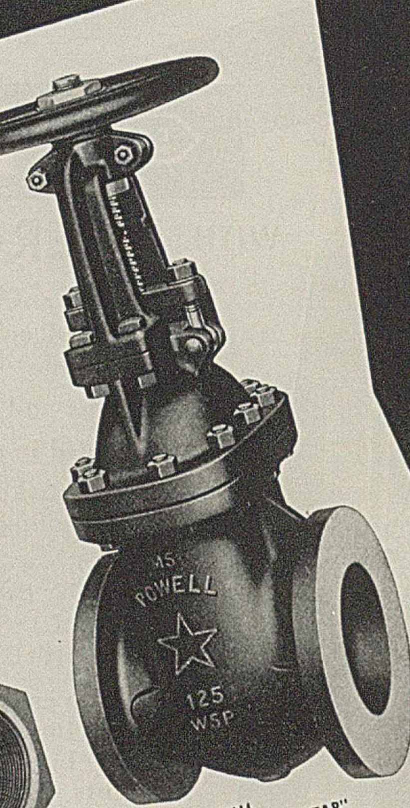

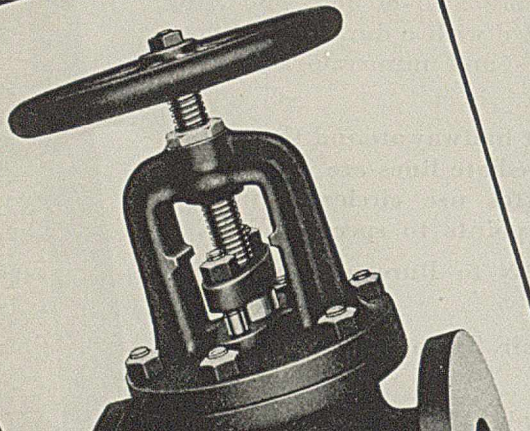

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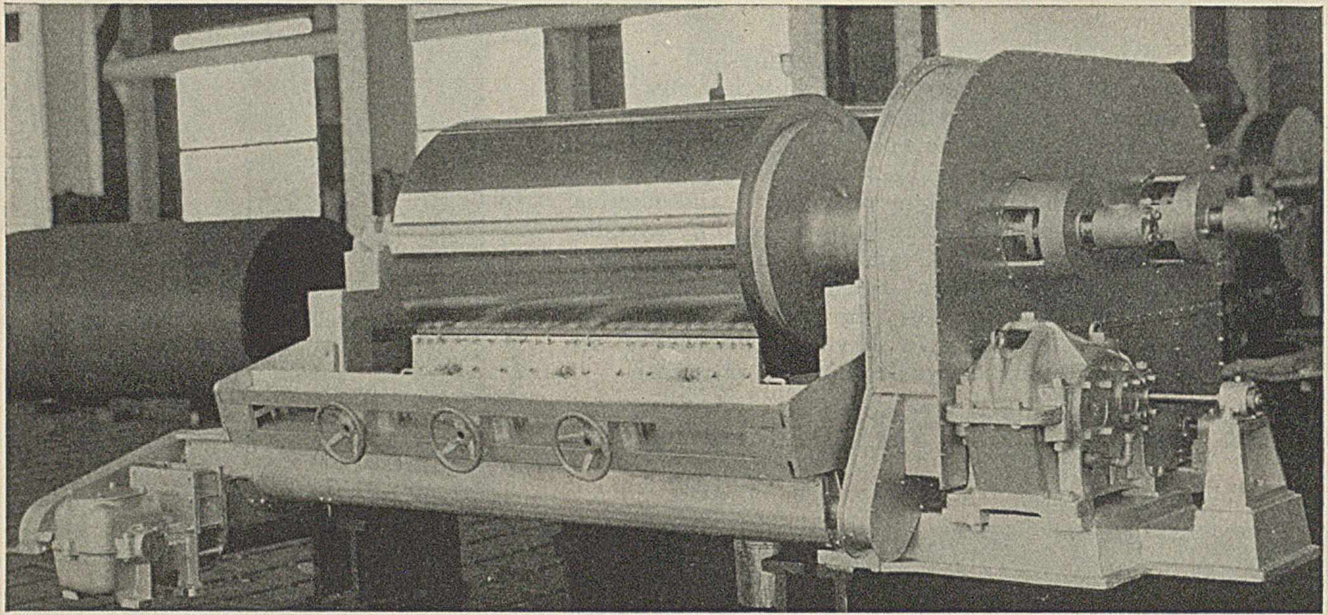

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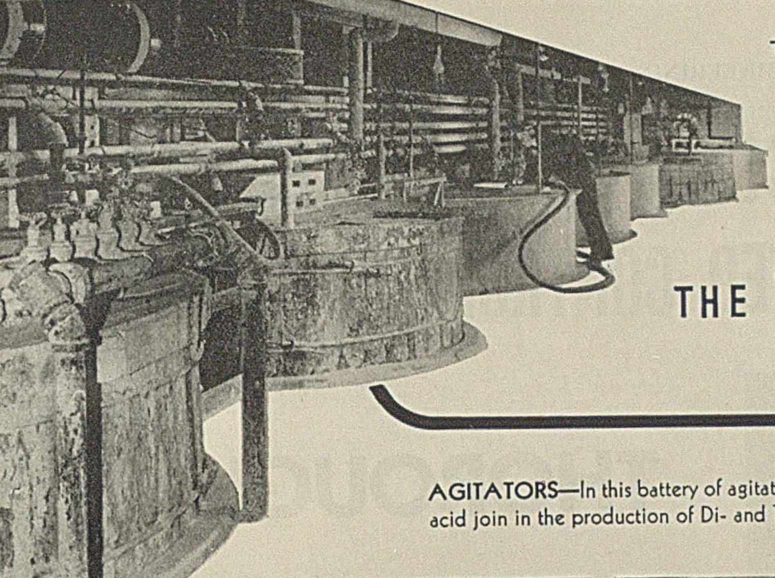

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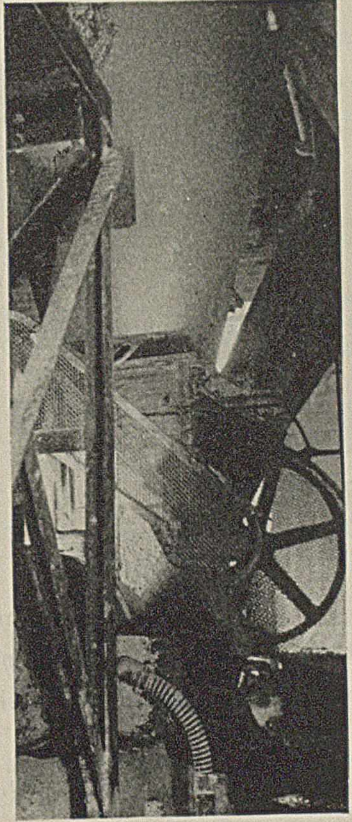
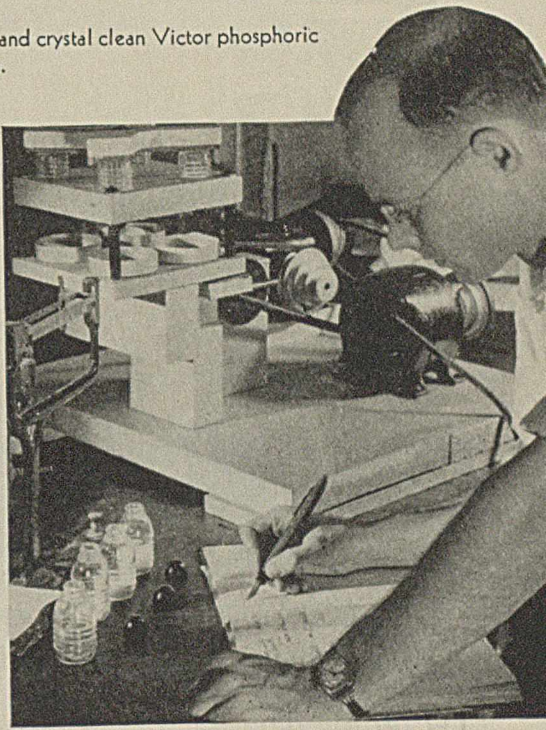
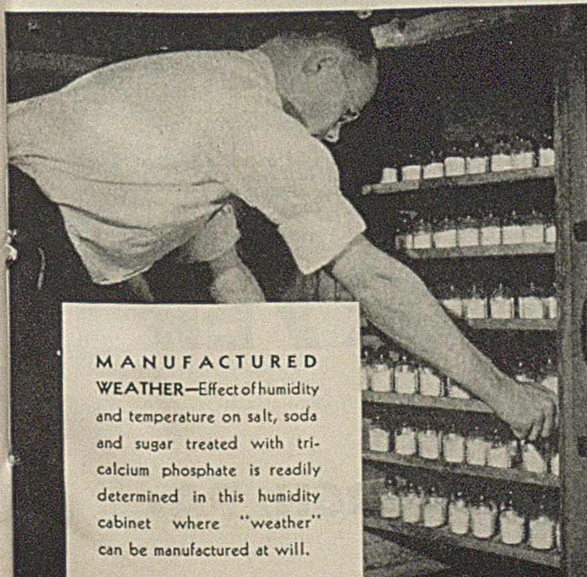




CONTROL—Accurate adjustment of the concentrations of lime and phosphoric acid is essential to the production of a pure product. Here goes a sample to the control laboratory.

MILLING—Milled to an impalpable powder so fine that the largest particle is less than 20 microns (1/1200 of an inch) in diameter, Victor Dicalcium Phosphate (Dentifrice Grade) is used as a polishing agent in non-alkaline tooth-pastes and powders.

SHAKER—Air-separated Victor Tricalcium Phosp is used as a conditioner for salt, soda, and suga prevent caking. Conditioning and lubricating ac is measured with the aid of this multiple shaker.



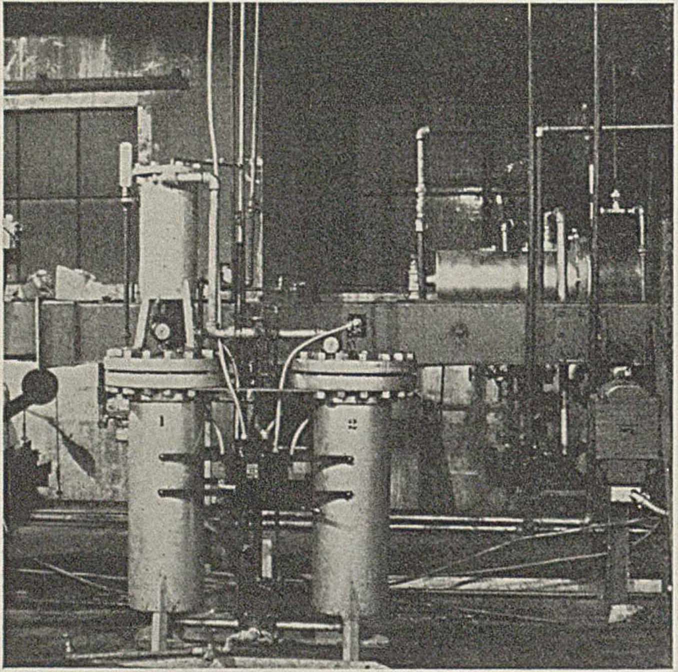
MANUFACTURED WEATHER—Effect of humidity and temperature on salt, soda and sugar treated with tricalcium phosphate is readily determined in this humidity cabinet where "weather" can be manufactured at will.

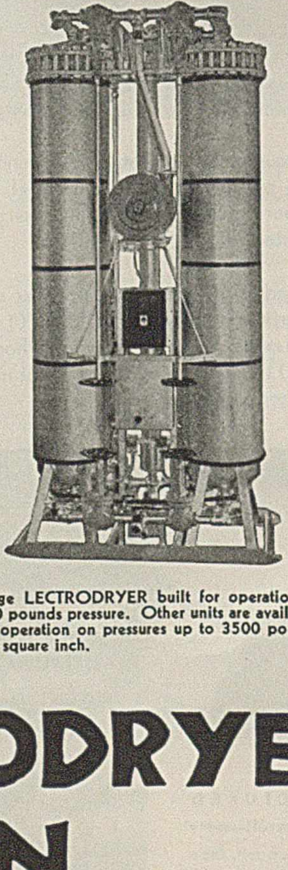
SEND FOR CATALOG OF VICTOR CHEMICALS

Phosphoric Acid
Pyrophosphoric Acid
Polyphosphoric Acid
Metaphosphoric Acid
Phosphorus
Phosphoric Anhydride
Phosphorous Acid
Alkylphosphoric Acids
Ammonium Hexaphosphate Dinitride
Ammonium Phosphates
Alkyl Ammonium Phosphates
Fireproofing Compounds
Calcium Phosphates
Magnesium Phosphates
Potassium Phosphates
Sodium Phosphates
Sodium Pyrophosphates
Potassium Pyrophosphate
Sodium Metaphosphate
Alkyl Acid Pyrophosphates
Formic Acid
Aluminum Formate
Nickel Formate
Sodium Formate
Sodium Boroformate
Oxalic Acid
Calcium Oxalate
Sodium Oxalate
Magnesium Sulphate
Sodium Aluminum Sulphate
Tuff-Lite
Ferrophosphorus
Triple Superphosphate

VICTOR CHEMICAL WORKS

3002 Board of Trade Building
Chicago, Ill.





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

USI SOLVENT *Reg. U.S. Pat. Off.* NEWS USI

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

Solox Widely Used For Plane Propeller Anti-Icing Fluids

Mixed With Glycerine to Avert Dangerous Flight Conditions

Rapid growth of airplane transportation is expected to result in an increased demand for Solox, U.S.I.'s alcohol-type solvent, which is reported to find extensive use in propeller anti-icing mixtures.

All planes operating in commercial transport service are equipped with a device for supplying a de-icing mixture to a slinger ring at the propeller hub. From this point the mixture is further spread over the propeller surface by centrifugal force, preventing ice formations on the propeller which might result in dangerous flight conditions.

A suitable mixture for the purpose is said to consist of 85 parts of Solox and 15 parts of C. P. Glycerine. The average plane carries 10 gallons of de-icing solution on regular flights—more than enough for a trip from New York to Chicago under ordinary conditions.

WINTER FLYING. A mixture of Solox and glycerine, supplied to airplane propellers, aids in preventing ice formations.

Finds Way of Making Foam For Extinguishing Fires

FRANKFORT-ON-THE-MAIN, Germany—A new process of producing fire-extinguishing foam is revealed in a U.S. patent granted jointly to inventors here and at Bad Soden.

The foam, it is claimed, is prepared from a gas, a large quantity of water, and a relatively small amount of a concentrated aqueous solution of an organic foam-forming agent. In addition, the solution contains a hydrophilic organic solvent, such as alcohol, glycol, or ethyl acetate, which, the inventors say, facilitates the dissolving of the foaming agent in the water.

Alcohol and Ethyl Acetate are U.S.I. Products.

Alcohol Proves Helpful In Bleaching of Wood

BUFFALO, N. Y.—That alcohol can be used to facilitate the bleaching of wood has been revealed in a patent granted to an inventor here.

The alcohol, according to the patent, is used in connection with a peroxide and an alkali. The alcohol is allowed to evaporate from the wood, and thus increases the concentration of the bleaching agent.

Treatment With Curbay X Aids Efficiency of Coal Combustion

U.S.I. Product Valuable Medium Promoting Quick Ignition and Free Burning; Overcomes Caking and Air Slaking

Curbay X powder, specialty product manufactured exclusively by U.S.I., has definitely established its value as a medium for treating coal to increase the efficiency of combustion, Mr. F. A. Schleindl, coal conditioning specialist, told Solvent News.

"Coal should be considered a raw material and not a finished product. In order to attain its maximum usefulness, it must be processed like any other raw material to suit the specific job it is to do. In this processing, Curbay X has proved itself a valuable and versatile assisting medium.

"This conclusion was reached after extensive laboratory research over several years here and abroad, followed by large-scale commercial applications on every type of hand- and stoker-fired equipment, involving hundreds of thousands of tons of coal from practically every mining field.

Many Advantages Indicated

"From this broad experience with Curbay X for coal conditioning, the following advantages in attaining fuel economy are noted:

"1. It reduces caking, with its concomitant disadvantage of high stack losses, caused by the excess air needed for combustion.

"2. It minimizes air-slaking.

"3. Substandard or low grade coals with inferior burning characteristics can often, through Curbay X treatment, be brought up to standard performance with obvious money savings.

"4. It reduces soot deposits and smoke.

"5. Curbay X under proper formulation with certain additions, serves to raise or depress the fusion point of the ash, as desired, resulting in a neutral ash and clinkers easy to remove.

"6. It aids in preventing spontaneous combustion.

Wide Usefulness Foreseen

"A particularly striking feature of Curbay X is the readiness with which it can be adapted to the processing of different types of coal. It is, of course, a recognized fact that

(Continued on next page)

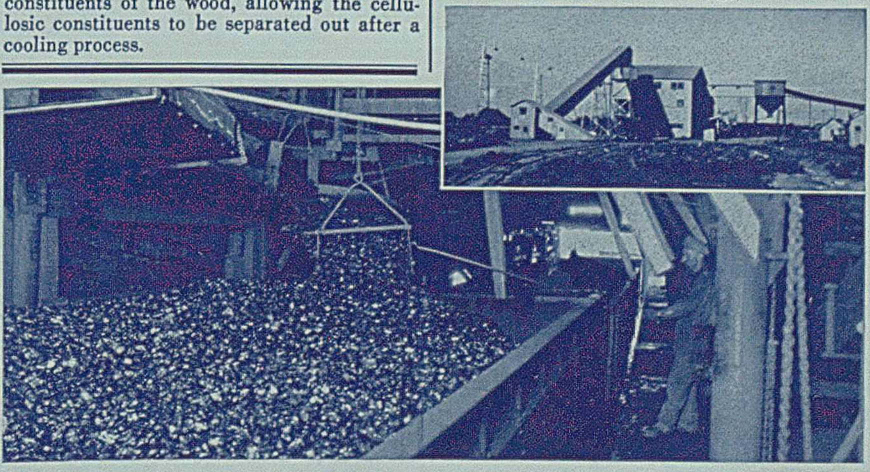
Here is U.S.I.'s new 1-gallon Solox can, designed for easy storing and quick sales in retail outlets. Its attractive colors make it particularly adaptable to display purposes, and rectangular shape helps save valuable shelf space. The can is provided with a convenient carrying handle, and is equipped with a closure of the popular "U-Press-It" type.

Higher Alcohols Used to Extract Pure Cellulose

ST. PAUL, Minn.—How alcohol can be used to obtain relatively pure cellulose from wood is revealed in a patent granted to an inventor here.

Process is reported to consist in treating the wood with a water solution of a monohydroxy alcohol. The alcohol, it is said, should have at least four carbon atoms, and at least three of them in a straight chain; should be substantially insoluble in water at normal temperatures, but soluble at temperatures between 100° and 200° C. In addition to the alcohol, an inorganic alkali is used in amounts ranging from 2 to 10%.

The process, it is said, serves to dissolve in the water practically all of the non-cellulosic constituents of the wood, allowing the cellulosic constituents to be separated out after a cooling process.



Curbay X, reported to have shown excellent results in coal conditioning. Desirable point of application is the chute between breaker and gondolas, as shown in large photograph. Insert shows plant of Pittsburg and Midway Coal Mining Co., where treatment with Curbay X is a feature of coal processing.

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

January ★ **SOLVENT NEWS** ★ 1940

Soybean Oil Paints Show Up Well in Exposure Tests

WASHINGTON, D. C.—Paints and varnishes made with soybean oil compare satisfactorily with those made from tung, perilla, and linseed oils when subjected to exposure tests, it is indicated by reports received at the Department of Agriculture here from the Government soybean laboratory at Urbana, Ill.

While it is recognized that the soybean paints harden and dry a little more slowly than other types, the tests indicated that this factor did not have a harmful effect on the durability of the paint, it is said.

White exterior paints made from commonly used pigments with soybean oil appeared to be in good condition after two years' exposure on outside fences, it is stated. Cheaper varnishes made with soybean oil are believed to offer interesting possibilities.

Discusses Production And Uses of Industrial Alcohol

BALTIMORE, Md.—L. A. Helfrich, Production Manager of U.S.I.'s plant here, delivered an address on Production and Uses of Industrial Alcohol before the Baltimore branch of the American Pharmaceutical Association on Thursday, December 14, in the School of Pharmacy Building, University of Maryland.

Curbay X Conditions Coal

(*Continued from previous page*)

coals vary widely in their chemical composition, and processing for fuel economy must take into account both the chemical composition of the coal and the nature of the application. By varying the proportions of Curbay X and using it either alone or in combination with other materials, it is possible to condition a wide variety of coals for specific applications.

Action Considered Catalytic

"Mixed with water, and with or without other chemical additions, Curbay X is applied to the coal in the form of a spray. Only a trifling amount per ton is needed with corresponding low cost.

"The action of Curbay X in increasing the efficiency of fuel combustion is both mechanical and catalytic. That the action is catalytic rather than chemical is indicated by the relatively small amount of Curbay X required in the conditioning process. In fact, this application of Curbay X may be regarded as an extension of catalytic chemistry into the coal combustion field.

"It is the custom to buy coal on a B.T.U. basis, rather than on a basis of *recoverable* heat—the factor in which the user should be primarily interested. Coal conditioning, properly applied, may serve to bring about a reconsideration of such purchasing policy. Curbay X is not, of course, to be regarded as a panacea for all coal troubles and its use should be recommended only after a study of specific conditions."

U.S.I. invites both producers and users of coal who wish further information from Mr. Schleindl on coal conditioning with Curbay X to write to SOLVENT NEWS.

Prints Artificial Films And Foils with New Ink

LONDON, England—A printing ink said to be suitable for artificial foils, films, and similar products is described in a U. S. patent issued to an inventor here.

The ink is reported to consist of a pigment, an organic derivative of cellulose, such as cellulose acetate, and a plasticizer, used in a proportion at least five times as great as the total weight of the plasticizable material, suitably with the use of carbon black, iron oxide, benzyl alcohol, acetone, benzene, and alcohol.

Acetone and Alcohol are U.S.I. products.

U.S.I.'s Fairfield Plant Wins Safety Merit Award

Mr. F. C. Hettinger, Superintendent of U.S.I.'s Fairfield Plant, recently received, as representative of the plant employees, a certificate of merit awarded by the company's insurance carrier for the non-accident record established by the plant.

The record was established during the period from January 19 to August 6. During this time the plant operated for a total of 364,315 man-hours without a disabling injury.

Packs Food with Solid CO_2

NEW YORK, N. Y.—A package that is said to preserve the flavor of foodstuffs, such as coffee, sauerkraut, etc., has been patented by an inventor here. Package is made with an inner container, in which is inserted a pellet of solid carbon dioxide ("Dry-Ice"*). Outer container, says the inventor, is capable of supporting the walls of the inner flexible container when pressure is exerted by the vaporization of the pellet.

*Manufactured and supplied by Pure Carbonic, Incorporated, an associated Company of U.S.I.

TECHNICAL DEVELOPMENTS

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

A new industrial finish is said to have exceptional low-temperature speed baking characteristics. Curing temperatures are reported to be the lowest ever obtained for a speed-baking finish with similar properties of adhesion, flexibility, color retention, and toughness. The manufacturer claims that it can be used in conventional ovens. **(No. 290)**

U S I

A latex preservative is said to be non-volatile at ordinary temperatures, odorless, effective, and permanent. According to the manufacturer, it is toxic to algae, bacteria, protozoa, fungi, and other micro-organisms, while it is no more harmful to human beings than many other chemicals in common use. **(No. 291)**

U S I

A soap anti-oxidant is reported to be effective in minute quantities in restraining the oxidation and resulting rancidity, discoloration, and other adverse qualities of soap. It is said to be equally effective in soaps produced from animal or vegetable oils, filled or unfilled. **(No. 292)**

U S I

A protective coating is said to be suitable for wood or metal exposed to liquid acids or caustics. The manufacturer recommends it for lining tanks containing the usual commercial acids or caustics, or for protecting machinery from the spillage of these products. **(No. 293)**

U S I

A pH tester is described as a handy means of making approximate pH measurements. It is said to be a device for holding and dispensing pH paper in convenient form. According to the manufacturer, any desired length of paper can be drawn from the container, while at the same time the paper is protected from contamination by the atmosphere. **(No. 294)**

U S I

An adhesive cement has been released for sale on a restricted basis, it has been announced. According to the maker, the cement permits making strong, chemically-resistant joints between rubber and metals, and is useful in joining many other materials, such as woods, ceramics, and many synthetic resins. **(No. 295)**

U S I

A new mixer is said to be suitable for mixing viscous materials without incorporating air. The mixer is further reported to be silent and free from vibration. **(No. 296)**

U S I

White chromium plating is reported to be possible with a new chemical for converting ordinary chromium solutions into white chromium solutions. The process is said to produce a plate free from bluish tints, and to effect savings in plating time. **(No. 297)**

U S I

An aluminum finish is said to produce a soft patina resembling that of tarnished silver. It is baked on, and is reported to show excellent adhesion and high resistance to mechanical abrasion. **(No. 298)**

U S I

A pulley covering comes in the form of a plastic coating material which can be applied to a flat pulley after cleaning with benzol or carbon tetrachloride, it is reported. **(No. 299)**

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

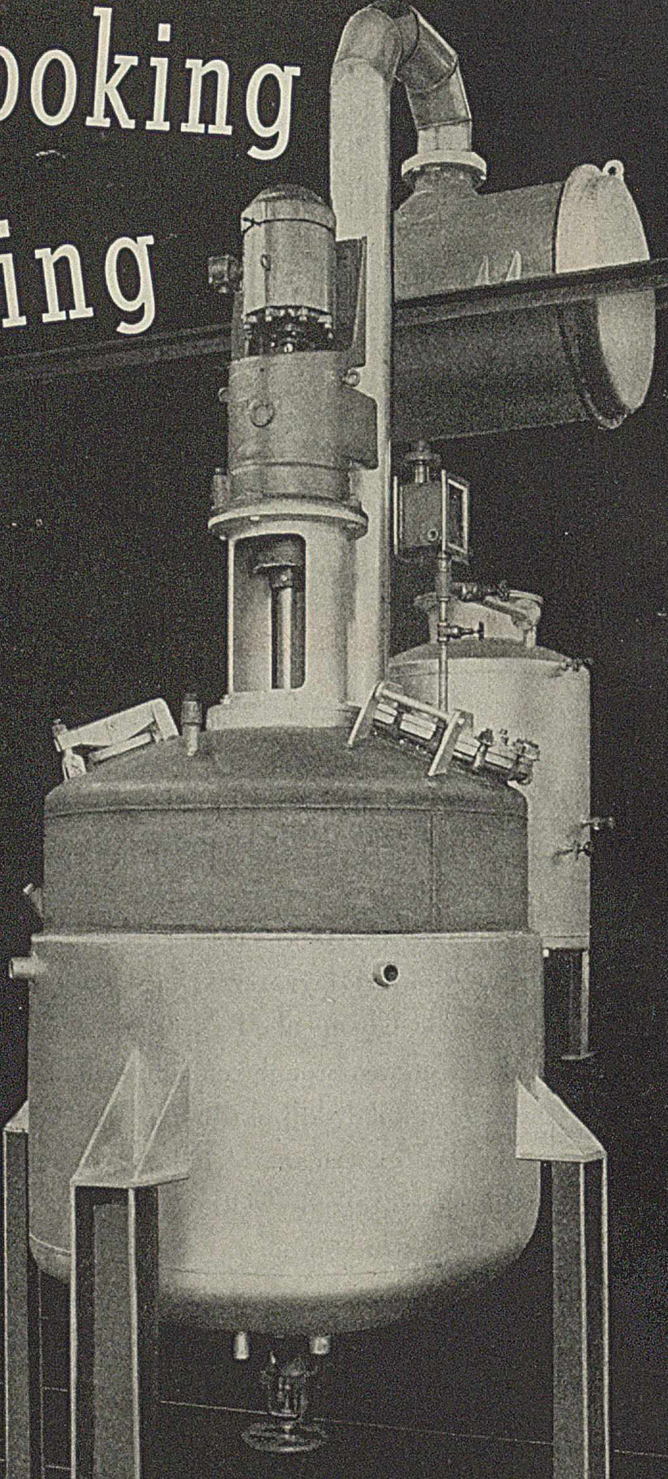
OTHER ESTERS
- Amyl Propionate
- Butyl Propionate
- Dibutyl Oxalate

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.
- Butyl-mesityl-oxide-oxalate
- Cellulose Acetate
- Collodions
- *Curbay Binders
- *Curbay X (Dried Curbay)
- *Derex
- Ethylene
- Methyl Acetone
- Nitrocellulose Solutions
- Potash, Agricultural
- *Vacatone

Synthetic Resins
Varnish Cooking
Oil Bodying



The photograph shows a Blaw-Knox stainless steel, low temperature, synthetic resin production unit, consisting of a steam jacketed and water cooled Process Autoclave, drip type surface condenser, special reflux measuring sight-box, and condensate receiver.

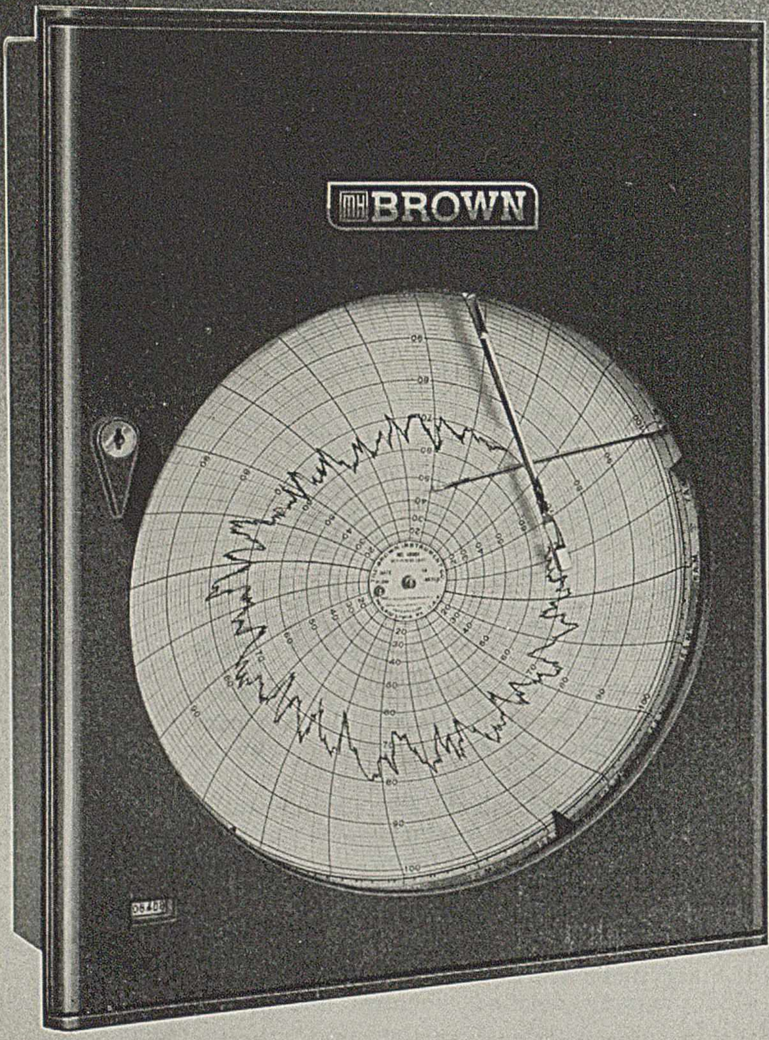
The Autoclave proper is equipped with an anchor type agitator, explosion proof drive unit, and a Blaw-Knox Flush Plug Type Valve.

Equipment for oil bodying, and varnish cooking, involving the use of special steels, are a part of the broad line of products designed and fabricated by Blaw-Knox for service in the process industries. We invite you to send for Catalog No. 1685—"Blaw-Knox Process Autoclaves."

BLAW-KNOX DIVISION
OF BLAW-KNOX CO.
Farmers Bank Building · Pittsburgh, Pa.

BLAW-KNOX

BROWN *Announce*



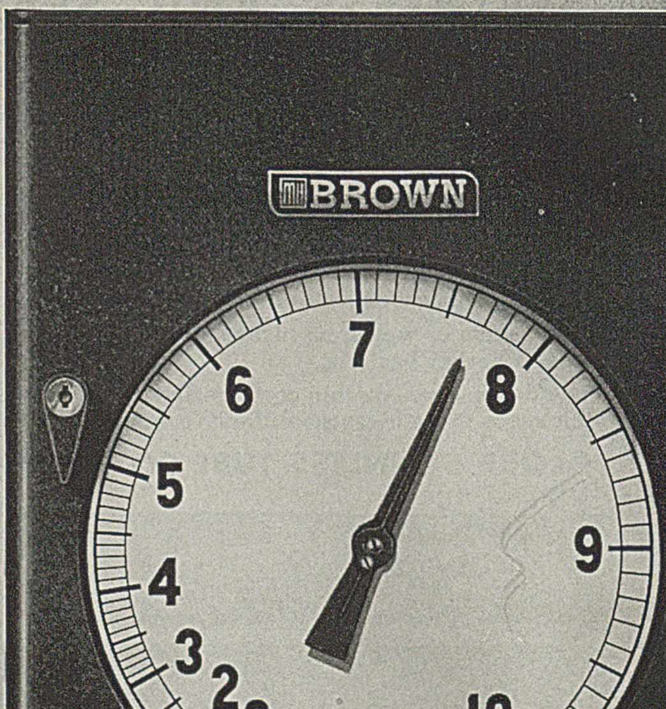
RECORDING, INTEGRATING FLOW METER

Modern RECTANGULAR CASE

Styled by HENRY DREYFUSS

Designer of the "Twentieth Century Limited"

BROWN ENGINEERS COLLABORATING WITH THIS WELL-KNOWN DESIGNER HAVE PRODUCED AN INSTRUMENT THAT IS NOT ONLY A THING OF BEAUTY, BUT A TRIUMPH OF ACCURACY AND SIMPLICITY.



INDICATING FLOW METER

Advanced Design

ASSURES ACCURATE MEASUREMENT WITH SIMPLICITY FOR METERING FLOW AND LIQUID LEVELS

A NEW LINE OF FLOW METERS

With justifiable pride The Brown Instrument Company presents the latest development in Flow and Liquid Level Recorders, Indicators and Controllers.

These new Flow and Liquid Level Instruments are entirely new inside as well as out. Advanced design of the operating mechanisms provides a new conception of *accurate measurement with simplicity*—the result of years of research and field testing under actual working conditions by Brown Engineers.

The classic, simple lines of the modern streamlined case—styled by Henry Dreyfuss, designer of the "Twentieth Century Limited"—give added beauty and distinction to practical and serviceable instruments.

For modern panel mounting they blend with the panel surface and surrounding instruments to provide the much-wanted flush appearance.

Available with electrical and mechanical meter bodies for the measurement and control of steam, air, oil, gas and other fluids.

Advanced Design Embodies:

NEW ELECTRIC FLOW METER: Operates on the Inductance Bridge Principle; inherently independent of voltage fluctuations.

AUTOMATIC PLANIMETER PEN: Gives a record on total flows over any period of time.

SIX INTERRELATED RANGE TUBES: With corresponding charts and scales make range changing easy, inexpensive.

INTERNAL MECHANISM: All moving parts have been designed to reduce wear and lost motion.

NEW INTEGRATOR: Insures highly accurate totalizing at all rates of flow from 0 to 100%.

DIAL INDICATOR: A 12" dial and new pointer provides better readability.

SIMPLE FLOAT MECHANISM of Mechanical Flow Meter: Insures unhampered float movement and long trouble-free operation. Single lever connects float to pressure-tight bearing shaft. No chains or complicated linkage to impede float movement or get out of order.

LARGE FLOAT: Provides ample power to accurately transmit to the pen minute variations in mercury level, thus assuring accurate measurement.

PRESSURE-TIGHT BEARING—Precision Made: Eliminates the necessity for a stuffing box. The bearing is packed with grease especially suited to the service and operating pressure for which the meter will be used. Automatic, built-in lubricator insures constant lubrication of the bearing under all conditions.

PRESSURE CHAMBERS: Designed to withstand the severe service demanded from this type of meter. High pressure chambers on all meters are forged steel. Sturdiness is built in to every part to insure long, trouble-free service.

MODERN RECTANGULAR CASE: Of die-cast aluminum, dust and moisture-proof and resistant to moist salt and acid atmospheres. Includes such desirable features as dust shield, concealed hinges with exceptionally heavy pins, door stop, oil resistant recessed gasket, and cam action handle-lock which draws the gasket firmly against the case.

UNIVERSAL MOUNTING: Universal case permits mounting flush on panel with concealed clamps or on floor stand, wall bracket or pipe saddle.

IMPROVED RECORDING SYSTEM: Linkage is reduced to a minimum. Outboard bearing and hardened pivots on pen shaft insure unhampered pen movement and instant response. Stainless steel pen arm is 8" long, with ribbed reinforcement, permits pen travel of 4¾". Pen and pen arm are non-corroding, easily removed, cleaned and replaced with no effect on calibration. Micrometer adjustment on pen arm assures precision setting.

SIMPLE CHART DRIVE: New chart hub eliminates chart slippage, screw knob and chain—chart is placed on over two tapered studs. Chart hub acts as a time setting device and friction clutch facilitates setting chart for correct time.

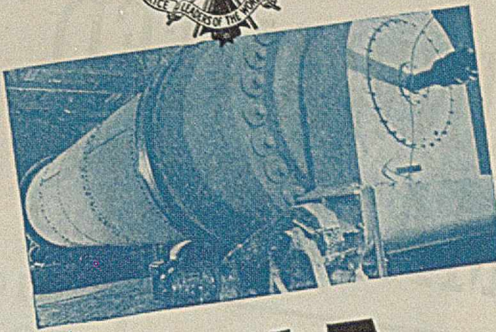
RESILIENT MOUNTING: A rigid, flat sub-plate with 3-point, resilient suspension mounting carries all moving parts. Insures permanent alignment.

ELECTRIC AND MECHANICAL METER BODIES: Are available in various models. Each meter body is tested at double its rated working range up to 5000 lbs. pressure.

The above-mentioned features are but a few of the many new developments found in the New Brown Electric and Mechanical Flow Meters

For full details write THE BROWN INSTRUMENT COMPANY, *a division of Minneapolis-Honeywell Regulator Co.*, 4480 Wayne Avenue, Philadelphia, Pa. Offices in all principal cities. Toronto, Canada: 117 Peter Street . . . Amsterdam-C, Holland: Wijdesteeg 4 . . . England: Wadsworth Road, Perivale, Greenford, Middlesex . . . Stockholm, 16, Sweden: Nybrokajen 7.

BROWN Flow Meters



LOUISVILLE DRYER INCREASES COSTS—YET SAVES $41,650 ANNUALLY!

Here is a case in which Louisville engineers saved a customer $41,650 per year *by increasing his drying cost!*

Briefly, a manufacturer of a delicate and heat-sensitive by-product was using a dryer which operated at low cost, but which was burning out some of the important elements of the by-product. As a result, the by-product could not be sold for more than $20 per ton.

After several weeks of pilot-plant experimentation, Louisville engineers demonstrated that a more "gentle" type of dryer could turn out a somewhat greater yield from the same tonnage of wet material, and that the dried product could then be easily sold at $27 per ton. Even though the recommended dryer increased drying costs by a few cents per ton, this Louisville customer is now earning an *extra* $41,650 annually from his new Louisville equipment!

PREVIOUS DRYER (5-Month Season)	
Tons raw material	20,000
Tons dried product	4,320
Value @ $20 per ton	$86,400
All drying costs	$10,600
Net annual return	$75,800

LOUISVILLE DRYER (5-Month Season)	
Tons raw material	20,000
Tons dried product	4,800
Value @ $27 per ton	$129,600
All drying costs	$12,150
Net annual return	$117,450
Net Annual Increase from Louisville Dryer	$41,650
(Cost of Louisville Dryer	$45,000)

Unless you are *certain* that your dryer is giving you absolutely top performance, Louisville engineers would be glad to study *your* drying processes, without cost. *Address:* Louisville Drying Machinery Co., *Incorporated,* 451 Baxter Avenue, Louisville, Kentucky.

DISPOSE OF UNWANTED MATERIALS

QUICKLY AND ECONOMICALLY

For example: (COAGULATION)

Suspended matter from river or lake is flocculated quickly, with the aid of PQ Silicate so that a clear effluent results. Rates of filtration are also increased. Thus various industrial waste disposal problems find economical solution thru PQ Silicates.

And, of course: (CLEANING)

Grease, oil, grime and dirt are removed efficiently from all sorts of surfaces—glass, metal, fabric—by Metso Detergents. Soluble silica in these detergents keeps dirt dispersed and prevents re-settling. And the balanced properties of Metso give more cleaning for less cost.

Also here: (ORE FLOTATION)

PQ Silicate of the correct type causes undesired particles to sink, floating the valuable minerals such as gold, lead, zinc, tungsten. Recoveries from tailings and lean ores also are made commercially profitable with the silicate of soda reagents.

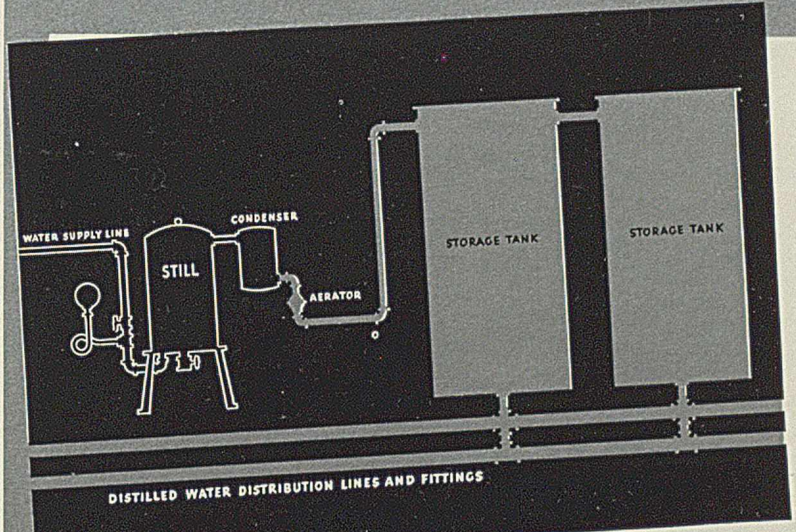
PQ

Silicates of Soda

MAYBE the separation of wanted materials from those unwanted in your process is different from any of these specific cases. Remember PQ Silicates' versatile properties can be adapted to many other uses. Let's talk over your problem soon.

PHILADELPHIA QUARTZ COMPANY

General Offices and Laboratory: 125 S. Third St., Philadelphia, Pa. Chicago Sales Office: Engineering Bldg. Sold in Canada by National Silicates Ltd., Toronto, Ont. Nine plants. Distributors in over 60 cities.


WATER SUPPLY LINE
STILL
CONDENSER
AERATOR
STORAGE TANK
STORAGE TANK
DISTILLED WATER DISTRIBUTION LINES AND FITTINGS

THE industrial history of the 60 new chemicals described in this book is just beginning. They are so new that we have not, as yet, given them a collective name—the term "Fine Chemicals" being adopted from our plant men. Once rare and costly curiosities with valuable properties, these so-called "fine" chemicals, including members of ten organic families, should not be considered laboratory reagents but rather as important commercial products. Many of them are being shipped in 5- and 10-drum lots and several in tank-car quantities.

Their properties, specifications, and applications have been compiled for the first time to make this attractive new book. Its 32 pages are filled with myriads of new product ideas, new means for process savings, and new ways to meet the changing needs of industry. For instance, Morpholine, one of the sixteen new amines described, has made it possible for manufacturers of floor wax to produce a product that is unaffected by wet-mopping. Also included is a complete list of 150 products of Carbide and Carbon Chemicals Corporation with their physical properties tabulated for quick reference—a veritable summary of commercial aliphatic chemistry.

Everyone interested in keeping up with the newer things in synthetic organic chemistry should have this book. A request on your company letterhead to the Fine Chemicals Division will bring you a copy.

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

INDUSTRIAL AND ENGINEERING CHEMISTRY

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

EDITORIALS

Our President's Greetings

TO THE ever increasing membership of the AMERICAN CHEMICAL SOCIETY I am glad to send greetings at the beginning of the New Year. We are all gratified by the steady progress which not only our SOCIETY but also chemical science and industry have continued to make in the United States, even through the years of industrial depression.

Now that the world is again plunged into war, we can compare with satisfaction our position of chemical independence and preparedness with that at the beginning of the World War, twenty-five years ago.

We are all united in the abhorence of war and in the hope that chemists will not again be called upon for emergency service, either commercial or military. But if we should be faced with that necessity, we have the certainty of our enhanced ability to meet every need adequately and completely.

Through its highly trained members, its various publications, its organization of scientific and technical divisions, of local sections, of national committees, and of student affiliates, the AMERICAN CHEMICAL SOCIETY is able and glad to serve all branches of chemistry and related sciences, as well as industry, in this country and throughout the world.

To our members and colleagues in other countries, especially those where progress is halted by the disorders of war, we send greetings and the hope that they will soon be permitted to resume their scientific activities in the midst of peace re-established on a firm international basis.

S. C. LIND

Work

FEW things are more confusing than the employment situation. If there is anything cheering about it, it is that we are far from alone in our inability to think the thing through. The picture is a mixture of extremes and inexplicable conflicts. A college graduate, unable to find employment in the field for which he was trained, to say nothing of the stipend, was willing to accept employment at the going wage as a garbage collector in the town where he lived. He preferred this to relief. In the same town lived an artisan who would rather accept relief than to take jobs at less than union wages. There was no market at any price for the college man's specialty. There was no market for the artisan's work at the price he demanded. It should be remembered that at least in some localities today it requires $27 to buy seven hours' labor on the part of a plasterer and his helper. We are not economists or social scientists, but such cases call for a lot of explanation, if not for some sort of remedial action.

Practically all professions today are overcrowded, with the pressure felt most by the poorer trained. Perhaps there is no other way now known of assuring the public a reasonable number of highly skilled professional men than by the wasteful process of training too many so that out of an excess number there may evolve the few with extraordinary talents. On the other hand, the cry arises from all sides that there are too few really expert mechanics with one or another specialty. Lists of the unemployed undoubtedly contain numbers of well-trained men. However, the experience has been too often that those called from the ranks of the unemployed lack skill or because of long months of unemployment have lost efficiency, pride in their work, or even the will to do good work. One consequence is that it becomes increasingly difficult to interest employers in the possibility of finding among the ranks of the unemployed those who will deliver a reasonable day's work for a reasonable wage. There is still a long way to go before it will be generally accepted that the right to share cannot be separated from obligation to produce.

The growing airplane industry is one of those reported to be suffering from a lack of skilled workers. Thousands could be used where only scores can be found. There is much to be said on the side of those who feel that the training of skilled hands is not sufficiently emphasized in our educational system. But we suspect most of the fault lies with the people themselves. There has long been a trend to have the son of the skilled craftsman enter the professions, or at least become a member of the white-collar class. Many a parent has insisted on the son's becoming an accountant when he was far better suited and much more interested in becoming a master mechanic. Any piece of work that contributes to the welfare of the community is worthy of recognition, and if the public was more generous in its praise of the man who does well even the most menial task, the trend might be sufficiently shifted to turn likely young men and women into the occupations where they can do their best and enjoy their work.

Perhaps someone should invent a type of white collar that could be worn by every worker, or maybe what we need to preach is the dignity of all labor honestly performed and really contributing to the public welfare.

Resolutions

IF YOU are one of those who find it necessary to wait for the first of January to make good resolutions and turn over new pages, this will reach you after you have passed through that ordeal for 1940. However, we see no reason why new and improved leaves should not be turned every morning, nor why good resolutions should not be made and kept whenever the occasion arises.

We have been told that in an office in Louisville the following statement of policy was framed and hung on the wall: "No complaints entertained unless accompanied by a remedy." Therein lies all the elements for a good resolution, solemnly vowed and rigorously maintained. If it could be adopted on a wider scale, it should at least train critics to study their complaints before offering them. The effort to furnish the remedy may lead to much more constructive thought than is sometimes evidenced.

A still stronger and perhaps more potent resolution would be "I will offer no complaint unless I can accompany it with a remedy." That would change the procedure from a negative to a positive requirement, and might go still further toward provoking constructive thought and criticism. It is trite to say that it is easy to criticize. We have all tried that and know it to be true. But the idea of accompanying our destructive remarks with those which are believed to be truly helpful would be a new experience to a great many people. We recommend it for trial at least during the new year.

Resources

FOR some years numerous agencies have busied themselves in taking a census of various resources. Details of manufacturing plants capable of certain types of production, transportation, and agricultural resources are subjects of some projects. European war conditions have led to inquiries designed to give us useful information regarding the deposits of minerals and all details concerning them. Still another group has determined the location of special types of scientific equipment and knows something of what might be expected from the men who have access to it.

There remains, however, a very important though large task to be performed. We refer to details concerning the location, the abilities, and the scientific productivity of the research and technical men of the United States. A comprehensive survey is already under way with regard to industrial research facilities, and within a few months it is expected that a far-reaching report can be prepared on that subject. This has its importance, but we still need to know what our resources are in terms of capable, efficient, scientific man power.

There are many who will recall that twenty-five years ago, not only here but in countries overseas, insufficient care was exercised in the beginning to learn the value of scientific personnel. Some men were lost before the mistake was realized, and many readjustments had to be made besides the effort involved in calling men of special capabilities and scientific training back to the places where they could do the most.

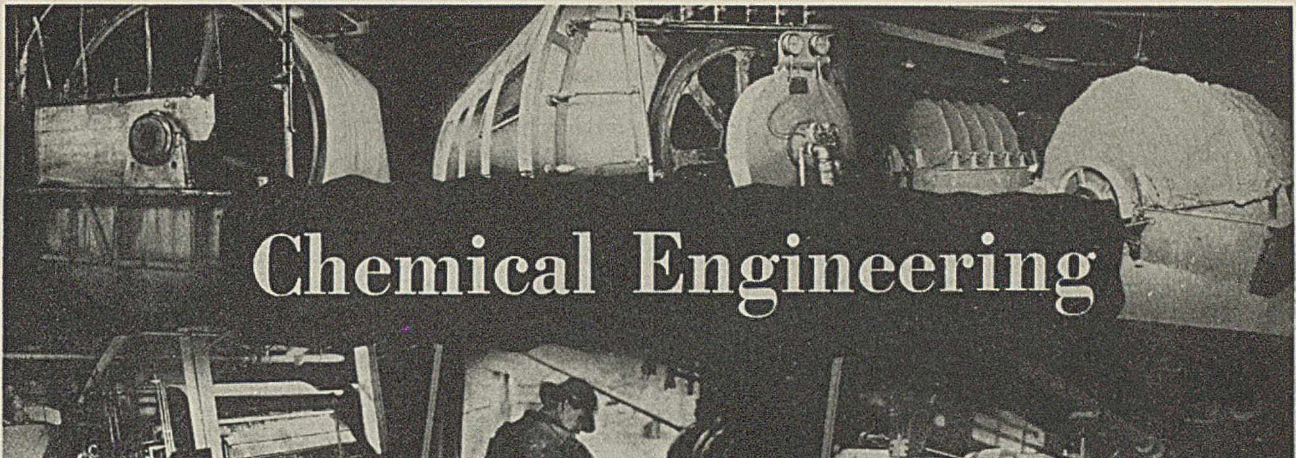
Such a mistake is not being made in Great Britain this year. British scientists have been indexed and classified, and a voluntary register containing more than eighty thousand names has been prepared. This is not regimentation. From this list some seven thousand names have been selected for work immediately in hand. The total represents a surplus over present requirements, but the mistake of twenty-five years ago will not be repeated and the chances are good that when men of special qualifications are needed they will be assigned to the work in hand without the hazard of the wasteful process once in vogue.

To collect such a register in the United States would be a large task. The several scientific societies might undertake it, with financial assistance, for their respective specialties. But there might be much duplication of work in such a procedure and we are more inclined to suggest that it is a job for the National Research Council, where the sciences are represented and where, with financial assistance, machinery could be set up to make such a census.

We all hope that the United States can remain neutral, but there is nothing warlike in determining just what the scientific resources of the country are. Many a peacetime problem of national significance could be attacked with greater likelihood of success if there were available somewhere lists of the type we have in mind. A little consideration will show many uses for such information. Its collection should proceed in a vigorous orderly fashion without delay.

The English language is the most important scientific instrument at your disposal. Learn to use it with precision.—C. W. Foulk

Engineering is the adaptation of knowledge written by research.—Henry P. Kendall



Photographs by —
E. B. BADGER & SONS COMPANY
OLIVER UNITED FILTERS Inc

CHEMICAL INDUSTRY MOVES AHEAD IN 1939

WHETHER or not the business boom which began to make itself felt in the late summer of 1939 was the result of war in Europe need not trouble us. Important is the fact that distinct improvement in all lines of business has developed at an accelerating pace during the past several months.

Partly this has been caused by optimism and partly by pessimism. Optimists have long been impressed by the necessity for re-establishing economic base lines at new values as a result of years of depression. Pessimists, already alarmed by war clouds over Asia, saw in threats to Europe's peace, now unhappily realized, cause to build up inventories against rising prices. They joined the optimists in laying in all manner of supplies, both groups expecting higher prices, albeit for opposite reasons.

The same cause, which spurred your wife and mine in early September to stock up the family larder with sugar, flour, and other staples, has operated in industry. The results in industry's markets were the same as those in neighborhood groceries: Low existing stocks were promptly moved, and prices took a sudden spurt upward. This ceased almost as quickly as it started when the inertia of idling production machinery was overcome. Strangely enough, when the first hurried rush of buying had spent itself by the end of September, prices and demand failed to react as much as had been anticipated and a comfortably active business boom was under way.

Obviously, war in Europe has been an important factor in the situation, but it has not been the sole cause. Memories of 1914 and the years of stringency following were easily revived, and not for some time was it possible to lay this ghost of former industrial unpreparedness. This reaction to war in Europe was intuitive and subsided readily when time allowed facts to be considered.

These facts completely refute fear of shortages. Production within the United States had profited by its lesson in diversification learned in World War days. Progress toward a completely integrated industrial economy has been so signally effective as to care for domestic as well as somewhat increased export demands, without dislocation. Certainly the chemical industry, once the prime offender, has been able to meet its problems of enlarged output with minimum inconvenience to anyone.

Satisfying variety of chemical production, achieved through years of effort, has so far proved its efficacy that no shortages of any chemical products are to be feared. Plant capacities have been great enough to meet the situation by the mere taking up of slack in the reduced schedules of the past few years. No lack of essential products has appeared to nullify claims of adequacy in this respect. But even more important, no gaps are discernible in the ranks of experienced men to form the cadres of expanded personnel which may be required to increase output materially should need require it.

Effects of the War in Europe

The war in Europe raised frequent questions as to what constitutes contraband. Wood pulp was so considered in the sinking of one Swedish ship. In the United States the matter was determined by a list of exports prohibited under the so-called Neutrality Act. This was repealed subsequent to the beginning of hostilities in Europe and its place taken by a "cash-and-carry" act permitting sale of any American products to warring purchasers who would take title to goods here and transport them in their own ships. One result was to force many ships previously under the American flag to seek foreign registry and foreign crews.

What is perhaps the most significant development of the European war from our point of view is the virtual cessation of Europe's exports to South America. This has turned the eyes of our southern neighbors rather definitely on the United States as a source of supply of the goods formerly bought in Europe.

The demand for chemical products thus engendered has been indirect rather than direct. Although it is true that some products of American chemical industry are enjoying increased demand from Latin America, the greater part of our required chemical output has found its way south only after passing through various other industries here. A few of the heavy chemicals, alkalies, ammonia, and phosphatic fertilizers, have been sold direct, but the greater effective bulk of chemical demand thus created has taken the form of consumers' goods, automobiles, paints, and a variety of other items, whose manufacture here has consumed chemical products.

Noteworthy, too, has been the effect of stoppage of supplies of salt cake from Europe for use in our new southern paper industry. Cheapness and low water freights had encouraged makers of kraft and bleached sulfate pulp to supply their needs of salt cake largely by imports from Germany, among others. Natural deposits of sodium sulfate in the Southwest were at a disadvantage because of freight costs, and the output of salt cake furnaces in the United States has never been large. However, the rise of ocean freight rates from Europe, necessitated by the enlarged hazards of war, and the inability of European producers to deliver have operated to arouse new interest in domestic natural sources and to promote new activity on the part of possible domestic producers in this item. The result has been a substantial development in the recovery of salt cake from mineral sources in West Texas and Arizona, particularly, and the manufacture of "synthetic salt cake" by the Mathieson Alkali Works at Lake Charles, La. The process for making synthetic salt cake uses soda ash and sulfur as its raw materials; the product, which is not sodium sulfate, is reported to be equivalent to salt cake when used in the sulfate pulp process.

Further supplies for this branch of the paper industry are coming from the viscose rayon process. The spinning baths in which viscose sirup is coagulated to filaments are initially made acid with sulfuric acid. As the process progresses, the soda from the sirup neutralizes this acid and the spent liquor contains substantial amounts of sodium sulfate. This is being recovered in view of the increased demand for salt cake and has become an important source of this raw material.

Other suggestions for amplifying the supply of salt cake include operation of salt cake furnaces with electrolysis of the hydrochloric acid by-product to yield chlorine and the use of the hydrochloric acid to acidulate phosphate for fertilizer purposes. These processes are being seriously investigated, and plans are reported to be under way to operate them, but no definite confirmation of production is yet obtainable.

Generally throughout the chemical industry the year has been one of expansion. Confidence coupled with increased earnings by chemical companies has been effective in promoting numerous new plants in a variety of fields. In addition to the natural salt cake recovery units and the synthetic salt cake plant, potash production has increased in the Carlsbad district of New Mexico where International Agricultural Corporation is expanding the output of its subsidiary, Union Potash & Chemical Company, by some 140,000 tons annually, equally divided between sulfate and chloride. Beyond these, it is difficult to trace chemical expansions to the present war.

Expositions

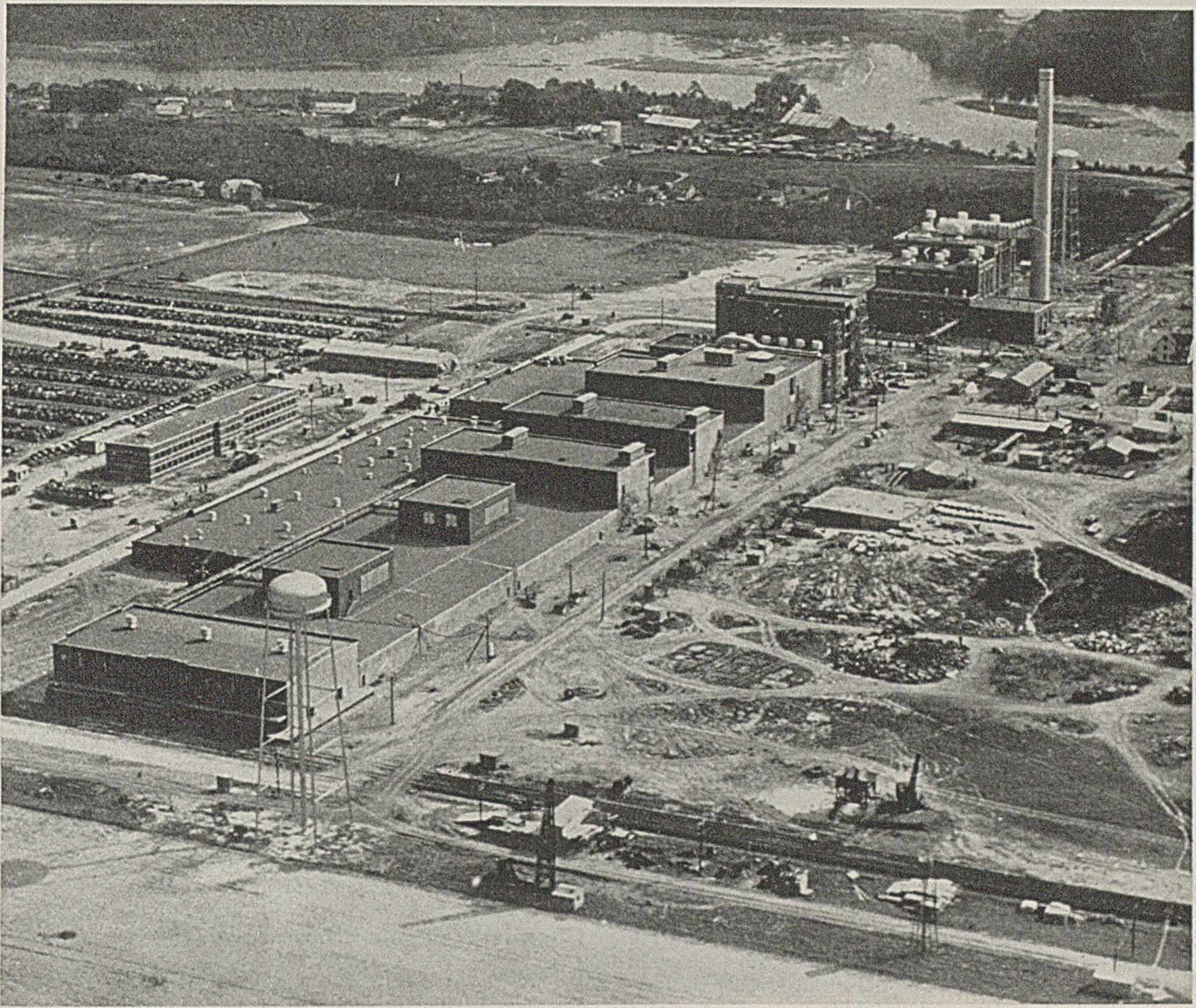
Three expositions were of special chemical interest during 1939. Both the New York World's Fair and the San Francisco Golden Gate Exposition showed many chemical products, notably in the field of synthetic resins which virtually dominated both fairs.

The Seventeenth Exposition of Chemical Industries at Grand Central Palace, New York, devoted itself primarily to the display of new developments in equipment for the process industries and showed some new chemical products.

The AMERICAN CHEMICAL SOCIETY's booth at the latter exposition contained exhibits of products newly commercialized since the preceding exposition in 1937. Included were nylon, Vinyon, castor oil paint vehicle, castor oil resins, hydrogenated rosin, glass centrifugal pump, rubber filter media, threshold treatment of water, sulfamic acid and derivatives, nitroparaffins, organic phosphorus compounds, ethylcellulose rayon, products from waste sulfite liquor, and the synthetic vitamins. The pictures on pages 3 and 7 show two of the panels in the AMERICAN CHEMICAL SOCIETY booth.

Industrial Developments

Industry generally has been able to step up production and to expand plants with a minimum of dislocation. Ethyl Gasoline Corporation recently completed a large new plant at Baton Rouge, La., and is already planning further expansion there. Along with this greater production of tetraethyllead and ethylene dibromide has had to go enlarged output of



First Plant for Commercial Production of Nylon, Seaford Del. *Courtesy, E. I. du Pont de Nemours & Company, Inc.*

bromine by the Ethyl-Dow Company at Kure Beach, N. C. Both nylon and Vinyon (synthetic resin fibers more like silk than customary rayons are, and hence usable in hosiery to replace silk from this last stronghold) went into production during the year. The former is a du Pont product and $11,000,000 are being invested in a plant for its production, now nearing completion. Vinyon, a vinyl resin derivative, was developed by Carbide and Carbon Chemicals Corporation and is now on the market as fiber made by the American Viscose Corporation; as felt by American Felt Company; and as filter cloth, where its high resistance to acids and alkalies make it particularly valuable, by Wellington Sears Company. Both of these developments, coming to commercial importance at the same time, are significant in view of the advancing prices of oriental silk which has heretofore held a monopoly of the hosiery market, and because both fibers are made of materials polymerized from small original molecules involving no cellulose in their composition.

In regard to cellulose fiber, the important developments have been in the expanded production of viscose rayons and in the announcement by the Dow Chemical Company that its ethylcellulose rayon is nearing commercial production.

Bearing upon the question of war stringencies is the development of a process for utilizing low-grade manganese ores now operated by a subsidiary of the Freeport Sulphur Company, the Cuban American Manganese Corporation, in Cuba. Operators of the process point out that it makes available vast deposits of similar ores in the United States hitherto unusable by the steel industry. Thus any extraordinary situation which might interrupt imports (supplying about 90 per cent of United States consumption) or substantially increase the demand for steel and its alloys becomes decidedly less significant. The process yields a high-grade manganese sinter, reported to be superior from a metallurgical point of view to natural high-grade ores. Manganese is expected to be removed from the list of critically strategic raw materials as application of this or equivalent processes spreads.

Deposits of tungsten ore have been discovered in the state of Coahuila, Mexico, about 70 miles from the Texas border. Plans are already under way for their development and involve bringing the ore to Eagle Pass, Texas, for concentration. The Molybdenum Corporation of America is interested.

Important, too, is the commercial-scale utilization of waste sulfite liquor from the paper process to produce fuel, resins, vanillin, and other lignin derivatives at the plant of the Marathon Paper Company, Rothschild, Wis. This recovery of waste not only prevents pollution of streams but is reported to yield an actual profit to its operators, a distinctly important advance for the pulp and paper industry.

Other important new plants completed or well under way include:

Southland Paper Mills, Inc., Lufkin, Texas, newsprint from southern pine, announced operations to begin in December, 1939.

Krebs Pigment & Color Corporation, Edge Moor, Del., enlarged titanium pigment plant.

Victor Chemical Works, Mt. Pleasant, Tenn., increased phosphorus output.

National Oil Products Company, Harrison, N. J., greater plant capacity.

Eastman Kodak Company, Rochester, N. Y., new and larger plant.

Union Carbide and Carbon Corporation, new alloy plant at Sheffield, Ala., and new oxygen plant and enlarged ethylene glycol plant at South Charleston, W. Va.

Air Reduction Company, enlarged plants.

The Barrett Company, Philadelphia, Penna., synthetic phenol plant.

U. S. Industrial Chemicals, Inc., Curtis Bay, Md., ethylene glycol plant.

Commercial Solvents Corporation, Peoria, Ill., new plant for nitroparaffins.

E. I. du Pont de Nemours & Co., Inc., Belle, W. Va., ethylene glycol plant.

Hercules Powder Company, various locations, new plants for chlorine and caustic, chlorinated rubber, ethylcellulose, hydrogenated rosin, heavy acids, and a large addition to cellulose acetate plant.

Rumford Chemical Works, Providence, R. I., sodium tetraphosphate plant.

Among the important corporation changes of the year were:

Purchase of Great Western Electro-Chemical Company by Dow Chemical Company.

Fred L. Lavanburg Company, Inc., sold to Reichhold Chemicals, Inc.

Resinox Corporation bought by Monsanto Chemical Company.

American Gypsum Company bought by Celotex Corporation.

Bakelite Corporation purchased by Union Carbide and Carbon Corporation.

Several important changes in associations are interesting. Newly formed were the National Council of Textile Industries, bringing together all textile interests; the Council of Industrial Alcohol Users; and the American Council of Commercial Laboratories. The Industrial Alcohol Institute was dissolved after a long and useful life.

Unusual was the merger of two technical schools, the Armour Institute and the Lewis Institute, both of Chicago, to form the Illinois Institute of Technology.

New Products

Technological developments have been numerous in many fields. A second pilot plant to explore further possibilities in the chemical elaboration of water gas by-products is being erected by the United Gas Improvement Company. Future chemical developments by the company depend on the results of marketing the products of pilot plant operation.

An all-glass centrifugal pump, comparable in efficiency with metal pumps of the kind but avoiding destructive corrosion and contamination of product, has been developed through the joint efforts of the Corning Glass Works and the Nash Engineering Company.

Two new highly resistance filter media have been developed. One of them is of rubber sheeting made with minute conical pores of controllable size comparable with the interstices in fabric filter cloths. The process of manufacture was developed by the United States Rubber Company, and the product is marketed by Filter Media Corporation. Vinyon fabric, combining the extreme inertness to reagents of vinyl resins with a textile structure, has proved highly efficient as a filter cloth.

A new technique of electroforming iron provides a convenient method of cheaply duplicating molds for plastic articles. The process, which involves plating iron as much as $^3/_8$ of an inch thick on an original pattern of any convenient material, was originally developed by United States Rubber Company to duplicate molds for tires. Already it is being widely used in other fields, particularly in plastic molding.

A new alloy of tungsten, titanium, and carbon is proving useful as a material for machine tools. The alloy, which corresponds to the formula $W_2Ti_2C_4$, is marketed under the name "Kennametal" by the McKenna Metals Company.

Two developments in glass technology have been noteworthy. Within a single year of its commercial introduction the improved glass fiber known as Fiberglas has found no less than 565 applications, in spite of the fact that glass wool has long been known. A new type of glass comparable in properties with fused quartz was developed and marketed during the year by Corning Glass Works. The process involves separation of an acid-soluble phase from a special borosilicate glass and annealing the insoluble phase. The final product represents a substantial shrinkage from the original piece but it has a coefficient of expansion about as low as that of fused silica.

A new plastic is made by the Agricultural By-Products Laboratory at Ames, Iowa, from sugar cane bagasse by hydrolysis in the presence of aniline at a cost reported to be about 4.5 cents per pound.

Pecan shells are yielding a highly absorptive charcoal.

Silver as an addition to stainless steel to increase its resistance to corrosion by sea water is the subject of a series of patents.

Noise is now employed as a controlling factor in grinding through the use of a microphone operating the feeding mechanism of the mill.

Plastics have been employed in the construction of an airplane. Considerable secrecy has surrounded details pending full tests, but the scant information available points to the use of laminated phenolic plastic in the wings and fuselage.

Chemistry of Life Processes

Vitamin B_1 achieved headlines late in the year when it was administered to Lou Gehrig, retired baseball idol, in an effort to cure amyotrophic lateral sclerosis which has forced him to abandon baseball. The treatment and its effects in this and other paralytic cases were reported by W. J. McCormick, of Toronto, in the *Medical Record*.

Added to the list of synthetic vitamins commercially available was vitamin K. Announcement of its first synthesis by Fieser at Harvard followed shortly on the determination of its structure by Doisy and others at St. Louis, and preceded by only a few months its commercial preparation in minute amounts. Vitamin K is an antihemorrhagic.

Other synthetic vitamins now on the market are B_1, B_2, B_6, C, E, K, nicotinic acid, and riboflavin.

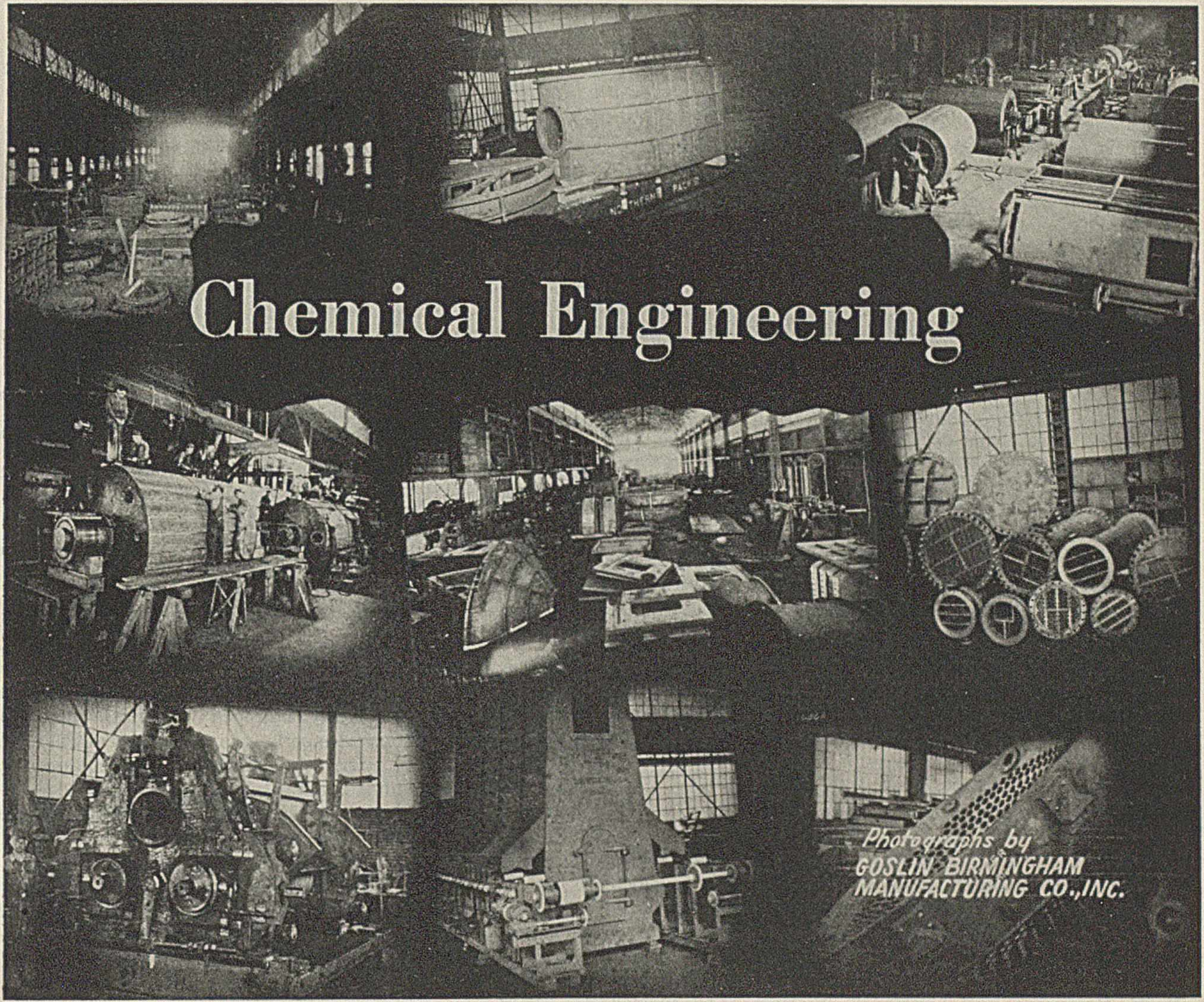
A new concentrated vitamin product is made from distillery waste and marketed as Curbay BG by U. S. Industrial Chemicals, Inc. It contains riboflavin and pantothenic acid and is principally used in poultry and stock feeds.

Vitamin D is being produced from ergosterol of corn oil, and the cholesterol of wool fat has been found to be a satisfactory source of this vitamin.

A patent on the production of crystalline insulin was issued during the year.

Gallium was discovered to be essential to life processes in minute amounts.

Distinct advances in the study of plant hormones were made. Vitamin B_1, stimulating to the growth of roots of plants, was marketed in fertilizer tablets for garden use. Parthenogenesis of plants was accomplished by the use of



Chemical Engineering

Photographs by GOSLIN-BIRMINGHAM MANUFACTURING CO., INC.

substances, some of which are produced in the metabolism of plants, of a hormonelike character.

A number of new sulfanilamide derivatives were produced and their efficiencies under various clinical conditions tested.

Sulfapyridine and various chemical modifications were especially prominent. Its applications in pneumonia, in pneumococcic meningitis, and with heparin in acute endocarditis were favorably reported to the medical profession. Gerhard Domagk, a German, was declared the winner of the 1939 Nobel Prize for physiology and medicine for his discovery of prontosil (sulfanilamide derivative).

Gelatin taken in relatively large doses has been found to relieve fatigue in men and to increase energy. Tests made by G. R. Ray and his co-workers at Long Island College Hospital, Brooklyn, N. Y., resulting in this conclusion have been widely exploited.

A new type of metathetical organic reaction, resembling the usual metathesis of inorganic compounds, was produced catalytically by George Calingaert and reported at the Boston meeting of the AMERICAN CHEMICAL SOCIETY.

Controversies

Important was the disturbance created over the direction of laboratories engaged in making tests for clinical purposes. This argument was initiated by an attempt in the state of Pennsylvania to require that the direction of all such laboratories be in the hands of duly licensed M. D.'s. This view was upheld by the American Medical Association and was vigorously opposed by the AMERICAN CHEMICAL SOCIETY, particularly as contravening an agreement previously reached by the two societies and as being quite unrelated to the expertness of the persons involved.

This effort by the medical profession to limit the practice of chemistry on the one side was balanced by attempted inroads in another direction by labor unions on the basis that chemists and chemical engineers should join labor unions in unionized plants.

Full agreement and mutual understanding on the status of chemists were reached in the following summary by President William Green of the American Federation of Labor:

> If engineers and chemists perform professional work they should be classified accordingly. If they do production work they must be classified as production workers. ***It is a hardship and a detriment to production workers to have these professional workers wrongly classified and displacing bona fide production workers.
>
> Since the wrong classification persists, it is obvious that the distillery workers must have some device for protecting themselves and their jobs. An engineer or chemist working in his

profession and classified as such would then become a union member only upon his own volition.

The question of whether or not the chemist belongs to a recognized profession was a point argued before the Supreme Court in United States *v.* Harry L. Laws, 163 U. S. 256–269. The court held that a chemist belongs to a recognized profession, and we quote:

> Although the study of chemistry is the study of a science, yet a chemist who occupies himself in the practical use of his knowledge of chemistry as his services may be demanded may certainly at this time be fairly regarded as in the practice of a profession.***
>
> Formerly, theology, law, and medicine were specifically known as the professions; but as the applications of science and learning are extended to other departments of affairs, other vocations also receive the name. The word implies professed attainments in special knowledge as distinguished from mere skill. A practical dealing with affairs as distinguished from its pursuit for its own purposes. There are professors of chemistry in all the chief colleges of the country. It is a science the knowledge of which is to be acquired only after patient study and application. The chemist who places his knowledge acquired from a study of the science to the use of others as he may be employed by them, and as a vocation for the purpose of his own maintenance, must certainly be regarded as one engaged in the practice of a profession which is generally recognized in this country.

In both these controversies many prominent and thoughtful members of the chemical profession see reason for promoting the professional licensing of chemists and chemical engineers by states. Others are equally hearty in their opposition to such measures as tending to expand bureaucratic control unnecessarily. Meanwhile, efforts to pass a law requiring uch licensing through the state legislature of New York are being made but so far without result.

Honors Awarded

The Nobel Prize in Chemistry for 1938 was awarded this year to Richard Kuhn. Medalists for 1940 already named include V. N. Ipatieff (Willard Gibbs), J. M. Nelson (Nichols), and C. M. A. Stine (Perkin).

Lalor Foundation Awards for research in chemistry during 1939–40 went to O. K. Behrens, A. C. Bratton, R. B. Jacobs, W. E. Roseveare, and Charles E. Waring. The Weston Fellowship of the Electrochemical Society was awarded to W. P. Ruemmler, and the society's prize to young authors went to N. B. Nichols. Frank K. Pittman won the J. T. Baker Chemical Company's research fellowship in analytical chemistry.

Herman Frasch Foundation Awards were granted the University of Minnesota Department of Agriculture, Purdue University, and the Rutgers University College of Agriculture. Other chemical awards in 1939 were as follows:

Edward Goodrich Acheson Medal	F. C. Frary
American Institute Gold Medal	Sperry Gyroscope Company
Borden Award	Leroy S. Palmer
Chandler Medal	Thomas H. Chilton
Chemical & Metallurgical Engineering Achievement Award	Standard Oil Development Company
Chemical Industry Medal	R. E. Wilson
Willard Gibbs Medal	D. D. Van Slyke
Herty Medal	Frank K. Cameron
Hillebrand Prize	Raleigh Gilchrist and Edward Wichers
Eli Lilly and Company Award	George Wald
Mead, Johnson and Company Prize	C. A. Elvehjem
Associated Industries of Massachusetts Merit Award	Monsanto Chemical Company, Plastics Division
National Safety Council Award	E. I. du Pont de Nemours & Company, Inc., Rubber Laboratory
William H. Nichols Medal	J. H. Hildebrand
Nobel Prize in Chemistry	Adolph Butenandt and Leopold Ruzicka
Pennsylvania Public Health Association Award	C G. King
Perkin Medal	W. S. Landis
Francis C. Phillips Medal	C. J. Spiegl
Pittsburgh Award	G. H. Clapp
Howard N. Potts Gold Medal	N. K. Chaney and H. J. Creighton
Proctor Memorial Prize	R. O. Hull
Research Corporation Award	H. N. Taylor and Vannevar Bush
St. Louis Award	E. A. Doisy
Schoellkopf Medal	C. F. Vaughn
Leon P. Smith Award	J. S. Guy
Society of Chemical Industry (Canada) Medal	J. W. Bain

Research Facilities

New laboratories or substantial additions completed or planned in 1939 included, among others:

Four Federal Regional Research Laboratories at Wyndmoor, Penna., Peoria, Ill., New Orleans, La., and Albany, Calif.

Monsanto Chemical Company, Springfield, Mass., plastics laboratory.

Merck Institute of Therapeutic Research, Rahway, N. J., substantial addition.

American Telephone & Telegraph Company, Murray Hill, N. J., new laboratory.

Ethyl Gasoline Corporation, San Bernardino, Calif., new laboratory.

Battelle Memorial Institute, Columbus, Ohio, greatly enlarged.

Washington College, Chestertown, Md., new science building.

The Barrow-Agee Laboratories, Inc., at Memphis, Tenn., have a new three-story building with 12,000 feet of floor space which was formally opened last June. A new physical chemistry laboratory fully equipped with dark rooms for photographic and optical experiments was opened at Columbia University in July. It was planned, built, and equipped by members of the university staff.

Textile, leather, and dye research of the Commonwealth Color and Chemical Corporation is now housed in a three-story laboratory in Brooklyn.

V. N. Ipatieff has given $21,000 to Northwestern University to endow a chemical research laboratory for work in high pressure. Brown University's new Metcalf Research Laboratory is a three-story building housing the chemistry department and undergraduate physical chemistry laboratories, as well as combined libraries of three departments.

The Norwich Pharmacal Company, opened new laboratories in March as the finishing touch to a complete plant-modernization program.

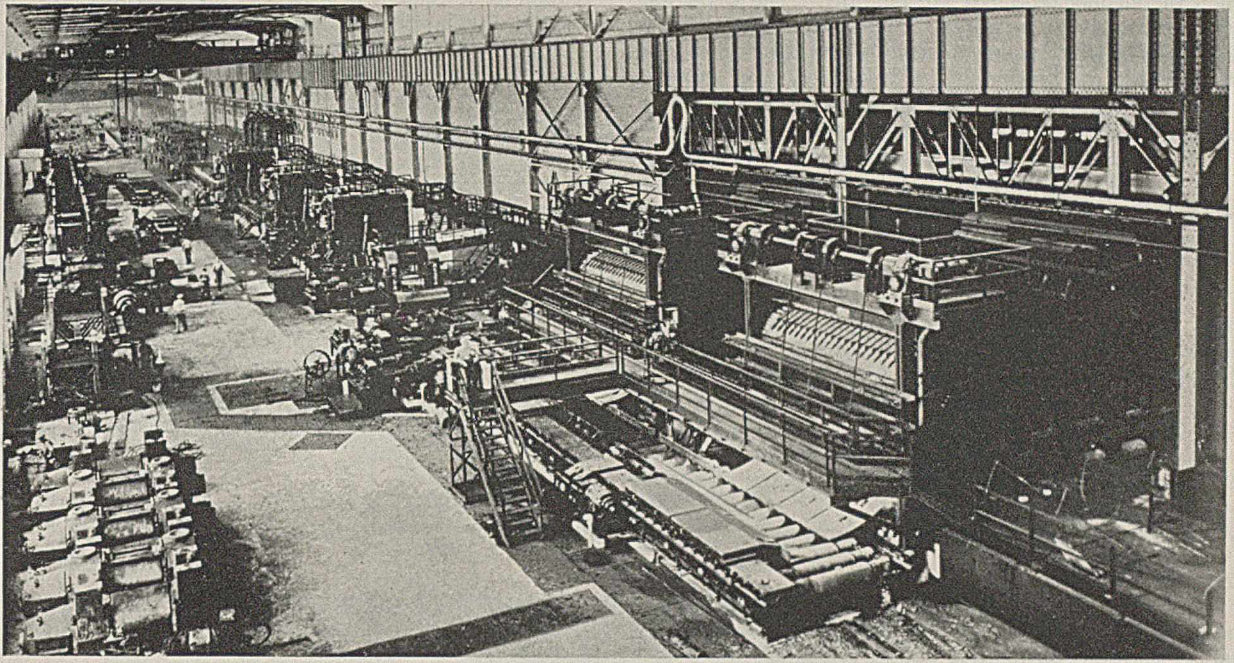
The first unit of the new chemical engineering building at Case School of Applied Science was completed and occupied in October. It houses laboratories for elementary and advanced chemical engineering, testing of fuels and lubricants, and physical and organic chemistry.

Asides

Interesting has been a running debate on the pronunciation of the Scandinavian word *Ångström;* considering the subject, it has reached voluminous proportions. Evidently there are many more possible pronunciations of the two vowels than anyone might have suspected.

As usual in a war period, talk has revived of a "death ray". The current inventor, whose claims might well have come from our most lurid fiction, is so overwhelmed by the potentialities of his weapon that he reports having destroyed it and, with it, his secret which will be revealed, he says, only if the United States is in imminent danger of invasion.

Growing melons were given special alcoholic flavors by introducing liquors and wines into their stems. A vast crowd was attracted to see this supposed wonder, much to the disgust of those performing the experiment. No significance could be attached to it.



Courtesy, Inland Steel Company

CONTINUOUS SHEET AND STRIP MILL

CHEMISTRY AND VITREOUS ENAMELS

EMERSON P. POSTE
309 McCallie Avenue, Chattanooga, Tenn.

SO MANY of the contributions of chemistry to modern life have involved the creation of entirely new products that we tend to overlook what the science has done to advance some of the older industries. Though the services of chemistry in the fields of textiles and metallurgy are well appreciated, there is probably a less clear conception in the case of ceramics, an industry or art as venerable as any of which we have historical record.

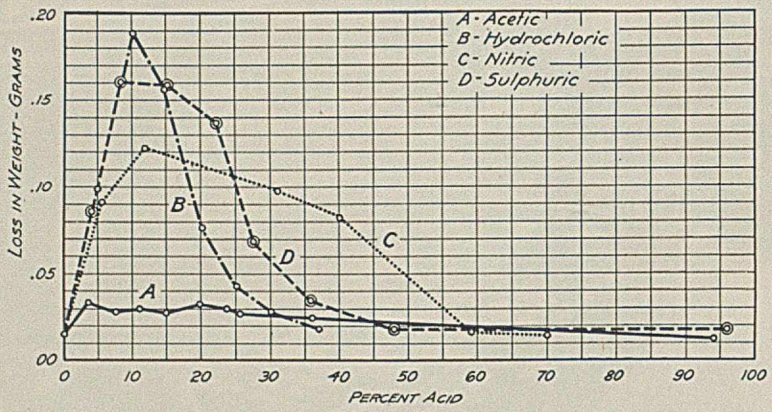
Recent developments in one of the ceramic industries—glass—have been called to the attention of the public in a creditable fashion. The closely related field of vitreous enamel has also contributed within the last few decades a product of unusual adaptability. Not long ago it was chiefly evident as sanitary and cooking ware, but the enameled bathtub and dishpan were the forerunners of a large family—stove parts, signs, table tops, refrigerators, washing machines, chemical ware, and, more recently, extensive architectural features as well as a numerous line of miscellaneous items. This progress has been made possible largely through the application of chemistry to a rule-of-thumb industry whose roots go far back into the ancient coating of metals with glass as a means of artistic decoration.

Vitreous enamel is a silicate coating that has been fused onto a metal base. It should not be confused with certain organic coatings which are also termed "enamel". As a means of avoiding misunderstanding in this regard, the industry has made use of two other terms, "porcelain enamel" and "glass enamel", suggestive of similarity in appearance and in properties to products in two other fields of ceramics.

At the turn of the century vitreous enameling in the United States was a relatively insignificant industry. A few plants were manufacturing cast iron sanitary ware, and a beginning had been made in the production of sheet iron hollow ware, though much of the latter was being imported from Europe. Early records indicate that the enameling of cast iron was particularly difficult because of the poor quality of castings, and that for reasonably satisfactory results with sheet iron enameling, the metal stock had to be imported. Probably one of the major factors making possible the tremendous growth of the industry was the development of proper sheet stock, specific attention to cast iron coming later. The particular application of chemistry first to be considered is, therefore, in the allied field of metallurgy.

Sheet Iron Base

One of the first points to be recognized was the relation between enamel and the carbon content of sheet steel. In one particular case it was learned that a certain type of blistering of the enamel came when the carbon content of the steel was of the order of 0.20 per cent; with 0.15 per cent carbon the enamel processed satisfactorily. The trend was to use steel safely below the latter figure in carbon. There were plenty of troubles due to steel defects other than high carbon, however. Nothing is a better criterion of low-carbon steel than its enameling characteristics. The steel producers attacked the problem from two points of view. One group strove to produce a low-carbon sheet of special quality, the other introduced stock of the ingot-iron type. Both met with marked success, and made available the various grades required for the several methods of fabrication—spinning, drawing, pressing, and welding. Today the cases of faulty enameling stock are rare, in spite of demands on the metal that would have been past hope a few years ago.



Relative Action of Acid on a 2-Gram Enamel Sample
(Powdered frit test)

Courtesy, Transactions of the American Ceramic Society

Another branch of metallurgy that has played a major role is fusion welding. Gradually the oxyacetylene process met the increasing demands of the industry and has now been so perfected as to materials and methods that range and refrigerator bodies are being fabricated as units prior to enameling. Arc welding, applicable to the fabrication of heavier units such as chemical ware, was not successfully used for seams to be enameled until the development of the coated electrode. The bare electrode produced oxides and nitrides in the weld, and unfavorable metallographic structures which did not permit satisfactory enameling. With protection from the atmosphere and other advantages characteristic of coated welding wire, the use of arc welding has become common practice for the fabrication of parts from heavy stock.

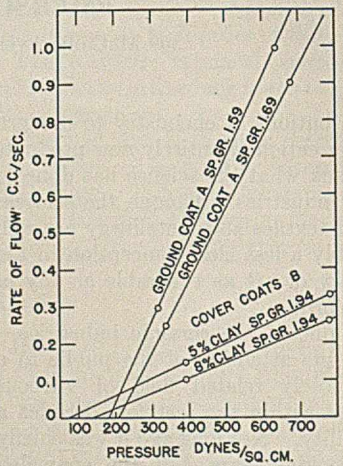
Preparation for Enameling

Satisfactory enameling is possible only on sheet that is free from fabrication strains, scale, and grease, and whose surface is properly related chemically to the enamel that is to be applied. Early practice involved scaling and annealing the shapes at a dull red heat to remove strains and pressing and drawing compounds. The metallurgist has produced stock and welding methods that render annealing unnecessary in most cases, and the chemist has developed a combination of forming compounds and chemical cleaning methods that produces a condition satisfactory for pickling.

"Drawing compounds for use prior to enameling should be an emulsion of fatty oils and/or fatty waxes with a bit of mineral oil permissible but with no cushion-agent or pigment. The removal of these materials by cleaners involves the proper combination of saponifying and emulsifying agents, with a proper soap as a wetting agent. The average formula, therefore, contains caustic soda, silicate of soda, trisodium phosphate, soda ash and soap" (*9*). A cleaner of this type is operated just below or at its boiling point, and the strength of the solution is generally judged by the sodium oxide content. The optimum varies with the type of drawing and pressing compounds used and the nature of a given cleaner. The sodium oxide content is usually of the order of 2.0 per cent, and the cleaning time varies from 10 to 25 minutes.

The use of cold hydrochloric acid for pickling was quite common when the preliminary treatment had been scaling and annealing, but with the advent of chemical cleaning there was, in general, a change to sulfuric acid. It is used at a strength of approximately 6 per cent and a temperature close to 150° F. Well cleaned stock will be properly pickled by a treatment of 10 to 20 minutes. The iron content of the pickle is carefully watched and the bath discarded when the concentration reaches 6 per cent. Some plants use organic inhibitors to reduce the solution of the iron in the acid, but this is not general practice since many feel that etching of the metal surface is essential to proper enameling.

Neutralization of the ware after pickling and prior to enamel application is necessary to prevent rusting and to present a chemical surface condition that is properly related to the enamel being used. Weak, hot solutions of soda ash, or mixtures of soda ash and borax, are in common use, though various excellent proprietary compounds are on the market. In some cases two neutralizing baths are employed, the first at about 0.4 per cent sodium oxide and the second at approximately 0.2 per cent. If a single bath is used, the strength is usually kept at about 0.3 per cent. Control at this point is essential if the ground-coat enamel is to be uniform.

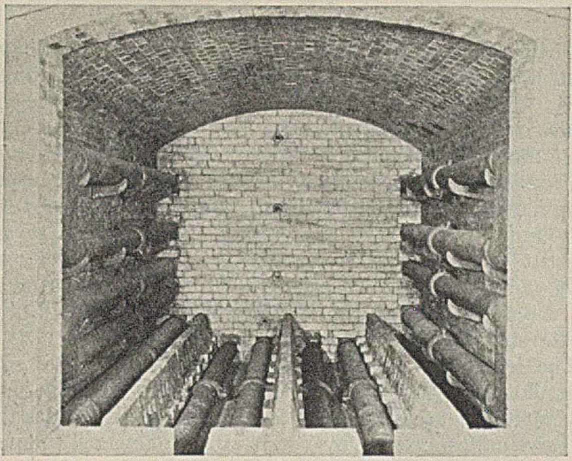


Courtesy, Ferro Enamel Corporation

Typical Plasticity Graphs

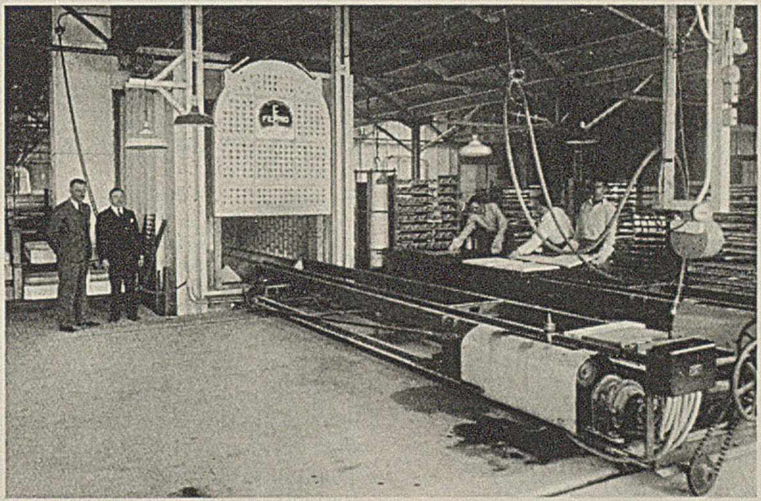
Two of the above operations are in some cases modified by the use of an electric current. Electrolytic cleaning involves an alkaline bath with a direct current, the ware serving as the cathode and the tank the anode. Less common is electrolytic pickling, though the use of alternating current in this operation is a recent development.

Enamelers are coming to recognize the nickel dip as good insurance against many of the troubles incident to subsequent processing. Following pickling, the ware is given a nickel "flash" by immersion in a bath containing 3 ounces per gallon of nickel sulfate ($NiSO_4.6H_2O$) and 0.25 ounce per gallon



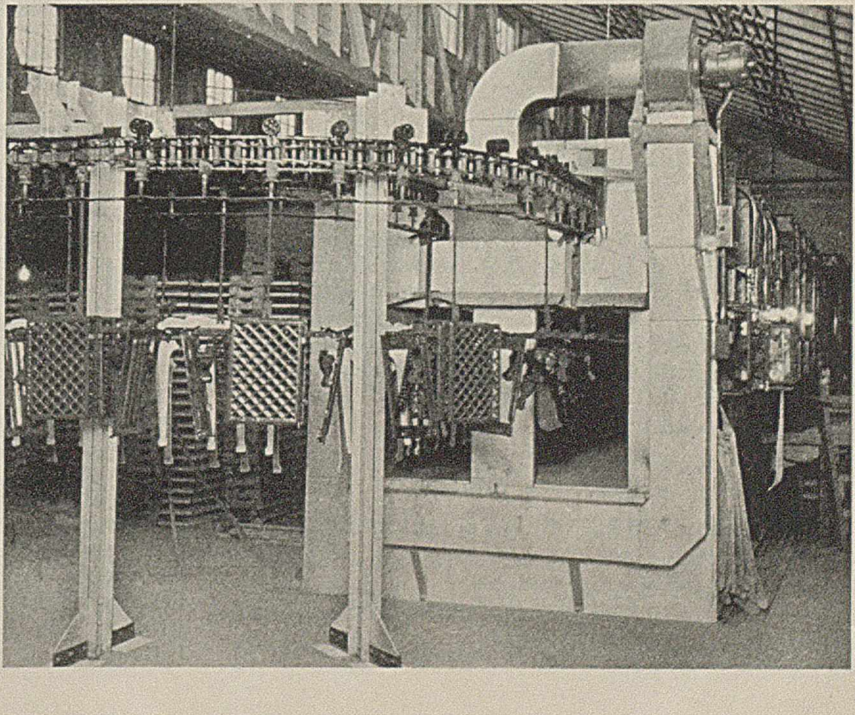
Courtesy, Ferro Enamel Corporation

INTERIOR OF RADIANT TUBE BOX-TYPE FURNACE



(*Right*)
BOX-TYPE MUFFLE FUEL-FIRED FURNACE WITH V-BOTTOM TO INCREASE RADIATING SURFACE

Courtesy, Ferro Enamel Corporation



(*Below*)
ELECTRIC CONTINUOUS FURNACE

Courtesy, Ferro Enamel Corporation

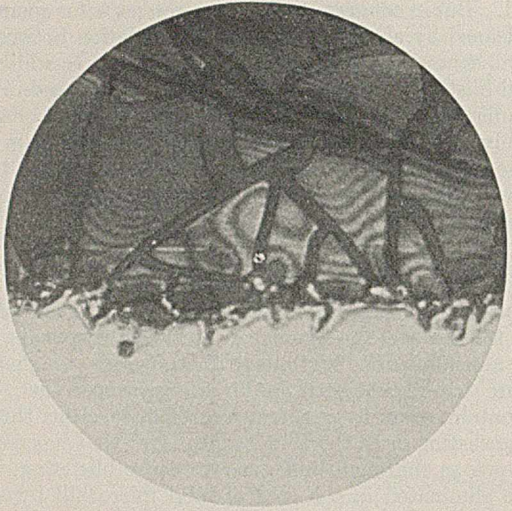
of boric acid. The control of pH within a range of 5.5 to 6.0, varying somewhat from one case to another, is essential. The bath is operated at a temperature range of 150° to 180° F., and the time of treatment is usually about 5 minutes.

In all well-operated plants the cleaning and pickling department is equipped with a chemical control outfit for the careful volumetric regulation of the several operations involved. A substitute is the use of standard "pills" for determining the strengths of the various solutions. Though not as accurate as titration methods, they serve well if properly used.

The foregoing statements as to processing have referred to ware made from relatively thin sheet stock. In the manufacture of large storage and processing units from thicker metal, preparation for enameling is by surface grinding and abrasive cleaning, and no chemical considerations are involved. But in connection with cast iron parts for enameling, also cleaned by abrasives, the chemical relation between the iron and enamel has received much attention. In addition to enamel blistering that may be caused by the escape of gases mechanically contained in the iron, there is a type of blistering (possibly more than one) that apparently comes from gases liberated by the graphitization or other reactions taking place within the casting, due to the heat incidental to burning the enamel.

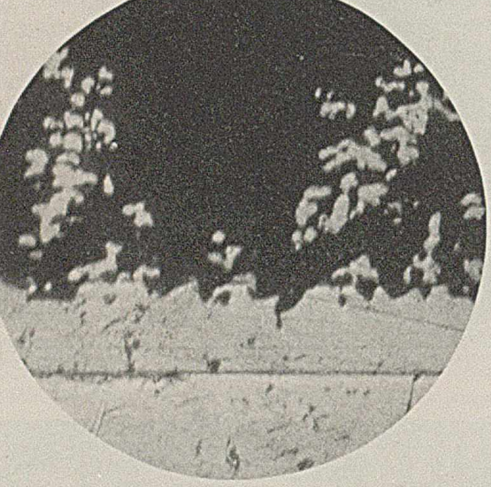
Cast Iron Base Metal

Irons that anneal readily so that the resulting gases pass off before the fusion of the enamel, give satisfactory results, while slowly annealing irons continue to give off gases at higher temperature that become entrapped in the viscous enamel. Irons that contain free or hypereutectoid cementite, either throughout the casting or in the thin surface layer that has come to be known as the microchill, tend to cause blistering. This can be eliminated in the case of mild microchill by severe abrasive treatment. Some special irons of the pearlitic type,



Courtesy, Better Enameling

IRON OXIDE FILM
Hydrochloric-acid-etched structure of iron-enamel interface of a normally fired commercial enamel on sheet steel; etchant attack on ferrous-oxide-rich areas (× 700).



Courtesy, R. M. King

DENDRITES IN ENAMEL
Iron-enamel interface of normally fired commercial enamel on sheet steel; dendrites precipitated in enamel on metal surface.

so stabilized as to resist graphitization by the heat of enameling, are also successfully enameled. There are other chemical factors connected with iron composition and blistering that may be involved; they are under study at the present time.

With proper foundry practice, iron of the following approximate analysis should give good results for stove plate. For thicker sections and the use of low-phosphorus pig, adjustments are required:

Silicon	2.50%	Manganese	0.70%
Sulfur	0.075	Total carbon	3.30–3.40
Phosphorus	0.75	Graphitic carbon	2.80–2.90

This composition is in line with the present theory that the carbon equivalent

$$\text{C. E.} = \frac{\%\,\text{Si} + \%\,\text{P}}{3} + \%\ \text{total carbon}$$

should be 4.3, or slightly above, for stove plate.

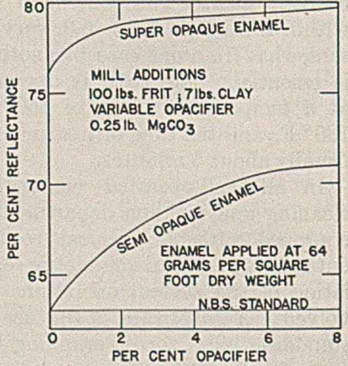
Chemical Raw Materials

Chemical processing and control have made conspicuous contributions to vitreous enameling through the raw materials used. Such chemicals as soda ash, sodium nitrate, borax, and oxides of tin, lead, and zinc have been well standardized for some time. By chemical treatment and control natural minerals, such as silica, feldspar, clay, cryolite, and fluorspar, have more recently been brought to high standards of purity and uniformity. Chemical research has produced several substitutes for the more expensive tin oxide, originally the chief white pigment and opacifier. Compounds of antimony and zirconium are now in wide use, either in place of or as partial substitutes for tin oxide.

The demand for attractive colors has resulted in the solution of some knotty problems. The color manufacturers have done an excellent job in developing coloring oxides that will give uniform results over wide ranges of enamel composition and processing conditions. Two types of coloring compounds are used—those that dissolve in the enamel matrix approaching a clear glass, supported by separate opacifiers if desired, and those that resist solution and contribute color and opacity through fine dispersion in the enamel. In making these colors the pigmenting constituents are mixed with certain carriers, so chosen as to give a product that will be properly related to the enamel involved. This mix is calcined, washed free of soluble matter, dried, and ground to a state of fine subdivision. Careful control of the entire process is necessary to ensure uniformity.

Enamel Compositions

Progress in the development of enamel compositions was slow in the hands of the enameler who jealously guarded his secret formulas, but with the advent of the technically trained man and the accompanying scientific approach, advancement became more rapid. From the chemical point of view early sheet iron enamels were just acid resistant enough to withstand the milder conditions encountered in the kitchen, but were attacked by strong fruit acids. Cast iron enamels were not so resistant as the sheet iron compositions. A little lemon juice carelessly dropped on the kitchen sink destroyed the glossy surface. Large equipment found use in the brewing and dairy industries but to only a limited extent in the canning, pharmaceutical, and chemical fields; the latter made use of highly acid-resisting cast iron ware from Europe. With the imported ware cut off by the war, the development of domestic acid-resisting enamels began. Cast iron and sheet steel enameled equipment was produced for the chemical trade and allied industries which was as resistant to acids as that formerly imported. A critical situation with reference to the manufacture of certain explosives, medicinals, and dyestuffs was thus met. The use of acid-resisting enamels has recently carried over into the cooking ware and sanitary fields so that enamels are now available for household use which are not attacked by any of the fruit acids or by the hydrochloric acid that the tile setter may drop on the bath-

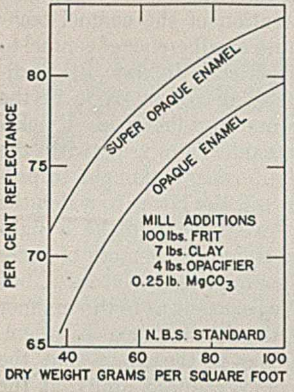


Courtesy, Ferro Enamel Corporation

REFLECTANCE *vs.* AMOUNT OF OPACIFIER

tub incidental to the removal of cement from the surface of wall tile.

Another important change in enamel composition is the elimination of lead from wet-process cast iron enamels used for stove parts and similar ware. Enamels of this type fuse at a lower temperature than do those for sheet iron, and lead oxide has been in common use as a flux. The leadless enamels often substituting barium carbonate for lead oxide, have been more difficult to process and more sensitive to defects in the casting, but recent improvements in the enamel and cast iron, accompanied by modified processing, have combined to make the leadless enamels commercially practical.



Courtesy, Ferro Enamel Corporation

Reflectance *vs.* Weight of Enamel

Consistency of Enamel Slips

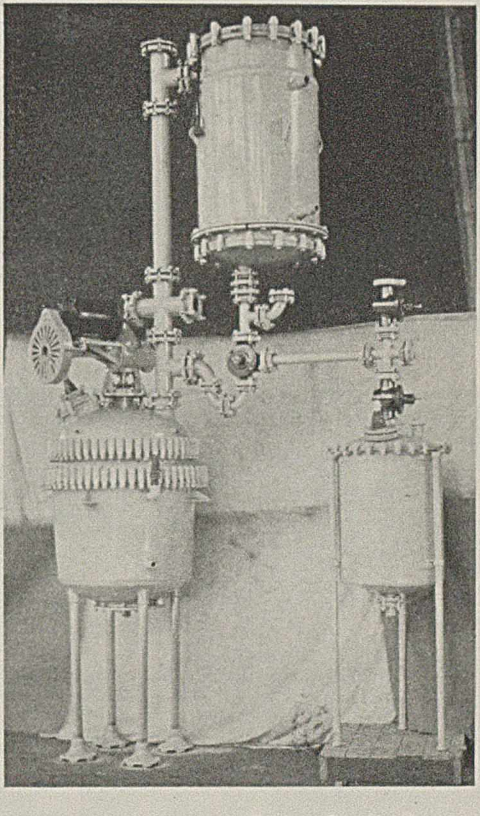
One of the most important points in the application of wet-process enamel is the consistency of the slip. This property is a determining factor in the production of a smooth, even coat of enamel by dipping or draining, less important, but not to be ignored, in application by spraying. Early methods of control involved the use of borax and sometimes magnesia for setting up ground coats and epsom salts for cover coats. The operator was guided in the use of these additions by the manner in which the slip drained from the hand. Early investigators realized that the basic principles of colloid chemistry were involved and that some accurate means of measuring consistency was needed. The effect on consistency of a variety of electrolytes was investigated, as indicated by apparently appropriate viscometers, but the data obtained did not lead to satisfactory interpretation. It was possible to determine standard requirements for a given enamel under definite operating conditions, but troublesome variables asserted themselves and no fundamental principles were recognized that permitted a scientific analysis.

A new day arrived when it was recognized that enamel slips follow the laws of plastic rather than those of viscous flow. By the use of simple plastometers it was possible to establish graphs corresponding to correct consistency for enamel slips for various conditions of application. The slope of the graph indicates "mobility" and the intercept the "yield value". Variations in one or both of these quantities offer means of adjustment. A rise in temperature increases mobility without change in the yield value; the addition of water increases the mobility and decreases the yield value; the use of more clay increases the yield value without change in mobility, and the addition of magnesium sulfate produces a like effect. Following the recognition of these facts, other electrolytes were studied and the important effect of the solution of sodium oxide, boron oxide, and other oxides from the frit in the mill liquor was appreciated. Various improvements of the early instruments are involved in the plastometers and mobilometers now on the market and in use in research and control. By the application of the principles of plastic flow through the above and auxiliary control methods, the consistency of enamel slips can be adjusted so as to make use of special enamels previously difficult to work and to make possible the application of enamel to constructions that could not previously be enameled.

Burning

It is a long step from the coal-fired fire clay muffles of a few decades ago to the modern furnaces heated by oil, gas, and electricity. This progress has come through improved refractories, the development of heat-resisting alloys, and a better understanding of the application of heat to the burning of enamel. Bearing on the proper maturing of the enamel, two important factors have been recognized—the proper time-temperature cycle and the necessity for correct furnace atmosphere. Several interesting chemical features are involved in the latter.

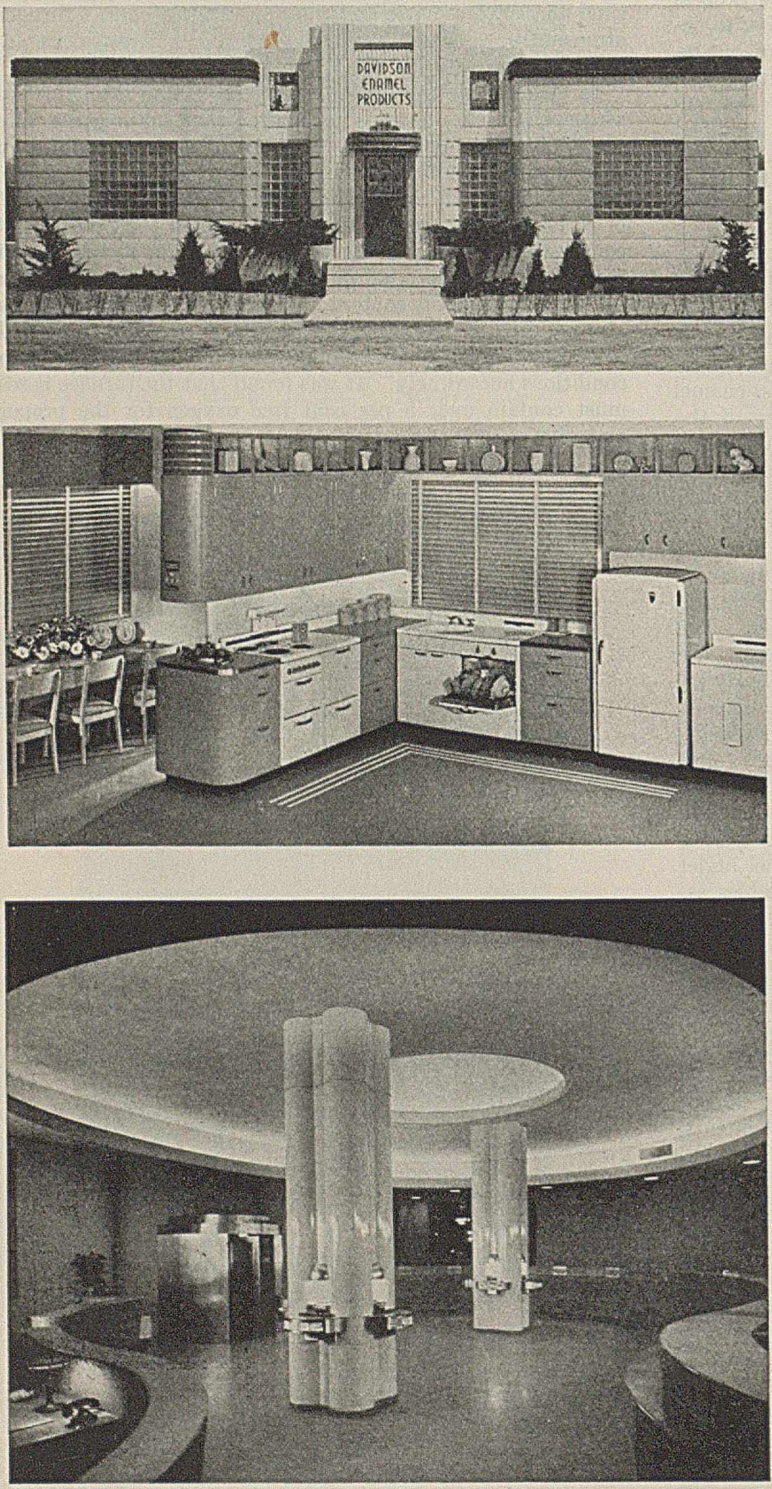
In general, air free from other gases is the ideal furnace atmosphere. It was early recognized that sulfur gases were detrimental to final finish. In muffle furnaces combustion gases carrying sulfur were excluded except in the frequent cases of defects in the muffle lining. With the development of certain direct-fired oil furnaces in which the products of combustion come in contact with the ware, it was found that "sulfur scum" did not develop with fuel oils below 0.5 per cent in sulfur content. In this type of furnace it was also required to determine the amount of free oxygen needed to mature a given enamel properly and to control combustion conditions accordingly. It was found that the furnace gases must contain over 5 per cent free oxygen for the proper maturity of the enamel involved.



Courtesy, Pfaudler Company

Acid-Resisting Enameled Still, Condenser, and Receiver

For furnaces using radiant heat from tight muffle walls, electric resistors, or fuel-heated radiant tubes, the problem includes proper ventilation of the burning chamber so as to avoid an excess of certain gases evolved from the enamel during firing. The chief of these is water vapor arising from moisture that may not have been previously removed, or that resulting from the dehydration of the clay and other constituents of the dried enamel film. Cases of defective enamel have been definitely associated with the presence of 4 per cent water vapor, and as much as 10 per cent has been found in extreme instances. There is ample evidence that certain other gases are harmful—for example, fluorine compounds—but when allowed to accumulate in a furnace they are usually accompanied by water vapor and there may be some doubt as to their effect. Some investigators hold that 0.5 per cent of these so-called acid gases can cause trouble with cast iron enamel.



Courtesy, Ferro Enamel Corporation

(*Top*) Vitreous Enamel Exterior, (*center*) Kitchen, (*bottom*) Interior Columns (Photo by F. S. Lincoln)

Adherence

One of the most interesting problems that has had the attention of the enamel technologist is the cause of adherence of enamel to sheet steel. Experience to date has indicated the necessity of cobalt oxide in the ground coat to assure adherence. Nickel and manganese oxides are used with the cobalt oxide; the former is thought to promote adherence, and the latter to widen the firing range. No effort to make a light ground coat free from one or more of these oxides has been commercially successful, but there is a lack of agreement as to the manner in which adherence is produced by them. The first theory was to the effect that the cobalt oxide becomes reduced and that the resulting alloy with the base metal produces a structure to which the enamel can adhere. Recent investigators have advanced more specific explanations.

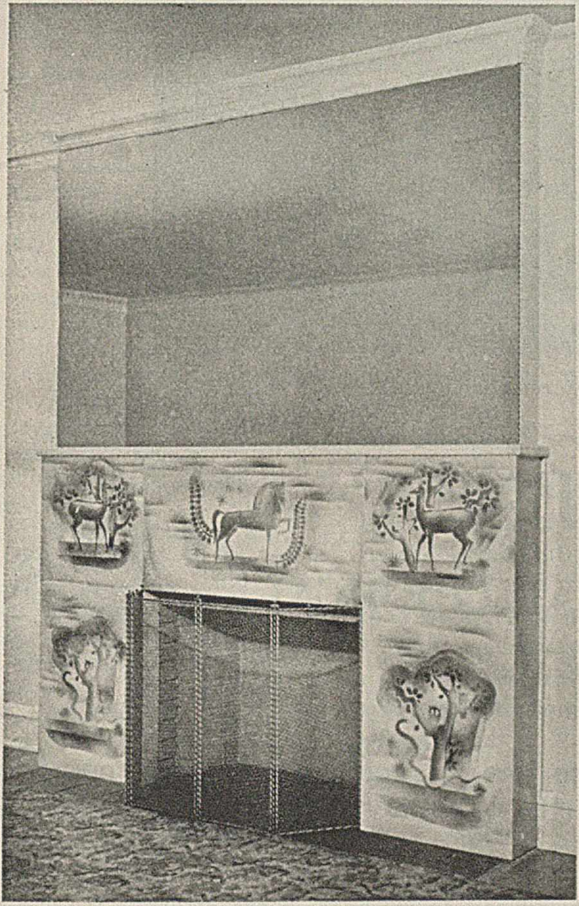
One school of thought holds that adherence is related to the formation of metallic dendrites which x-ray studies have indicated to be alpha-iron, cobalt, and nickel. Some of these dendrites as observed in a given section are attached to the metal; others penetrate some distance into the enamel. If these dendrites do not actually promote adherence in a mechanical way, they are at least present in cases of good adherence and absent under opposite conditions. A modification of this theory is that the dendrites are chiefly metallic cobalt that has been plated out by electrolytic action of the hot iron base during fusion of the enamel. All of the metals between iron and copper in the electromotive series, if dissolved in glasses, are plated out of solution when the glasses are fired as ground coats on steel. On this basis, cobalt and nickel are held to contribute to adherence by being deposited on the base metal, and possibly mechanically in addition by the dendrites formed.

In opposition to the above, adherence has been associated with the presence of certain iron oxide films at the interface between metal and enamel. "Neither gripping, electrolytic reaction or dendrites are the fundamental causes of commercial cobalt ground coat adherence to iron, but the enamel glass is rigidly held to the iron through the medium of a ferrous phase approximately 3×10^{-5} inches thick" (*4*). In at least one instance the formation of the desired oxide film is regulated by a controlled furnace atmosphere.

The most recent statements of the proponents of these theories are "iron oxides and metallic dendrites are precipitated at the interface; adherence is associated with precipitated metal in all cases, but not always with precipitated oxides" (*6*), and "the degree of adherence seems to depend upon the thickness of the ferrous oxide film between glass and iron. The thicker the film the poorer the adherence becomes" (*5*).

Opacity

Accompanying the development of more acid-resistant enamels, much progress has been made with regard to opacity. The result is better ware as to appearance and durability, the latter through the use of thinner coats with correspondingly greater mechanical resistance. This has come about through a more scientific understanding of the properties involved in the appearance of the finished coat and the manner in which various opacifiers contribute to it.



Courtesy, Ferro Enamel Corporation

Vitreous Enamel Mural Panels (Designed by Edwin H. Winter)

"Opacity" is a combined effect of reflection, refraction, and diffraction of light. Various devices for the individual and collective evaluation of these factors have proved useful tools. Opacity may be produced by the use of finely divided materials which are insoluble in the enamel matrix under commercial conditions, the development of a crystalline phase within the enamel through chemical reaction during firing, or the presence of immiscible phases, either solid or gaseous. In a given case the net effect may be a combination of two or all of these factors. X-ray studies have gone a long way in pointing out the mechanics of various types of opacity. For example, tin oxide remains as an insoluble, finely divided dispersion; certain fluorine compounds promote the formation of crystals of finely dispersed sodium fluoride; zirconium opacifiers produce immiscible phases, with an index of refraction different from that of the matrix.

Earlier practice was based on producing a fair amount of opacity in the frit, depending chiefly on opacifiers, such as tin oxide, in the mill. More recently, higher opacity has been produced in the frit and finer milling has increased the effect of opacifiers used. With these superopaque frits and more grinding, it is now possible to obtain a given net effect with a total enamel thickness much less than that previously required to produce enamels with less over-all opacity.

Uses

Vitreous enameled equipment plays an important part in many of the chemical industries. Resistance to the action of acids, with the exception of hydrofluoric, affords ample protection against corrosion and the contamination of materials by metals. There has been a steady and substantial increase in the maximum size and maximum pressure ratings of enameled vessels for use in severe chemical conditions. Units up to 1700 gallons in size are now available for such varied operations as nitration, chlorination, digestion, sulfonation, crystallization, and distillation. Much larger pieces are suitable for the handling and storage of materials of a less corrosive nature. Standard designs are such as to make possible assemblies of considerable complexity.

A majority of the new usages which have been found for enameled equipment during the past few years have been in the field of synthetic organics, particularly of the chlorinated type, and for such finished products as plastics, synthetic rubber such as Neoprene, chlorinated solvents, etc., either for the finished products themselves or for intermediates which enter into their manufacture.

Many of the everyday chemical and pharmaceutical compounds that make essential contributions to human welfare are most satisfactorily processed in enameled equipment. By way of illustration may be mentioned radium salts, vitamin compounds, glandular extracts, sedatives, and antiseptics. The use of glass enamel has also broadened greatly in the pharmaceutical field for synthetics such as sulfanilamide and in the preparation and concentration of biological products such as vitamins.

Thus, and in many other ways, modern ceramics and chemistry have worked hand in hand in the development of a product that is an everyday necessity in the household and in the factory. The sanitary and artistic excellence of the kitchen of today would hardly be possible but for this progress. Stores, filling stations, houses, and commercial structures are made more beautiful and durable through the application of the basic principles of chemistry and kindred sciences in the conversion of an ancient art into one of our most progressive modern industries.

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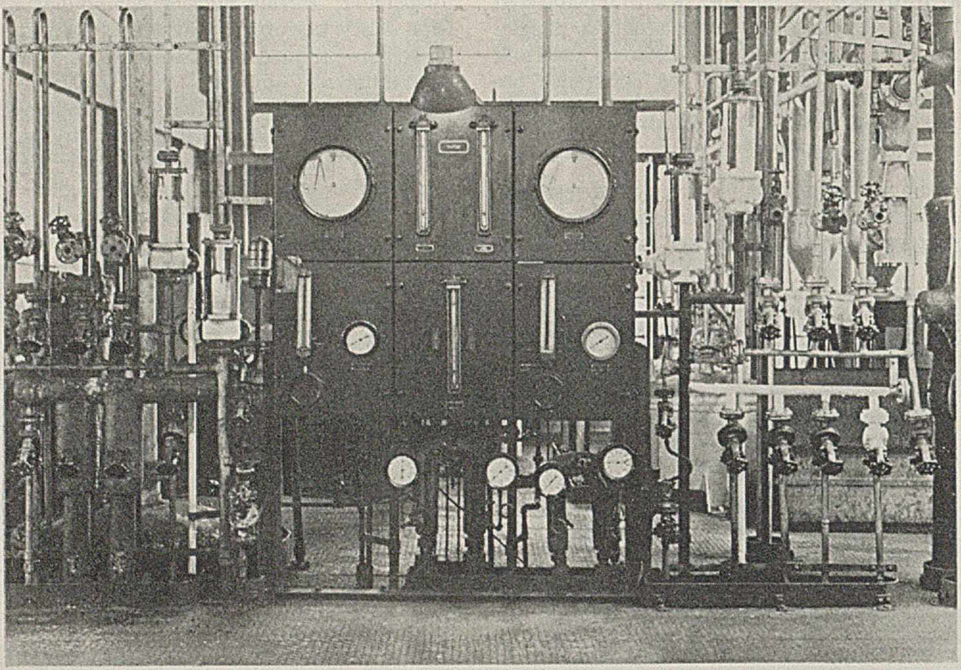


Control Area in the Manufacture of Diketene

DIKETENE

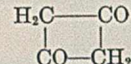
A NEW INDUSTRIAL CHEMICAL

A. B. BOESE, Jr.

Mellon Institute of Industrial Research, Pittsburgh, Penna.

COMPARED to the majority of aliphatic chemicals introduced to industry in recent years, the ketene dimer, or "diketene", which is now available in commercial quantities, is a comparatively new compound; it was discovered just thirty years ago. In 1907 the parent substance, monomeric ketene ($CH_2{=}C{=}O$) was first prepared by Wilsmore (*51*), who obtained it by immersing a glowing platinum wire in liquid acetic anhydride. Somewhat later Staudinger described its preparation by reacting bromoacetyl bromide with zinc (*48*). The great tendency of ketene to polymerize was soon observed by these investigators, and in 1908 Chick and Wilsmore first isolated diketene from the products obtained by allowing ketene to polymerize in sealed glass tubes (*14*). A more detailed description of the preparation and properties of this compound was published in 1910 by the same authors (*15*), who stated in their paper that "the preparation of cyclobutane-1,3-dione (diketene) may be recommended as a useful exercise for students in laboratories where a supply of liquid air is available". Hence, because of the obvious difficulties encountered in preparing adequate quantities of diketene, even on a laboratory scale for experimental purposes, it is not surprising that so little work has since been done on it. Now that a process has been developed for its commercial production, we may reasonably assume increased academic and industrial interest in the chemistry and uses of diketene and its derivatives.

Four structural formulas have at various times been proposed for diketene:

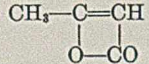


$$\begin{array}{ll} H_2C\text{—} & CO \\ | & | \\ CO\text{—} & CH_2 \end{array}$$

I

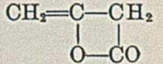
$CH_3COCH{=}C{=}O$

II



$$\begin{array}{ll} CH_3\text{—}C{=} & CH \\ | & | \\ O\text{—} & CO \end{array}$$

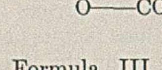
III



$$\begin{array}{ll} CH_2{=}C\text{—} & CH_2 \\ | & | \\ O\text{—} & CO \end{array}$$

IV

Formula I, cyclobutane-1,3-dione, proposed by Chick and Wilsmore (*15*), from a consideration of both the physical and chemical properties of diketene, has been found to be untenable (*33*). Formula II, acetylketene, also proposed by Chick and Wilsmore (*14*), fails adequately to account for the exclusive formation of γ-bromoacetoacetyl bromide ($BrCH_2COCH_2COBr$) by the addition of bromine, instead of the expected α-bromo compound, and for the formation of β-butyrolactone,



$$\begin{array}{ll} CH_3\text{—}CH\text{—} & CH_2 \\ \quad\ | & | \\ \quad\ O\text{—} & CO \end{array}$$

by hydrogenation. Formula III, β-crotonolactone, was recently postulated by Hurd (*33*) as a resonance isomer of acetylketene. Formula IV, vinylaceto-β-lactone, suggested by A. L. Wilson of this laboratory, with the exception of the formation of pyruvic aldehyde on ozonolysis (*34*), appears most satisfactorily to account for the reactions of diketene, including those involving halogenation and hydrogenation. In this paper the reactions of diketene to be described will be illustrated by the vinylaceto-β-lactone structure.

Physical Properties

Diketene is a colorless, nonhygroscopic liquid, insoluble in water but soluble in the common organic liquids inert toward it. It has an intensely pungent odor, and its vapors are extremely lachrymatory. Its physical properties are as follows:

Specific gravity, 20/20° C.	1.0897
Change in specific gravity, ° C.	0.0009
Pounds per gallon (grams/liter) at 20° C.	9.09 (1099)
Molecular weight	84.03
Boiling point, ° C.	127.4
Melting point, ° C.	−6.5
Vapor pressure at 20° C., mm.	8.0
Latent heat of vaporization, calcd., cal./gram	165
Heat of combustion (*2*), cal./mole	447
Heat of formation, obsvd. (*1*), cal./mole	1081
Parachor $(M\gamma^{1/4})/D - d$ (*34*)	181.5 (24.0° C.) 183.2 (20.4° C.)
Refractive index, n^{20}	1.4379

On standing at ordinary temperatures, it slowly polymerizes to a dark-colored, tarry material containing a substantial quantity of dehydroacetic acid, the dimer of diketene. The polymerization is greatly accelerated by mineral acids, alkali metal hydroxides, alkali metal alcoholates and phenolates, and tertiary aliphatic amines. As the reaction is exothermic, precautions must be taken to prevent these substances from coming in contact with large quantities of diketene. The tendency to polymerize is materially reduced by employing inert diluents, such as ethers, aromatic and aliphatic hydrocarbons, esters, and ketones. Acetone has been found to be of particular value in this connection. Certain organic antioxidants, such as hydroquinone and pyrogallol, have a slight inhibiting action, but organic peroxides, such as benzoyl peroxide and ascaridole, do not appear to act as catalysts. Low temperatures retard the polymerization until it becomes negligible at the freezing point (−6.5° C.). Samples of diketene have been stored in this laboratory under temperature conditions fluctuating between −30° and +10° C. for several years without any detectable change in physical or chemical properties. Of the common metals, aluminum has been found eminently satisfactory for storage and shipping containers. Accordingly, diketene may now be safely shipped and stored in a frozen condition in aluminum drums or other suitable containers. The availability of solid carbon dioxide affords an efficient and economical means of refrigeration. Diketene is best purified by distillation at subatmospheric pressure; the amount of polymerization occurring during distillation is a direct function of the temperature at which the distillation is carried out. Moreover, material distilled at a low temperature is more stable during storage than that distilled at a higher temperature.

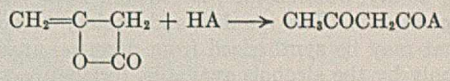
The ketene dimer, diketene, is now available in commercial quantities. Because of its exceptional reactivity, its industrial importance lies in the valuable products which may be synthesized from it.

Diketene reacts with hydroxyl groups to form acetoacetic esters such as ethyl acetoacetate, with amino groups to form acetoacetamides such as acetoacetanilide, and with phenyl hydrazines to form phenylmethylpyrazolones. When reacted with ureas, diketene forms 4-methyluracils, and the reaction between diketene and aromatic hydrocarbons in the presence of aluminum chloride yields 1,3-diketones such as benzoylacetone. Halogens add to diketene to form γ-haloacetoacetyl halides, and β-butyrolactone is formed when diketene is hydrogenated.

Diketene may be further polymerized by catalysts to yield a tetramer of ketene, dehydroacetic acid, which is noted for its varied chemical transformations.

By pyrolysis at 500–600° C., diketene is depolymerized almost completely to ketene and thus affords a method for the rapid production of high-purity ketene. Ketene is a powerful acetylating agent; it reacts in general with compounds having an active hydrogen atom to give the corresponding acetyl derivative.

In contrast to the majority of recently introduced aliphatic chemicals, whose chief values are their solvent powers or other specific properties, such as hygroscopicity, water miscibility, acidity, basicity, surface tension–depressing activity, and the like, the primary present and future industrial importance of diketene lies in its exceptional chemical reactivity and, consequently, in the products which may be synthesized from it. Because diketene is highly unsaturated, its most common reaction is the addition of substances having an active hydrogen atom to yield compounds containing the acetoacetyl group:

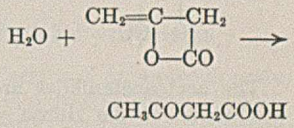


$$\underset{\text{O—CO}}{CH_2{=}C{-}CH_2} + HA \longrightarrow CH_3COCH_2COA$$

Thus a large number of products derived from acetoacetic ester by the usual metathetical reactions may be synthesized more economically and with greater ease from diketene. For example, when acetoacetanilide and phenylmethylpyrazolone, two compounds of recognized commercial importance, are manufactured from diketene instead of acetoacetic ester, higher yields and purer products are obtained and the reaction time is substantially reduced. Moreover, the marked exothermic nature of the reaction practically eliminates the necessity of externally applied heat. A summary of the more important reactions of diketene, together with a description of some of the products and their potential applications will be presented in the following pages (in several instances for the first time).

Reactions of Diketene

Diketene reacts with water in the presence of catalysts to give acetoacetic acid which, in turn, decomposes to acetone and carbon dioxide:

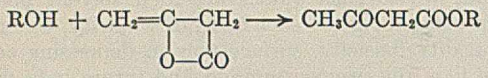


$$H_2O + \underset{\text{O—CO}}{CH_2{=}C{-}CH_2} \longrightarrow CH_3COCH_2COOH$$

$$CH_3COCH_2COOH \longrightarrow CH_3COCH_3 + CO_2$$

With pure water the reaction is quite slow even at elevated temperatures, for a mixture of diketene and water in the absence of catalysts may be distilled at atmospheric pressure as a constant boiling mixture, over 90 per cent of the diketene remaining unchanged.

The reaction between diketene and alcohols in the presence of acid catalysts yields the corresponding esters of acetoacetic acid (*11*):



$$ROH + \underset{O-CO}{CH_2=C-CH_2} \longrightarrow CH_3COCH_2COOR$$

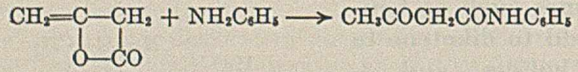
Thus, by this method ethyl acetoacetate can be produced in commercial quantities more easily and economically than by the classical sodium condensation of ethyl acetate. Also, the troublesome necessity of using sodium with its attendant hazards is eliminated. From both an academic and industrial standpoint, the importance of ethyl acetoacetate and its lower homolog, methyl acetoacetate, is too well known to require further comment. The number and variety of acetoacetic esters that may be synthesized from diketene appear to be limited only by the alcohols available, for the reaction is an extremely general one, applicable to all aliphatic alcohols from primary to tertiary, alcohol ethers, chlorohydrins, substituted alcohols, glycols, glycerol, and phenols. Acetoacetic esters similar to cellulose acetate have been reported as products of the reaction between diketene and cellulose (*50*).

Preparation of 2-Ethoxy Ethyl Acetoacetate

To 90 grams of 2-ethoxy ethanol ("Cellosolve") and 0.5 gram of benzene sulfonic acid at 100° C. were added dropwise, with agitation, 84 grams of diketene. Since an exothermic reaction occurred, the temperature was not allowed to rise above 110° C. When all the diketene had been added, the reaction mixture was kept at 100° C. for one hour, washed with water, and fractionally distilled under vacuum. An 84 per cent yield of ethoxy ethyl acetoacetate, $CH_3COCH_2COOC_2H_4OC_2H_5$, was obtained as a colorless, water-insoluble, pleasant-smelling liquid which distilled at 93–94° C. at 3 mm.

Since the acetoacetic esters, in general, have the solvent power of both an ester and a ketone, they are useful as solvents for lacquers and other surface coatings, while those of higher molecular weight may be of value as plasticizers. Certain of their metallic salts have shown promise as resin stabilizers and oil-conditioning agents.

Diketene and primary aromatic mono- and polyamines react smoothly to yield the corresponding acetoacetyl amines in a high degree of purity and with excellent yields (*10*). Representative of this type of compound is acetoacetanilide, prepared from diketene and aniline (*40*):



$$\underset{O-CO}{CH_2=C-CH_2} + NH_2C_6H_5 \longrightarrow CH_3COCH_2CONHC_6H_5$$

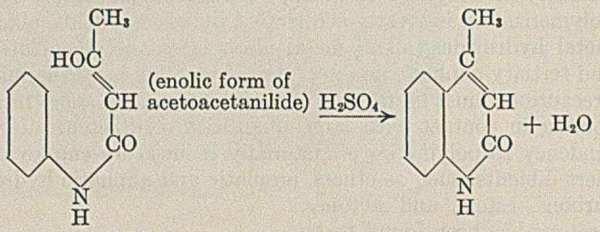
The acetoacetanilides are used as intermediates for the production of the Hansa yellow dyes, formed by coupling them with diazonium compounds (*30*). Because of their stability, light fastness, insolubility in the common organic solvents, and great tinctorial value, the Hansa yellows are becoming increasingly important as pigments for a wide variety of surface coatings.

Diacetoacetyl diamino compounds of the diaryl series are extensively used as developers for producing azo dyes directly on cotton (*39*). In this process an alkaline solution of the acetoacetyl amine is padded onto the fiber, then developed with a diazonium compound. Typical compounds of this series are *N*,*N*′-diacetoacetylbenzidine, $CH_3COCH_2CONHC_6H_4—C_6H_4—NHCOCH_2COCH_3$, and *N*,*N*′-diacetoacetyl-*o*-tolidine, $CH_3COCH_2CONHC_6H_3(CH_3).C_6H_3(CH_3)NHCOCH_2COCH_3$, commonly known as "Naphthol ASG", prepared by reacting two moles of diketene with one mole of benzidine and *o*-tolidine, respectively.

Diacetoacetyl-*o*-Tolidine

To a refluxing solution of 212 grams of *o*-tolidine in 1700 cc. of ethylene dichloride were added slowly, with agitation, 184 grams of diketene over a period of one hour. During this time the reaction was sufficiently exothermic to keep the solution refluxing without the application of external heat. When the diketene had all been added, the mixture was allowed to stand at room temperature for 16 hours and was then filtered. There were obtained 354 grams of pure diacetoacetyl-*o*-tolidine, melting at 206–207° C. and representing a yield of 93 per cent.

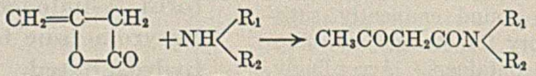
When treated with strong dehydrating agents such as sulfuric or phosphoric acid, acetoacetanilides undergo ring closure to form 4-methylcarbostyril and its derivatives. Thus, the simplest of these compounds, 4-methylcarbostyril itself, is obtained in practically quantitative yields by dissolving acetoacetanilide in concentrated sulfuric acid (*37*), followed by precipitation with water:



When dehydrated, substituted acetoacetanilides yield the correspondingly substituted 4-methylcarbostyrils. These compounds have shown activity as corrosion inhibitors and bactericides; their use as intermediates for dyestuffs and pharmaceuticals is also indicated.

Although in most cases the reaction between diketene and aromatic amines is most efficiently carried out in inert organic solvents as reaction media, the great difference in reactivity of diketene with water and primary amine groups makes it possible to run these reactions in water, the amine being either in solution or suspension (*9*). Diacetoacetylbenzidine can be prepared by adding diketene to an agitated suspension of finely divided benzidine in water; *N*,*N*′-diacetoacetyl-*p*-phenylene diamine is readily formed by introducing diketene into an aqueous solution of *p*-phenylene diamine.

Similarly, diketene reacts with aqueous solutions of ammonia and primary and secondary aliphatic amines, the products being acetoacetamide or nitrogen-substituted acetoacetamides (*9*):



$$\underset{O-CO}{CH_2=C-CH_2} + NH\begin{smallmatrix}R_1\\R_2\end{smallmatrix} \longrightarrow CH_3COCH_2CON\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$$

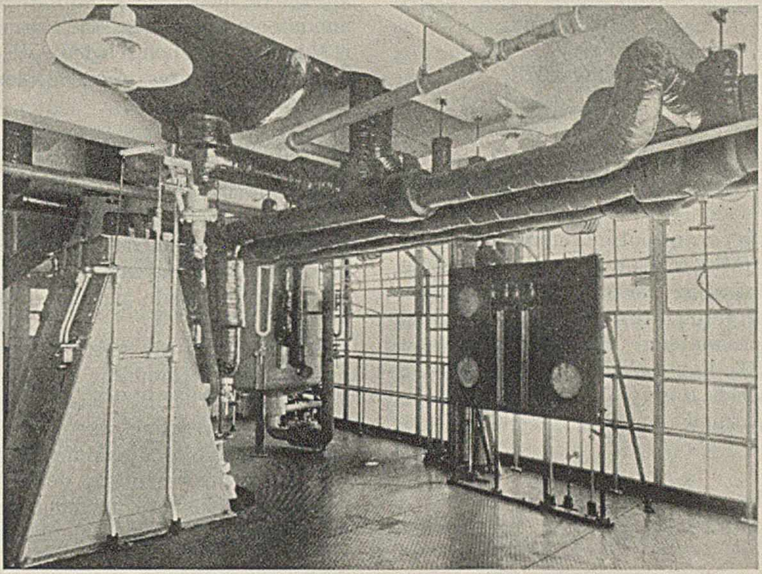
where R_1 and R_2 = H or alkyl groups

Here is presented a method for preparing acetoacetyl primary and secondary aliphatic amines which have not previously been described in the literature. As examples of such products might be mentioned acetoacetamide, *N*,*N*′-diacetoacetylethylene diamine, and *N*-acetoacetylmorpholine, obtained by reacting diketene with aqueous solutions of ammonia, ethylene diamine, and morpholine, respectively.

Diacetoacetylethylene Diamine

To a solution of 30 grams (one-half mole) of ethylene diamine in 500 cc. of water at 0° C. were added dropwise, with stirring, 84 grams (one mole) of diketene over a period of an hour; the temperature was kept below 20° C. During the reaction the product started to crystallize from solution.

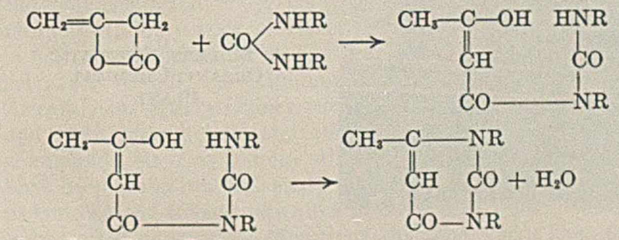
When all the diketene had been added, the mixture was stirred for one hour and filtered, and the product washed with water. A 72.4 per cent yield of *N*,*N'*-diacetoacetylethylene diamine, $CH_3COCH_2CONH—C_2H_4—NHCOCH_2COCH_3$, was obtained as a colorless, crystalline solid which melted at 168–169° C.



UNIT FOR THE REACTION OF DIKETENE WITH AN ARYL AMINE

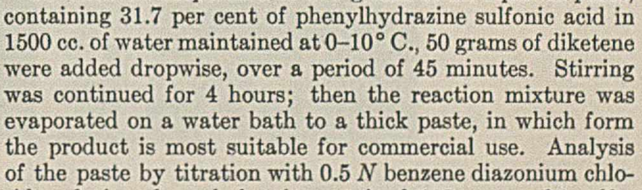
The aliphatic acetoacetamides are colorless, crystalline solids similar in chemical properties to acetoacetanilide and acetoacetic ester. They form metallic salts. They may be alkylated and acylated by the usual methods, and the nitrogen-substituted compounds form dyes when coupled with diazonium compounds. The lower members of the series have indicated value as dye solvents, constituents of wood stains, and as intermediates for the preparation of formaldehyde condensation resins. When heated, acetoacetamide condenses with itself to form lutidone carboxylic acid and lutidone, compounds of interest as intermediates for further syntheses (*18*).

When diketene is reacted with urea or symmetrical disubstituted ureas in an inert solvent, 4-methyluracil or its homologs are formed (*8*). The reaction involves the intermediate formation of an *N*-acetoacetylurea, which then undergoes ring closure through elimination of water to yield the uracil:



where R = H or alkyl group

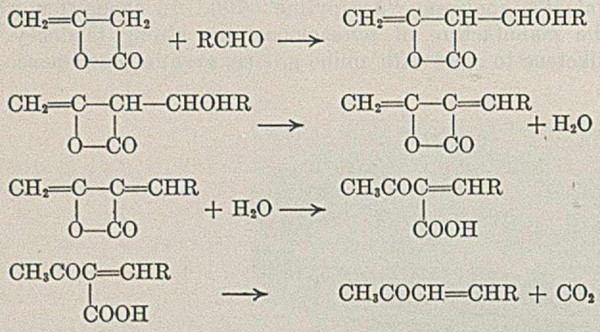
At temperatures around room temperature, diketene reacts with phenylhydrazine in an inert solvent to form the phenylhydrazone of acetoacetylphenylhydrazine, $CH_3C(=N—NHC_6H_5)CH_2CONHNHC_6H_5$ (*15*). If, however, higher temperatures are employed, the reaction takes a different course, yielding 1-phenyl-3-methyl-5-pyrazolone in high efficiency (*36*). Phenylmethylpyrazolone, known to the dyestuff trade as "Developer Z", and its derivatives are constituents of an important class of azo dyes formed by coupling with diazonium compounds (*19*). Phenylmethylpyrazolone also serves as the starting material in the synthesis of the valuable analgesic, "Antipyrine" (*38*). In connection with the manufacture of pyrazolones, the strong tendency of diketene to react with amino groups, even in the presence of water, makes it possible to prepare sulfophenylmethylpyrazolone, also a well known dye intermediate (*20*), by this method. The starting material, phenylhydrazine sulfonic acid, is practically insoluble in inert organic solvents; consequently no reaction takes place with diketene under such conditions. But when diketene is added to an aqueous suspension of phenylhydrazine sulfonic acid, smooth reaction takes place and good yields of 1-sulfophenyl-3-methyl-5-pyrazolone result:



1-Sulfophenyl-3-Methyl-5-Pyrazolone

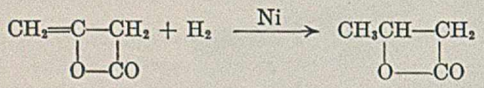
To a stirred suspension of 315 grams of an aqueous paste, containing 31.7 per cent of phenylhydrazine sulfonic acid in 1500 cc. of water maintained at 0–10° C., 50 grams of diketene were added dropwise, over a period of 45 minutes. Stirring was continued for 4 hours; then the reaction mixture was evaporated on a water bath to a thick paste, in which form the product is most suitable for commercial use. Analysis of the paste by titration with 0.5 *N* benzene diazonium chloride solution showed that it contained 112 grams of 1-sulfophenyl-3-methyl-5-pyrazolone, representing a yield of 80 per cent.

Ketones, esters, and ethers apparently do not react with diketene. With aldehydes higher than formaldehyde, an aldol-type condensation takes place, the final products being alpha-beta-unsaturated ketones (*7*). In this reaction an intermediate hydroxy diketene is believed to be formed, which subsequently loses water. The water eliminated reacts with the condensation product and results in the formation of a β-ketocarboxylic acid, which, in turn, loses carbon dioxide; the end product is the unsaturated ketone:

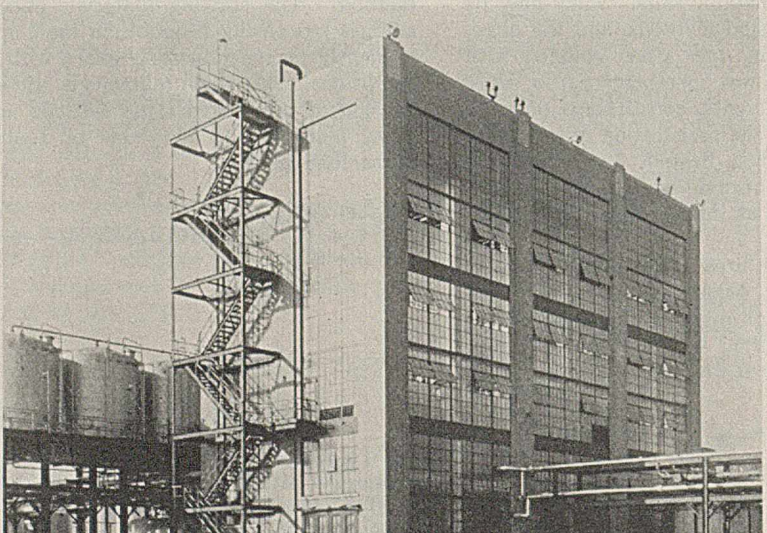


In practice the reaction is carried out by refluxing diketene and the aldehyde in molar ratio, with or without a solvent for 24–48 hours, and then separating the product by fractional distillation. When heated, formaldehyde and diketene react to form a polymeric resinous material (*6*).

When hydrogenated in the liquid phase in the presence of Raney nickel, diketene yields β-butyrolactone in high efficiency and, in addition, a small amount of butyric acid (*35*, *43*):

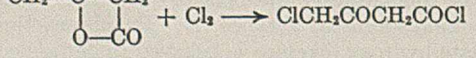


β-Butyrolactone may be readily hydrolyzed to β-hydroxybutyric acid, a compound of pharmaceutical importance and an intermediate for the preparation of a great number of esters and acyl derivatives useful as solvents and plasticizers.



A Modern Synthetic Organic Chemical Plant

Diketene, either in the pure state or dissolved in an inert solvent, rapidly absorbs chlorine at low temperatures to yield γ-chloroacetoacetyl chloride, a reaction readily accounted for by the vinylaceto-β-lactone structure:



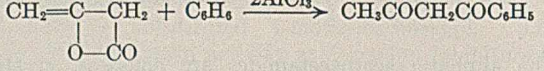
Similarly, bromine adds to diketene to form γ-bromoacetoacetyl bromide (*15*).

Chloroacetoacetyl chloride is stable only at low temperatures and cannot be purified by distillation. It reacts as an acid chloride and is of value for synthesizing compounds containing the chloroacetoacetyl group, such as γ-chloroethyl acetoacetate, $ClCH_2COCH_2COOC_2H_5$, and γ-chloroacetoacetanilide, $ClCH_2COCH_2CONHC_6H_5$. Since, in addition to an active methylene group, these compounds contain an amide or ester linkage, their use as synthetic intermediates is suggested. When reacted with water, γ-chloroacetoacetyl chloride hydrolyzes to monochloroacetone, carbon dioxide, and hydrochloric acid:

$$ClCH_2COCH_2COCl + H_2O \longrightarrow ClCH_2COCH_3 + CO_2 + HCl$$

The chloroacetone obtained in this manner is free of higher chlorinated acetones; hence the chlorination and subsequent hydrolysis of diketene offer a convenient method for preparing this material in a pure state. Starting with γ-bromoacetoacetyl bromide, pure monobromoacetone is obtained in like manner.

Another series of derivatives of diketene of considerable interest are the aromatic 1,3-diketones typified by benzoylacetone, $CH_3COCH_2COC_6H_5$, which can be economically prepared by reacting diketene with aromatic hydrocarbons in the presence of aluminum chloride. Diketene appears to function in this reaction as do acid anhydrides in the Friedel-Crafts synthesis, the maximum yields being obtained when two moles of aluminum chloride are employed with one mole of diketene:



An addition compound of aluminum chloride and diketene is probably first formed as an intermediate, which then adds to the hydrocarbon under the activating influence of a second mole of aluminum chloride.

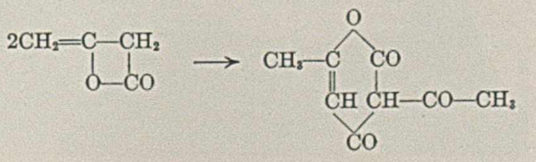
Benzoylacetone

A 2-liter three-neck flask, fitted with a reflux condenser, mercury-sealed stirrer, and dropping funnel, was charged with 532 grams (four moles) of anhydrous aluminum chloride and 1100 cc. of benzene. Over a period of 90 minutes 168 grams (two moles) of diketene were added dropwise with stirring, while the temperature was kept between 45° and 50° C. A vigorous exothermic reaction took place, accompanied by a copious evolution of hydrogen chloride. When all the diketene had been added, the reaction mixture was heated, with stirring, at 65–75° C. for 2 hours, and was then cooled and decomposed by pouring onto 1500 grams of chopped ice. After excess benzene was removed by steam distillation, 250 cc. of concentrated hydrochloric acid were added and the mixture was refluxed for 2 hours. On cooling, benzoyl acetone separated in an impure form as a brown, crystalline solid, which was separated on a filter, washed with cold water, dried, and purified by fractional distillation under reduced pressure. There were obtained 237 grams of benzoylacetone as a colorless solid which distilled at 140–141° C. at 15 mm. and melted at 58–59° C. The yield was 73 per cent, based on the diketene used.

The aromatic 1,3-diketones are colorless, crystalline solids or pale yellow, high-boiling liquids soluble in alcohols, ethers, esters, ketones, chlorinated solvents, and aromatic hydrocarbons, sparingly soluble in water, but completely soluble in dilute alkali solutions. The presence in the molecule of an aromatic nucleus combined with two ketone groups confers unique solvent properties, which make them of interest as plasticizers, particularly for resins of the vinyl type. Chemically they exhibit all the typical reactions of 1,3-diketones. They may be alkylated or acylated at the methylene carbon atom by the usual methods, they form extremely stable chelated compounds with polyvalent metals (*12*) which show promise as resin stabilizers and oil-conditioning agents, and they are converted into dyes when coupled in alkaline solution with diazonium compounds (*31*). Primary aromatic amines condense with benzoylacetone to give imino derivatives which, on dehydration, yield quinaldines (*5*); the latter are of interest in the photographic field. Also, when reacted with hydroxylamines and hydrazines, isoxazoles (*17*) and pyrazoles (*27*), respectively, are formed.

Dehydroacetic Acid

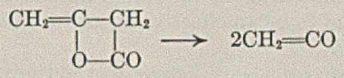
As has been pointed out, one of the characteristic properties of diketene is its tendency to polymerize to higher ketene polymers. Slow polymerization or polymerization induced by a catalyst and then allowed to proceed uncontrolled, results in the formation of dark-colored, tarry products from which only a small amount of dehydroacetic acid can be isolated with difficulty. In order to obtain dehydroacetic acid economically from diketene, it is essential to carry out the polymerization under controlled conditions which will minimize the formation of higher polymers. This treatment is best accomplished by adding diketene slowly to an inert solvent at 70–120° C., containing a small amount of catalyst. As catalysts, tertiary amines, such as pyridine, triethylamine, and methylmorpholine, and alkali metal salts of hydroxyl compounds, such as sodium ethylate and sodium butylate, have been found most efficient; aromatic hydrocarbons, such as benzene and toluene, are most suitable as solvents. When polymerized under these conditions, diketene, yields from 60 to 80 per cent of dehydroacetic acid:



Dehydroacetic acid is a colorless, crystalline compound melting at 109° and boiling at 274° C.; from a chemical standpoint it is noteworthy for the large number of derivatives into which it may be transformed by the action of acids and alkalies under varying conditions. Among them might be mentioned the formation of triacetic lactone (*22*), acetylacetone (*22*), and isodehydroacetic acid (*24*) by the action of strong sulfuric acid, and of diacetylacetone (*25*) and dimethylpyrone (*3*) which result from the hydrolysis of dehydroacetic acid with concentrated hydrochloric acid. Diacetylacetone and dimethylpyrone, in turn, react with ammonia and primary amines to yield a series of lutidone derivatives which deserve investigation in the pharmaceutical and dyestuffs fields. Orcinol, a dihydric phenol which has interesting possibilities as a photographic developer and antioxidant, and malonic acid are reported as products resulting from the action of concentrated alkali on dehydroacetic acid (*23*, *45*).

Ketene

Just as diketene may be converted largely to its dimer, dehydroacetic acid, by polymerization under the proper conditions, conversely it may be depolymerized quantitatively to its monomer ketene by pyrolysis; thus for the first time a convenient and simple process for rapidly producing pure ketene uncontaminated by methane and other hydrocarbons and oxides of carbon is available:



The pyrolysis may be carried out efficiently either by refluxing diketene over metal filaments, such as platinum or other resistant metal, heated to a dull redness, or by passing the vapor through a tube heated to 550–600° C. For the laboratory preparation of ketene, a modification of the Ott ketene lamp (*42*) was found most satisfactory. This device consists of a 200-cc. flask surmounted by a pyrolysis chamber of glass, 18 cm. long and 5 cm. in diameter, in which is suspended a filament of 70 cm. of No. 30 B. and S. gage platinum wire; the glass frame on which the wire is mounted is sealed to a ground-glass stopper so that the filament can be removed easily. The pyrolysis chamber is fitted at the top with a reflux condenser leading to a flask immersed in an ice bath to collect unchanged diketene entrained by the ketene vapors. From this flask the ketene is led into and condensed in a cold trap cooled by a solid carbon dioxide–acetone bath. The data from a typical run, where 100 grams of diketene were refluxed for 25 minutes over platinum filament heated to a dull redness by a current of 5 amperes, are as follows:

Residue, grams	5.6
Unchanged diketene condensed in first ice-cooled trap, grams	38.5
Ketene condensed, grams	55.5
Material accounted for, grams	99.6
Ketene from pyrolyzed diketene, %	99.1
Rate of ketene production:	
Grams per minute	2.2
Moles per hour	3.17

On a larger scale ketene is produced with equal efficiency by passing the vapors of diketene through a tube heated to 550–600° C., liquid diketene being first vaporized by flash evaporation or other convenient means.

Ketene is a colorless, highly toxic gas boiling at −56° and melting at −134.6° C. (*44*). When inhaled in low concentration, it leaves a peculiarly disagreeable taste in the mouth and slight irritation in the lungs and nasal passages which persists for several hours or longer after exposure. Curiously this effect is greatly heightened by smoking or by the mere presence of tobacco smoke in the atmosphere. The tendency of ketene to polymerize is even more marked than that of diketene; hence it cannot be stored or shipped in the gaseous state or in solution but must be reacted immediately after preparation.

Ketene, which is the internal anhydride of acetic acid, is a powerful acetylating agent; it reacts, in general, with compounds having an active hydrogen atom to give an acetyl derivative:

$$CH_2{=}C{=}O + HA \longrightarrow CH_3COA$$

Aliphatic alcohols from primary to tertiary react with ketene to give the corresponding acetic acid esters. Ketene has also been used as an acetylating agent for polyhydroxy compounds, such as glycols and glycerols (*29*), vegetable oils (*28*), resins of the glyptal type (*13*), and cellulosic materials (*41*). Phenyl acetate (*47*) and acetylsalicylic acid (aspirin) (*1*) have been prepared in almost quantitative yields by reacting ketene with phenol and salicylic acid, respectively. Thioacetates are obtained from ketene and thioalcohols (*32*).

Ketene reacts with gaseous or aqueous ammonia to give acetamide and with primary and secondary aliphatic amines to yield nitrogen-substituted acetamides. For example, from monoethanolamine and aniline, respectively, *N*-hydroxyethylacetamide and acetanilide are formed. *N*-chloroacetamide, $CH_3CONClH$, results from the addition of chloramine, NH_2Cl, to ketene (*21*).

Ketene reacts preferentially with amino groups in the presence of water and has been reported as a valuable means for acetylating amino acids in aqueous solution (*4*). Ketene has also been found to be an effective agent for the detoxification of vaccines (*49*).

Organic acids react with ketene to yield mixed anhydrides which, on distillation, break down to acetic anhydride and the anhydride of the acid (*46*). Chloroacetyl chloride is easily prepared by the addition of chlorine to ketene, either in the vapor phase or in solution:

$$CH_2{=}C{=}O + Cl_2 \longrightarrow ClCH_2COCl$$

Chloroacetyl chloride is a useful intermediate for the preparation of a number of commercially important products, such as chloroacetic acid, the hydrolysis product of chloroacetyl chloride, chloroacetamide, prepared by reacting chloroacetyl chloride with ammonia, and chloroacetophenone, the important vesicant which is obtained by reacting chloroacetyl chloride with benzene in the presence of aluminum chloride. Anhydrous hydrogen chloride adds to ketene to produce acetyl chloride (*26*). Liquid hydrogen sulfide and ketene form thioacetic anhydride, $(CH_3CO)_2S$ (*16*); malonyl chloride, $CH_2(COCl)_2$, which can be hydrolyzed to malonic acid, may be obtained from ketene and phosgene.

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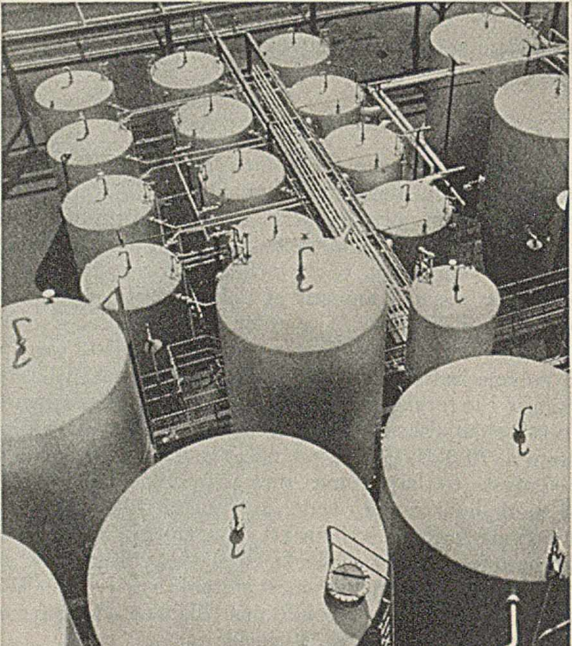
PRESENTED before the Division of Industrial and Engineering Chemistry at the 98th Meeting of the American Chemical Society, Boston, Mass.



STORAGE TANK AREA OF CARBIDE AND CARBON CHEMICALS CORPORATION

THE CHANDLER LECTURE

Thomas H. Chilton

THE Charles Frederick Chandler Medal for 1939 was presented to Thomas H. Chilton, director of the Technical Division of the Engineering Department of E. I. du Pont de Nemours & Company, Inc., at Columbia University, New York, on November 16, 1939. The honor was bestowed upon Mr. Chilton "for his outstanding achievements in the discovery and formulation of principles underlying the unit operations of chemical engineering, and in the application of these principles to process development, to equipment design, and to chemical plant construction and operation".

After Mr. Chilton finished his lecture, Dean Barker of the School of Engineering presented the medal with the following remarks:

> It is indeed appropriate on this seventy-fifth anniversary of the School of Engineering which Professor Chandler helped to found in 1864 as the School of Mines and of which he was the distinguished first dean, that the recipient of the medal is an alumnus of Columbia, having won the degree of chemical engineer in 1922.
>
> The President of the university has delegated to me the great privilege of acting in his behalf on this occasion of our seventy-fifth anniversary. Therefore by authority of the President of this university and in the name of the Trustees, I present the 1939 Charles Frederick Chandler Medal to Thomas Hamilton Chilton, chemical engineer, Columbia, 1922.
>
> Tom, it is with great pleasure and deep satisfaction that I convey the Chandler Medal to you and it is with sincere delight that I ask Mrs. Chandler to hand you this Medal.

The Charles Frederick Chandler Foundation was established in 1910 when friends of Professor Chandler presented to the trustees of Columbia University a sum of money, and stipulated that the income was to be used to provide a lecture by an eminent chemist and also a medal to be presented to this lecturer in further recognition of his achievements in the chemical field.

The previous lecturers and the titles of their lectures are as follows:

1914	L. H. Baekeland	Some Aspects of Industrial Chemistry
1916	W. F. Hillebrand	Our Analytical Chemistry and Its Future
1920	W. R. Whitney	The Littlest Things in Chemistry
1921	F. G. Hopkins	Newer Aspects of the Nutrition Problem
1922	E. F. Smith	Samuel Latham Mitchill—A Father in American Chemistry
1923	R. E. Swain	Atmospheric Pollution by Industrial Wastes
1925	E. C. Kendall	Influence of the Thyroid Gland on Oxidation in Animal Organism
1926	S. W. Parr	The Constitution of Coal—Having Special Reference to the Problems of Carbonization
1927	Moses Gomberg	Radicals in Chemistry, Past and Present
1928	J. A. Wilson	Chemistry and Leather
1929	Irving Langmuir	Electrochemical Interactions of Tungsten, Thorium, Caesium, and Oxygen
1931	James B. Conant	Equilibria and Rates of Some Organic Reactions
1932	George O. Curme, Jr.	Synthetic Organic Chemistry in Industry
1934	Jacob G. Lipman	The Stuff of Life
1936	William F. Giauque	Temperatures below 1° Absolute
1937	John H. Northrup	Chemical Nature and Mode of Formation of Pepsin, Trypsin, and Bacteriophage

Engineering in the Service of Chemistry

THOMAS H. CHILTON

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

THE triumphs of chemistry, to the man in the street, appear like miracles. And little wonder chemistry is so regarded! Synthetic ammonia and nitrates now supply every nation with the essential ingredient of explosives and with means to maintain a sufficiency of nitrogen for agriculture. Synthetic organic chemicals, based on coal, air, water, petroleum, and a few minerals such as limestone and salt, have themselves or through their derived products revolutionized industries and have become established as an industry in their own right. Consider, for instance, derivatives only of methane and ethane as examples of products now available from synthetic processes. From methane are derived (though not commonly thus produced) methanol, formaldehyde, formic acid, liquid and solid carbon dioxide; methylamine, urea, formamide, and hydrocyanic acid; methyl chloride, methylene chloride, chloroform, carbon tetrachloride; dichlorodifluoromethane. Of ethane derivatives we may mention ethanol, acetaldehyde, acetic acid, ethylene glycol; ethanolamine, ethylene diamine; ethylene dichloride, trichloroethylene, tetrachloroethylene (perchloroethylene); dichlorotetrafluoroethane.

The commercial production of these synthetic materials, from which the public benefits, is not miraculous but is the result of painstaking application of sound engineering, as well as of brilliant chemical research. These triumphs are no more miraculous, and no less so, than the George Washington Bridge, the Holland Tunnel, and the Empire State Building; the Zephyr trains, the *Queen Mary*, and the *Atlantic Clipper;*

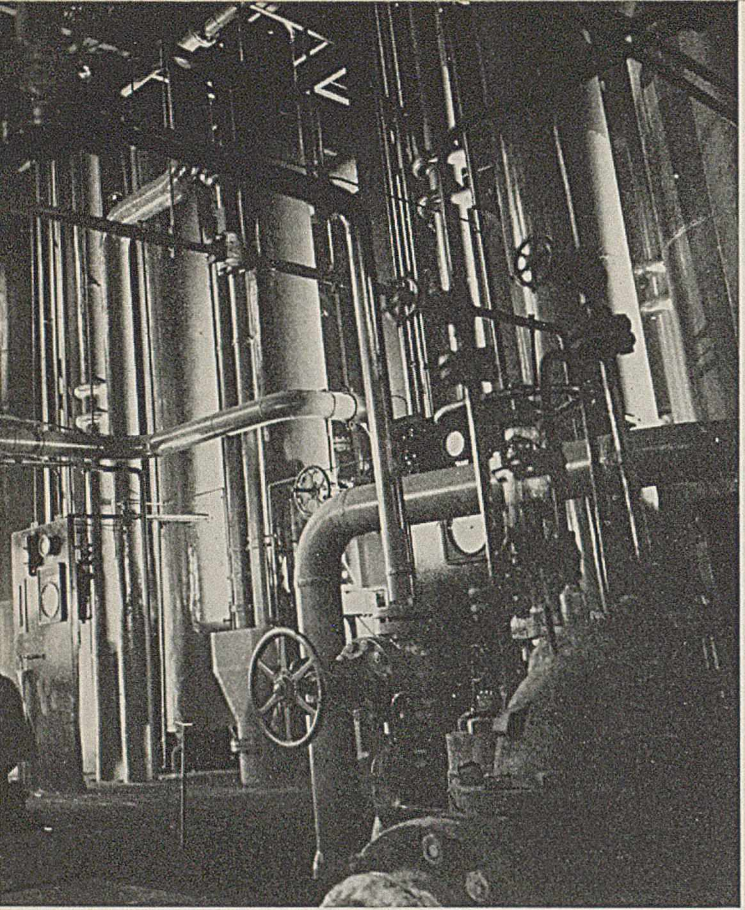


Figure 1. Equipment for Contact Conversion of Carbon Monoxide in Water Gas

or the Hell Gate power station, the New York telephone exchange, and Station WJZ. Although the work of the engineer is more apparent in some of these than in others, they are all the result of engineering effort. The work of the civil engineer may thus be prominent, and his place, developed over a long period of years, is readily acknowledged. The mechanical engineer emerged after the invention of the steam engine and the consequent transition from home industries to the factory system a hundred years ago. The metallurgical engineer found his calling when the blast furnace and steel mill supplanted the iron puddler and the smith. The electrical engineer filled the need resulting from the discoveries of Faraday, Henry, and Edison. Likewise researches in theoretical and organic chemistry, each paving the way for others, have demanded for their adaptation to practical use what we now call the "chemical engineer".

An accelerating pace of research and development has brought the chemical engineer to his present place in industry. It is not necessary to revert to the time when the Columbia School of Mines was founded, 75 years ago, when petroleum had just been discovered, before coal tar dyes had been made, and before electrical machinery had been invented. Contrast the chemical operations carried on today, and especially the scale of operations, with those even of 1910 (when this medal was first presented to Chandler) or those of 1914 (when Baekeland gave the first Chandler Lecture). High-pressure synthesis was then unknown, at least in the United States. Organic processes were relatively few and simple. Inorganic operations were then carried out on a scale of roughly one fifth to one tenth of the production now expected from each manufacturing unit.

Chemical engineering plays its principal part in the translation of a chemical process from the laboratory to the industrial scale. Sometimes, indeed, engineering is called for even before the laboratory research can be completed. Fritz Haber's work on the equilibrium of the ammonia synthesis at high pressures, demonstrating the application of LeChatelier's principle, could not have been completed without engineering assistance, and it was the brilliant engineer, Carl Bosch, who subsequently carried the process through to a successful conclusion. Georges Claude, who extended Haber's work to still higher pressures, was also a versatile engineer.

Nitric Acid from Ammonia

One example of this function of the chemical engineer can be cited here (*22*). In the development of a process for the production of nitric acid from ammonia, the ground work was laid in 1839 by the researches of Kuhlmann (*12*) on the catalytic oxidation of ammonia to nitric oxide on the platinum gauze catalyst,

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad (1)$$

by researches of Bodenstein (*2*) and Briner (*3*) on equilibrium and rate of reaction between nitric oxide and oxygen,

$$2NO + O_2 = 2NO_2 \qquad (2)$$

and by the researches of Burdick (*4*, *5*) on the equilibrium between oxides of nitrogen and solutions of nitric acid,

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (3)$$

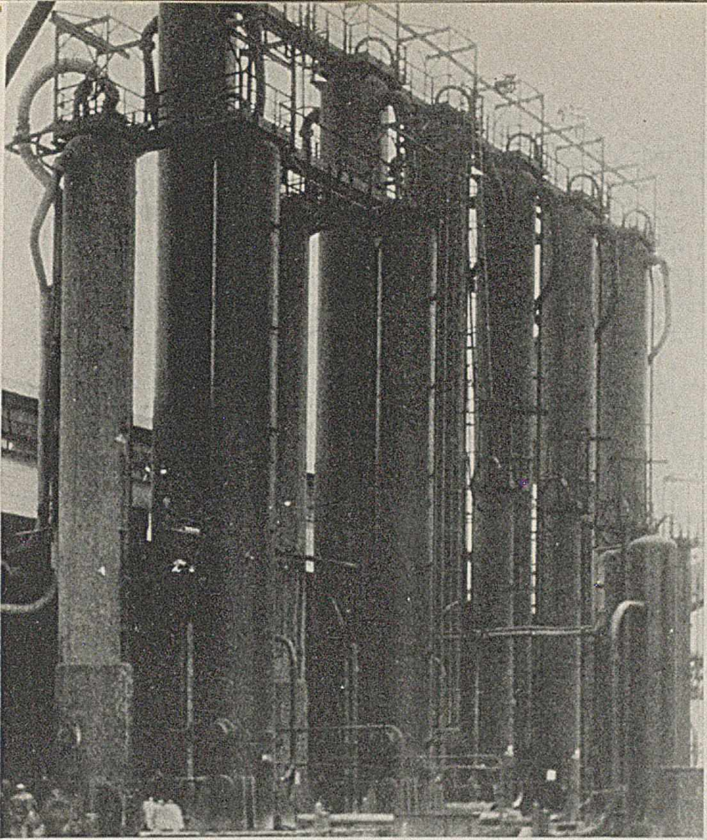
The latter pointed to a highly favorable influence of increased pressure, not so much from LeChatelier's principle as applied to Equation 3, as from the increase in reaction rate of the slow trimolecular reaction (Equation 2) owing to increase in concentration of the reactants. One phase of the development therefore centered around the application of pressure; and converters and absorption systems were successively designed for ammonia consumptions of about 1, 10, and 100 pounds per hour. Preliminary tests on the smallest scale, using absorption equipment made from $^3/_8$- and 3-inch stainless steel tubing, demonstrated the general correctness of these conclusions. Engineering and performance data obtained on a scale of 10 pounds per hour, proving 100 pounds per square inch to be an advantageous pressure, were used in the design of a pilot-plant unit rated at 100 pounds per hour of ammonia. Units only double this size appeared to be the largest then justified, and the full-scale plant was built employing such units. Further improvements in the design of the converter and in provision of cooling surfaces at critical points in the absorption system have raised the capacity of each unit to about 1000 pounds per hour.

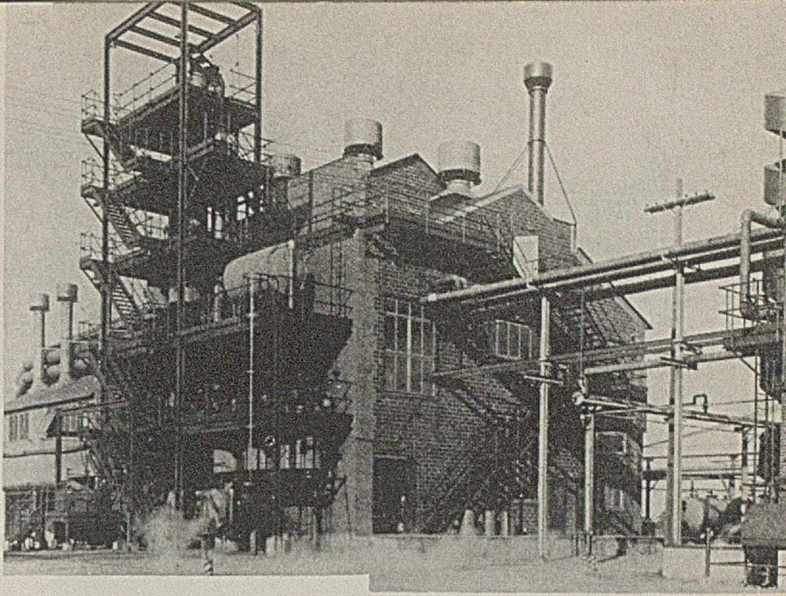
This was a straightforward application of engineering principles, building upon a basis of thorough chemical research, and proceeding in constant collaboration with metallurgists in the specification and fabrication of materials.

With this as an example, the imagination will perhaps supply an idea of the engineering development work behind such plants as that for synthetic ammonia production, comprising units for contact conversion of water gas (Figure 1), absorption of the carbon dioxide (Figure 2), and the synthesis units and their accessories (Figure 6). The same quality of engineering design was required in all other successful new ventures: viscose rayon (Figure 7 shows cellulose xanthate dissolvers), synthetic camphor which is made in the autoclaves of Figure 3, neoprene (Figure 5), titanium dioxide pigments calcined in the kilns of Figure 8, and vinyl resins such as "Butacite" (Figure 4).

Principles of Chemical Engineering

We may now ask, are there engineering principles which provide a foundation for chemical engineering practice?





Left, from top to bottom

Figure 2. Scrubbers for Removal of Carbon Dioxide in Water Gas

Figure 3. Camphor Process Autoclaves

Figure 4. Precipitators Used in "Butacite" Production

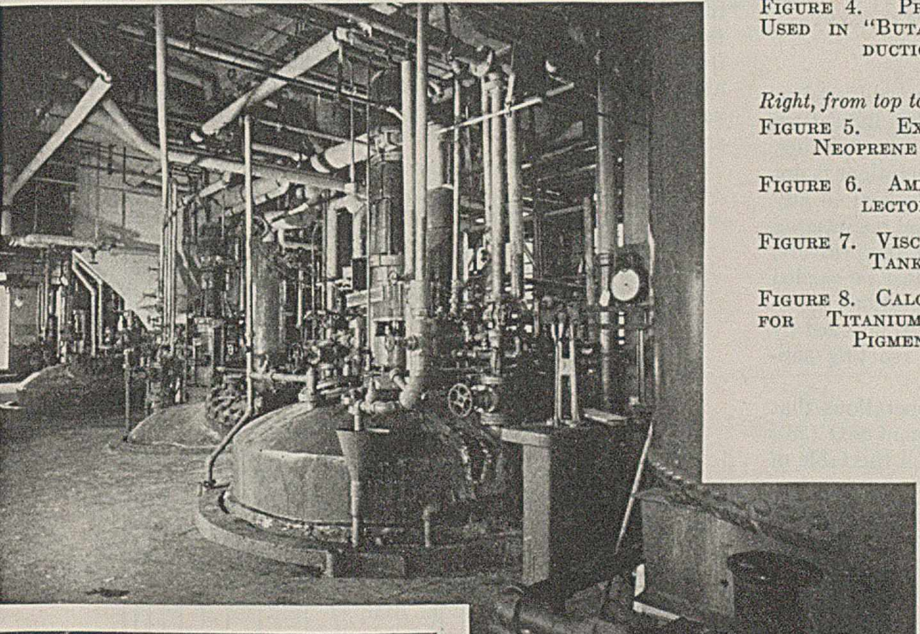
Right, from top to bottom

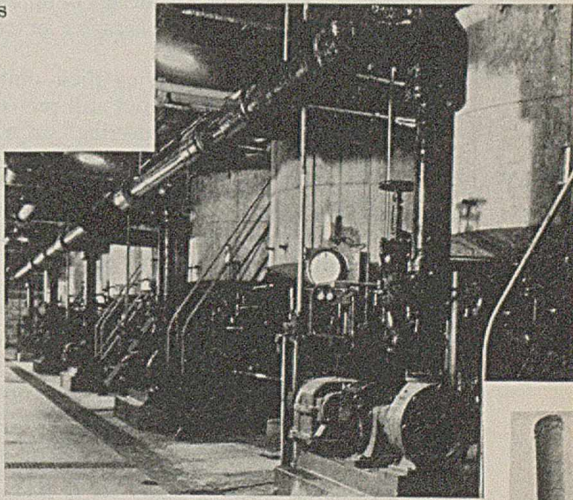
Figure 5. Exterior of Neoprene Plant

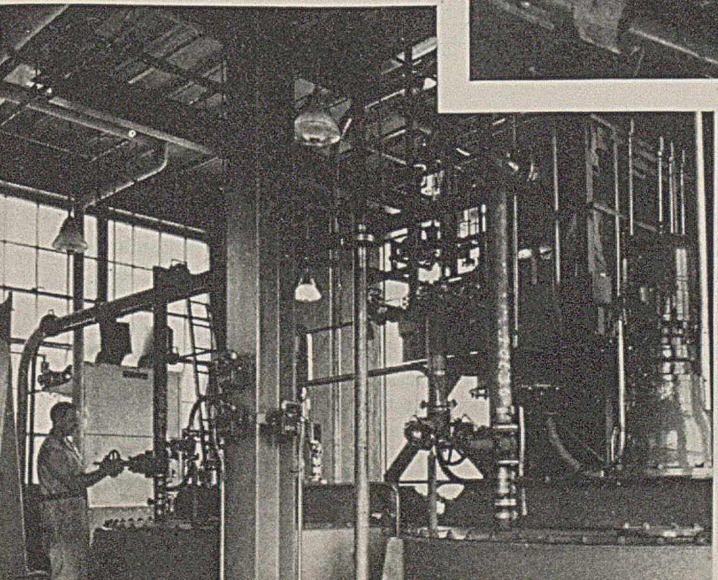
Figure 6. Ammonia Collectors

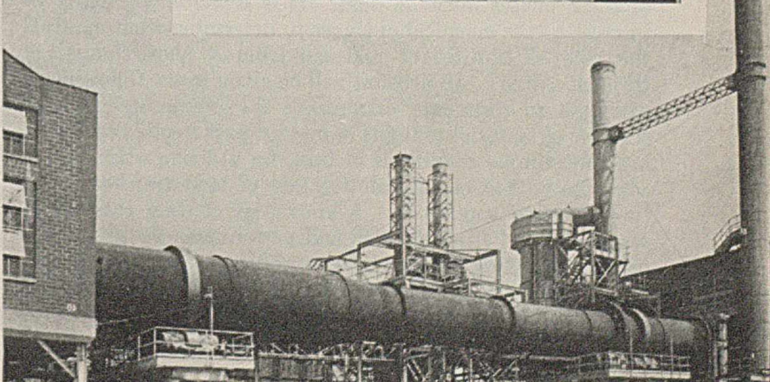
Figure 7. Viscose Mixing Tanks

Figure 8. Calcining Kiln for Titanium Dioxide Pigments









There are, and progress in chemical engineering has been more rapid since it has been recognized that this is the case.

Chemical engineering has as its basis "those unit operations which in their proper sequence and coordination constitute a chemical process as conducted on the industrial scale" (*26*). To quote again: "Any chemical process, on whatever scale conducted, may be resolved into a coordinated series of what may be termed 'unit actions', as pulverizing, mixing, heating, roasting, absorbing, condensing, lixiviating, precipitating, crystallizing, filtering, dissolving, electrolyzing, and so on. The number of these basic unit operations is not very large and relatively few of them are involved in any particular process. The complexity of chemical engineering results from the variety of conditions as to temperature, pressure, etc., under which the unit actions must be carried out in different processes and from the limitations as to materials of construction and design of apparatus imposed by the physical and chemical character of the reacting substances" (*13*).

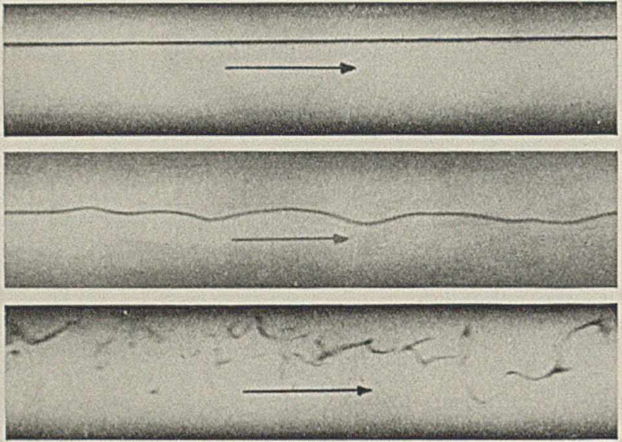


FIGURE 9. TRANSITION FROM LAMINAR TO TURBULENT FLOW (*1*)

It is the principles underlying these unit operations that are meant in the pioneering and still pre-eminent text (*25*), "Principles of Chemical Engineering", of which the table of contents includes flow of fluids, flow of heat, combustion, crushing and grinding, mechanical separation, filtration, evaporation, absorption and extraction, distillation, and drying. Certain of these operations are the same as those employed in processes not strictly considered chemical. The problems of fluid motion are of interest in hydraulics and aerodynamics. Problems of heat transfer occur in power generation and refrigeration. The handling and treatment of solids have been the concern of the metallurgist.

The distinctly chemical engineering operations may be taken as those involving contact between separate phases and the transfer of material from one to the other. Since diffusion in the solid state is too slow to be of much consequence, one of these phases must be fluid. It is therefore primarily of interest to the chemical engineer to determine what controls the rate of transfer of material from a phase boundary through a fluid. An account will be given in the following of attempts to formulate expressions for predicting rates of transfer of material to fluids in motion past a solid boundary, for some simple conditions of flow, by utilizing what knowledge can be had of fluid motion and of heat transfer under the same flow conditions. A knowledge of these rates is essential in predicting the size and performance of equipment used for effecting changes in composition—partial condensation, absorption, distillation, extraction, and humidification.

Fluid Flow Problems

If fluids always followed the laws of viscous motion, the problems of the chemical engineer would be simpler, or so it seems, since they would be susceptible to mathematical solution—fluid flow problems on the basis of viscosity, heat flow problems on the basis of thermal conductivity and the flow pattern determined by the laws of viscous motion, and mass transfer problems on the basis of molecular diffusivity. Formulations for these cases are available, though the mathematics is not always simple. But industrial problems would be made more difficult if viscous motion always prevailed, since heat conduction and molecular diffusion are slow processes compared to transport of heat or material by the mixing or convection that is characteristic of turbulent motion.

Fortunately from this standpoint, turbulent flow is often unavoidable on account of the inherent instability of the fluid motion at high velocities. By means of a thread of colored fluid introduced into the center of a stream flowing in a glass tube, Figure 9 shows the effect of increasing the velocity (*1*). The criterion which has been found to control the transition from the smooth streamline flow to the irregular turbulent flow is called the "Reynolds number" since it was proposed by him. This criterion expresses the ratio of the values representing the inertial characteristics of the motion (or terms in the equation of motion), $V^2\rho/D$, to those representing the viscous characteristics, $V\mu/D^2$, or upon cancellation, $DV\rho/\mu$ (*20*). For flow in straight pipes, the transition from streamline to turbulent motion occurs at a Reynolds number of about 2300. (This criterion is dimensionless, and values do not depend upon the units chosen, provided they are self-consistent.)

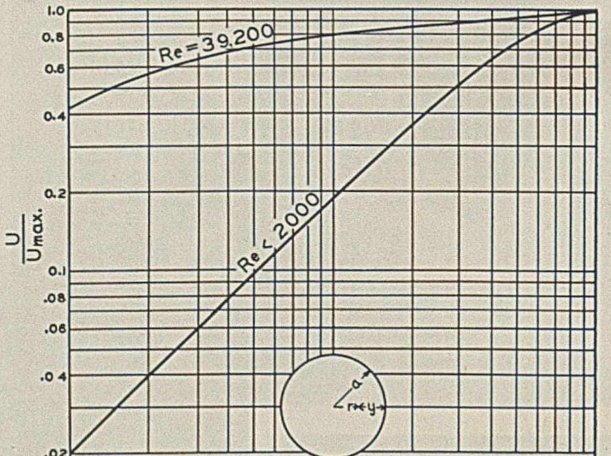
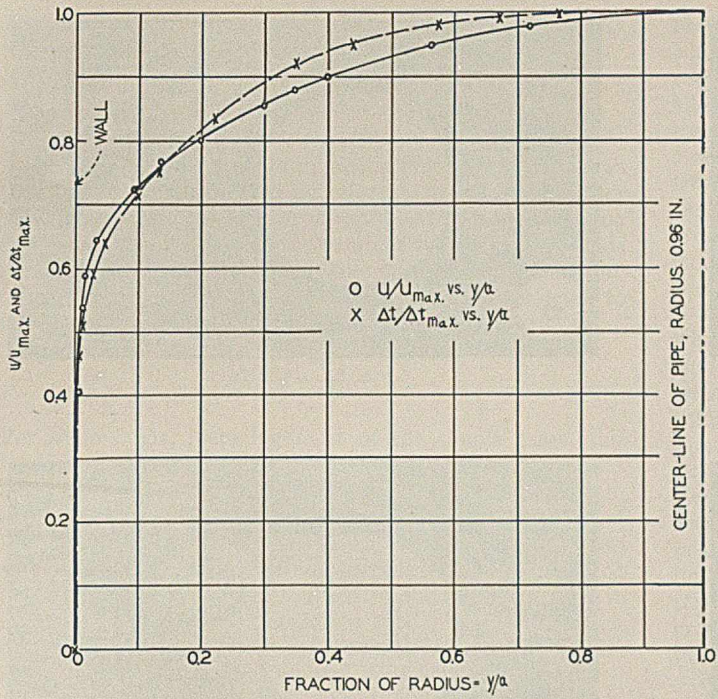


FIGURE 10. VELOCITY DISTRIBUTION IN CIRCULAR TUBES

The process of convective mixing is evidently absent at low velocities (small Reynolds numbers) and predominant at higher values. The velocity distribution under the former condition is found to be parabolic, as it ought to be; in turbulent flow the velocity is much more nearly uniform throughout the cross section, and produces a high shear at the walls and greatly increased friction. Figure 10 shows that in viscous motion the velocity at the edge of an annulus comprising 2 per cent of the cross section (0.01 of the radius from the wall) is close to 2 per cent of the centerline velocity (*17*); at a Reynolds number of about 40,000, it is over 40 per cent.



Courtesy, W. H. McAdams

FIGURE 11. EXPLORATION OF VELOCITY AND TEMPERATURE OF AIR FLOWING INSIDE A VERTICAL PIPE (*17*)

Turbulent Flow

If we now focus our attention on the phenomena of turbulent flow, where the velocity is so nearly uniform and the pressure loss is nearly proportional to the square of the average velocity, we may begin to consider by what mechanism momentum is lost, by what analogous mechanisms heat may be supplied to or withdrawn from the fluid, and later how its composition may be altered. This last was stated to be the problem of primary interest in chemical engineering.

A simplified analogy which leads to the desired useful relationships upon suitable modification was stated (*19*) by Reynolds in 1874: "The ratio of the momentum lost by skin friction between two sections a differential distance apart to the total momentum of the fluid will be the same as the ratio of the heat supplied by the surface to that which would have been supplied if the whole of the fluid had been carried up to the surface."

Expressed in symbols, the momentum of the fluid flowing (per unit time) in a circular tube is

$$\rho\, V \cdot \frac{\pi}{4} D^2\, V$$

and the momentum lost by friction is

$$(P_1 - P_2) \frac{\pi}{4} D^2$$

so that the first ratio becomes

$$(P_1 - P_2)/\rho\, V^2$$

The heat required to bring all the fluid to the temperature of the surface would be

$$C\, \rho\, V \frac{\pi}{4} D^2\, \Delta t_m$$

and the heat actually supplied is

$$C\, \rho\, V \frac{\pi}{4} D^2 (t_1 - t_2)$$

so that the second ratio is

$$(t_1 - t_2)\ /\ \Delta t_m$$

Reynolds' analogy states simply

$$\frac{(t_1 - t_2)}{\Delta t_m} = \frac{(P_1 - P_2)}{\rho\, V^2} \tag{4}$$

The momentum ratio is related to the pipe diameter and fluid properties by the friction factor, which is established as a function of the Reynolds number:

$$\frac{(P_1 - P_2)}{\rho\, V^2} \cdot \frac{D}{4L} = \frac{1}{2} f = \phi \left(\frac{D\, V\, \rho}{\mu} \right) \tag{5}$$

An expression, useful in design, for the rate at which heat is transferred from the surface to the fluid per unit time per unit area per unit difference in temperature, designated by h, may be defined by means of the following equation:

$$h\, \pi\, D\, L\, \Delta t_m = C\, V\, \rho \frac{\pi}{4}\, D^2 (t_1 - t_2) \tag{6}$$

Collecting terms to obtain the temperature ratio used above,

$$\frac{(t_1 - t_2)}{\Delta t_m} \cdot \frac{D}{4L} = \frac{h}{C\, V\, \rho} \tag{7}$$

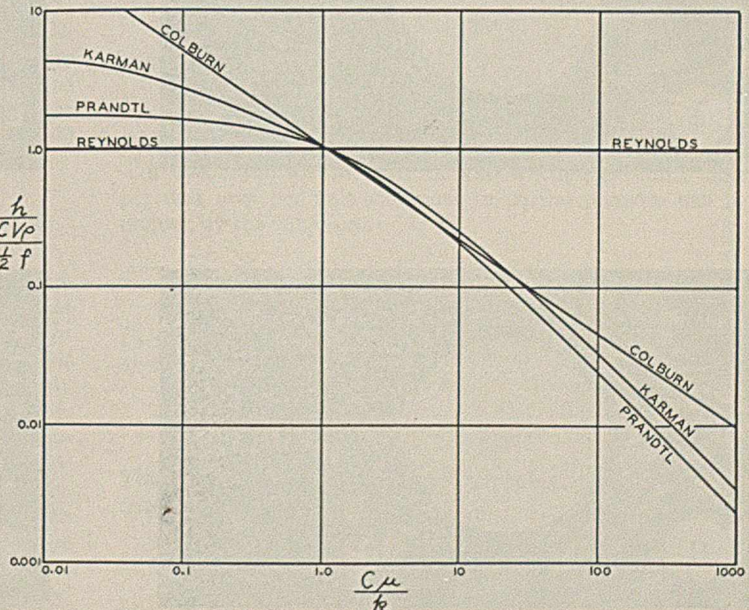
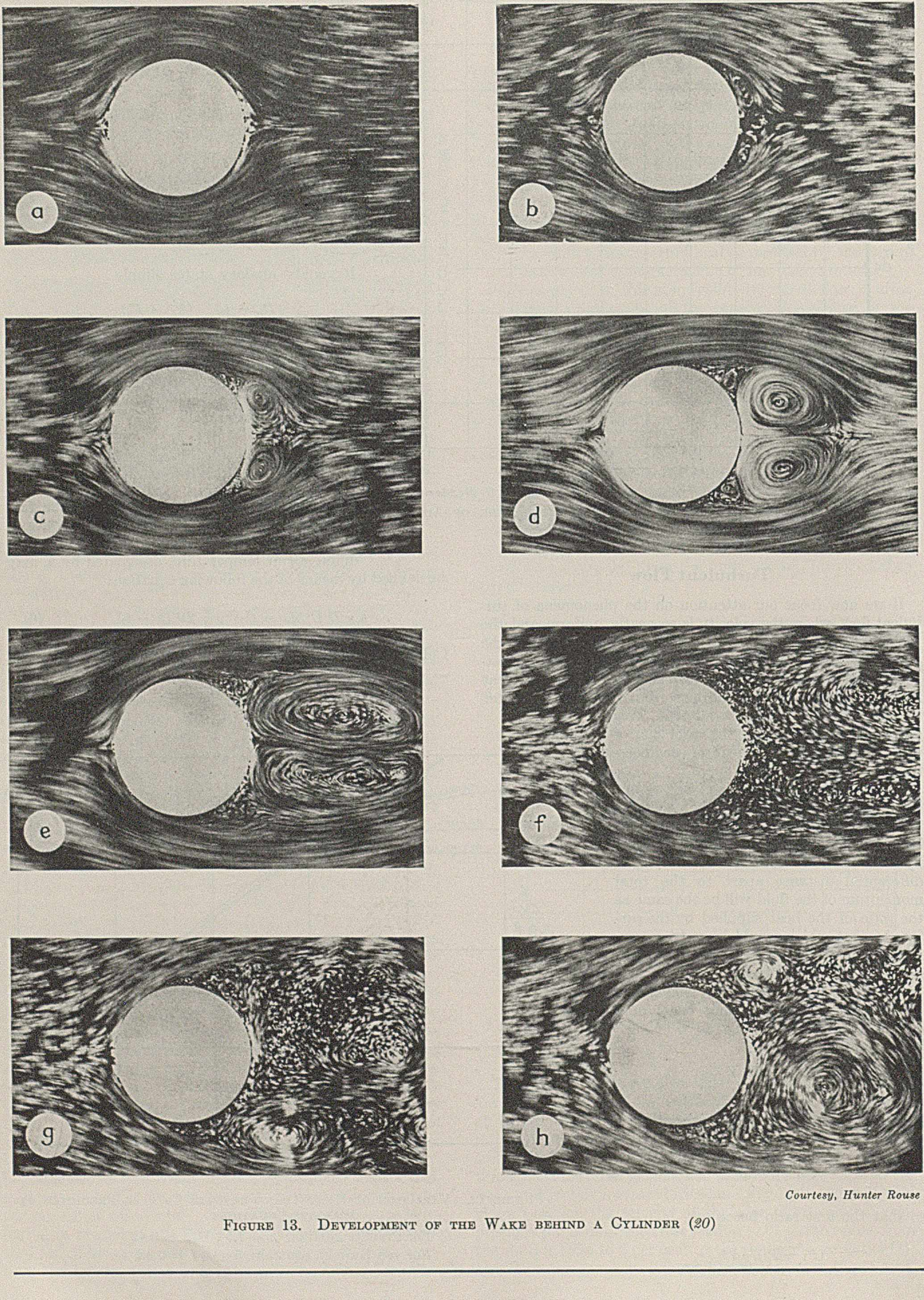


FIGURE 12. VARIATION OF HEAT TRANSFER WITH $C\mu/k$ AS PREDICTED BY VARIOUS EQUATIONS

For Prandtl equation, $r = 7.5\sqrt{{}^1/_2 f} = 0.42$
For von Karman equation, $5\sqrt{{}^1/_2 f} = 0.28$



Courtesy, Hunter Rouse

FIGURE 13. DEVELOPMENT OF THE WAKE BEHIND A CYLINDER (*20*)

If we make use of Equation 5, it is apparent that we may then extend Reynolds' analogy by writing

$$\frac{h}{C\,V\,\rho} = \frac{1}{2}f = \phi\left(\frac{D\,V\,\rho}{\mu}\right) \tag{8}$$

Problems of heat transfer involving fluids flowing through tubes could then be solved by reference to a friction factor plot, such as is given in textbooks (*25*), by the use of Equation 8 if Reynolds' analogy were found to be valid. Reynolds recognized that it would be valid only if the momentum diffusivity (or kinematic viscosity, $\nu = \mu/\rho$), were equal to the thermal diffusivity, $\alpha = k/C\rho$—that is, if

$$\frac{(\mu/\rho)}{(k/C\rho)} = \frac{C\mu}{k} = 1$$

For some fluids, including most of the simple gases, this relationship is nearly fulfilled. Figure 11 shows explorations of the velocity and temperature distributions for air flowing in a heated pipe (*17*). For other fluids, for which values of $(C\mu/k)$ are much higher than unity, such a correspondence would not be expected. In the turbulent "core" something like this could be natural but not in the "film" of fluid in streamline motion adjacent to the wall. The problem has been attacked theoretically by Prandtl (*18*) and by Taylor (*23*); the resulting expression is:

$$\frac{(h/C\,V\,\rho)}{\left(\frac{1}{2}f\right)} = \frac{1}{1 - 7.5\sqrt{\frac{1}{2}f}\left(\frac{C\mu}{k} - 1\right)} \tag{9}$$

More recently von Karman (*11*) submitted a solution in the form:

$$\frac{(h/C\ V\ \rho)}{\left(\frac{1}{2}f\right)} = \frac{1}{1 + 5\sqrt{\frac{1}{2}}\ \left\{\left(\frac{C\mu}{k} - 1\right) + \ln\left[1 + \frac{5}{6}\left(\frac{C\mu}{k} - 1\right)\right]\right\}}$$

These both propose a relation between $(h/C\ V\ \rho)$ and $(^1/_2\ f)$ in terms of functions of $(C\mu/k)$ relating to the velocity distribution in the turbulent core, laminar zone, and buffer layer. A simpler expression, based on empirical correlations but seen from Figure 12 to be a good approximation for these theoretical equations over the range from, say, 0.75 to 100 for values of $(C\mu/k)$, was proposed by Colburn (*8*):

$$j = \left(\frac{h}{C\,V\,\rho}\right)\left(\frac{C\,\mu}{k}\right)^{2/3} = \frac{1}{2}f \tag{10}$$

A test of this expression for predicting heat transfer coefficients for turbulent flow in tubes is given by Nusselt's data for heating air and carbon dioxide (*8, 16*) and by data of later investigators on heating water (*8*). For more viscous fluids few data have been obtained in the turbulent region. Clearly no analogy between friction and heat transfer factors is expected for viscous flow in tubes. These cases are susceptible to mathematical solution. That for friction leads to Poiseuille's equation involving only the linear velocity, viscosity, and tube dimension; and that for heat transfer leads to an equation attributed to Graetz (*10*), involving neither the viscosity of the fluid nor the diameter of the tube but the heat capacity of the fluid flowing, the thermal conductivity, and the heated length. Heat transfer factors are, however, subject to complications at these low velocities due to natural thermal convection effects, and the theoretical equations do not take account of changes in viscosity and velocity distribution as the fluid is heated or cooled. When plotted on the coordinates chosen for turbulent flow, the theoretical equations for viscous flow conditions (assuming a constant surface temperature), modified by empirical functions to allow for the considerations just mentioned, take on the form shown at the left in Colburn's résumé chart (*6, 8*); this is in striking contrast with the agreement postulated between heat transfer and friction factors for turbulent flow conditions at the right of the figure. The intermediate transition region is discussed fully by Colburn (*6, 21*); it is naturally dependent on many more variables than the transition for isothermal friction.

For flow across tubes, an equally important case industrially in the design of heat exchangers and condensers, no analogy would be expected between heat transfer and friction factors. For as Figure 13 (*20*) shows, turbulence developed behind the cylinder evidently accounts for much of the pressure drop; and momentum transfer due to skin friction, which would parallel heat transfer, accounts for relatively little. Heat transfer data on flow across banks of tubes support the correlation proposed by Colburn (*8*) which implies that no relation exists between friction and heat transfer factors for this case. The use of the same empirical function of $(C\mu/k)$ as for flow inside tubes does not rest on theoretical grounds or on many data for banks of tubes, but does satisfactorily represent data on flow past single cylinders (*15*).

For flow relative to a plane surface of finite length, there is remarkable agreement between heat transfer and friction factors, not only in turbulent but also in viscous flow, as Colburn showed (*8*).

Mass Transfer

With this background of correlations of heat transfer, we are now ready to examine data on transfer of matter from a stationary boundary to a moving fluid, and to determine for what cases an analogy can be drawn between mass transfer and fluid friction. Extending in these terms the analogy attributed above to Reynolds, we note that the vapor required to bring up to saturation all the gas passing through a pipe wetted with a liquid is

$$\left(\frac{\rho\,V}{M}\right)\left(\frac{\pi}{4}\right)D^2\left(\frac{\Delta p_m}{P}\right)$$

and we write

$$\frac{(p_1 - p_2)}{\Delta p_m} = \frac{(P_1 - P_2)}{\rho\,V^2} \tag{11}$$

A coefficient for the rate of vaporization per unit time per unit area per unit difference in partial pressure can be defined by the equation:

$$K\pi\,D\,L\,\Delta p_m = \left(\frac{\rho\,V}{M}\right)\left(\frac{\pi}{4}\right)D^2\,\frac{(p_1 - p_2)}{P} \tag{12}$$

Collecting terms to obtain the partial pressure ratio used above,

$$\frac{(p_1 - p_2)}{\Delta p_m}\cdot\frac{D}{4L} = \frac{K\,P}{(\rho\,V/M)} \tag{13}$$

The corresponding extension of Reynolds' analogy to mass transfer would then read

$$\frac{K\,P}{(\rho\,V/M)} = \frac{1}{2}f = \phi\left(\frac{D\,V\,\rho}{\mu}\right) \tag{14}$$

The corresponding modifying factor, involving the molecular diffusivity, k_D, in relation to the momentum diffusivity, $\nu = \mu/\rho$, is naturally $\mu/\rho\,k_D$. We may proceed to test whether data taken under these conditions support the same function of this ratio as was found to be valid for heat transfer—

namely, the modified analogy equation, for the same flow conditions:

$$j = \left(\frac{KP}{\rho V/M}\right)\left(\frac{\mu}{\rho k_D}\right)^{2/3} = \frac{1}{2}f \qquad (15)$$

These flow conditions are represented by a "falling film tower" or tube in which a liquid flows downward along the wall while a gas passes through the center. Data on the vaporization of water into a current of warm air taken in the author's laboratory yield both heat transfer and mass transfer factors, which were shown (*6*) to agree reasonably well with the friction line. Data selected at random from a more extensive investigation (*9*) show equally good agreement and furnish support for the kind of function proposed for the modified analogy equation.

Not so many data are available under other flow conditions. For flow across a single cylinder, a set of experiments on the absorption of water by a stick of fused caustic (*6, 14*) agree within 25 per cent of the line representing heat transfer (j) factors from Colburn's correlation (*8*).

Data on evaporation from plane surfaces into an air stream (*6, 24*) likewise show good agreement.

The treatment of these mass transfer factors has been simplified in the present discussion; for a more rigorous treatment or detailed discussion of the various analogy equations, reference is made to the original sources. It is hoped that enough has been presented, however, to show the utility of methods for the prediction of coefficients for the rate of mass transfer under these more or less ideal flow conditions, and to suggest their application, with whatever modification may be found necessary, to such problems as those involving contact in packed towers (*7*), where the expression $(p_1 - p_2)/\Delta p_m$, representing the "number of transfer units", and the derived value, the "height of one transfer unit (H. T. U.)", are especially valuable.

Problems to Be Solved

The wrong impression would, however, be obtained if one concluded it was "as simple as that" in all problems of chemical engineering design. It may be that the success of these methods points the way to attacks still to be made on phenomena not so easily investigated—boiling, condensation, adsorption, drying (concerned as it is with diffusion within solids), if not to the problems of solid handling, size reduction, or separation. Yet with the experimental data accumulated or to be accumulated on these unit operations, the illustrations of actual equipment shown above should confirm that there will always be plenty of opportunity for the use of engineering skill and engineering judgment in the development of chemical processes, plenty of opportunity for engineering in the service of chemistry in its task of providing "better things for better living".

It is small wonder that, as chemistry appeals to those minded for research, chemical engineering appeals to those who desire to have a part in its application. The two dozen derivatives of the first two hydrocarbons mentioned early in this paper give only a hint of the developments being made or in store in organic chemistry, where the number of possible compounds reaches into astronomical figures in the higher members of the series. Nothing was said as to resins, fibers, colloids, or biochemical products; and no reference was made to inorganic developments, by no means yet exhausted. Likewise, although some of the advances in knowledge of chemical engineering principles have been stressed, there are unknowns to be encountered in every new undertaking. A handbook for chemical engineers has found wide acceptance, but chemical engineering is not a handbook science and is not likely to be for some time to come.

Doubtless it is the challenge thus presented as well as the opportunities in the rapidly growing chemical and allied industries that continue to attract an increasing number of men into chemical engineering. Unknown when the Columbia School of Mines was founded in 1864, it was almost nonexistent even in 1900, and by 1910 there were less than 1000 students in chemical engineering courses in the United States. In 1921 the number had grown to 7000, and in 1935 to over 10,000, representing one sixth of the total enrollment in all engineering courses. The latest figures show an enrollment of 12,500, so that chemical engineering, though only about half as old as the other branches of engineering—the American Institute of Chemical Engineers was founded in 1908—ranks with any of the others in numbers of students enrolled and graduating annually. The opportunities stand open wide for those who meet its challenge and prepare themselves for service to chemistry in its service to mankind.

Nomenclature

Any consistent set of units may be used. Pounds, feet, hours, and degrees centigrade have been chosen for convenience. For simplicity in setting up the equations, pressures have been converted to absolute units by including the conversion factor

$$g_c = \frac{\text{lb. (mass)} \times \text{hr.}^2}{\text{lb. (force)} \times \text{ft.}}$$

which in this system has the value 4.18×10^8.

C = specific heat (at constant pressure), P. c. u./(lb.) (° C.)
D = diameter, ft.
f = friction factor
j = heat transfer factor, mass transfer factor
k = thermal conductivity, P. c. u./(hr.) (sq. ft.) (° C./ft.)
K = mass transfer coefficient, lb. moles/(hr.) (sq. ft.) ($g_c \times$ lb./sq. ft.)
L = length, ft.
M = molecular weight
P = absolute pressure, $g_c \times$ lb./sq. ft.
p = partial pressure of diffusing vapor, $g_c \times$ lb./sq. ft.
Δp_m = mean partial pressure difference between vapor in gas and at saturation with surface, $g_c \times$ lb./sq. ft.
t = temperature, ° C.
Δt_m = mean temperature difference between fluid and surface, ° C.
V = velocity, ft./hr.
α = thermal diffusivity, sq. ft./hr.
ν = kinematic viscosity, sq. ft./hr.
μ = viscosity, lb./(hr.) (ft.)
ρ = density, lb./cu. ft.

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CASEIN PLASTICS

GEORGE H. BROTHER, U. S. Regional Soybean Industrial Products Laboratory, Urbana, Ill.[1]

FEW industries offer greater possibilities to the research chemist than the plastics industry. The polymerization and condensation reactions which form the plastic resins are not only complicated and little understood, but in many cases the starting materials are of unknown structure. Therefore, since so little is known about plastic materials, it is surprising how widely they have been successfully applied in spite of this handicap. With more fundamental knowledge of their structures and properties available, more intelligent applications would be possible in present fields and probably in fields not as yet considered.

This is especially true of casein plastics. Casein is a protein, a class of material that has baffled chemists since the time of Emil Fischer. However, there has been a change in the attitude of research chemists recently with the application of the x-ray, the infrared ray, the ultracentrifuge, the monomolecular film, etc., to the study of the structure of proteins. Preliminary results on the investigation of protein have already been obtained with these tools, which hold promise for the future of the whole class in general and for casein plastic material in particular.

Manufacture

Casein plastic is the result of a reaction between casein and formaldehyde. The commercial possibilities of the hornlike product of this reaction were first appreciated about 1897 by Adolf Spitteler (*21*, *25*), a German chemist. Through the early years of development considerable trouble was encountered chiefly because of the extremely clumsy process of production. This process consisted essentially of dispersing the casein in an aqueous solution of some alkali, coagulating the dispersion with an acid or an acid salt, pressing the wet curd into plates, and soaking these plates in formaldehyde solution until they harden. Throughout this period the industry was entirely controlled by the German-French firm, Internationale Galalith-Gesellschaft Hoff & Compagnie, located at Harburg, Germany, and the product was called "Galalith", meaning milkstone. This firm is still in business and is probably the largest casein plastics manufacturer in the world. Its product is so well known by the trade that Galalith has practically become a generic term applied to all casein plastic material.

During or shortly after the World War, it was found that rennet casein could be satisfactorily plasticized by heat and pressure if the total moisture content was about 40 per cent. The powdered casein used was dry, as far as appearance and methods of handling were concerned, and the process was consequently known as the dry process. The Erinoid Company of England (*1*, *10*), so named because of large Irish interests, after experimenting unsuccessfully with the wet process for a number of years finally succeeded with the dry process in making a product which is still the leading British casein plastic material today.

The first American casein plastic material was Aladdinite, followed by Karolith, Kyloid, Inda, and finally by American Erinoid. These were all satisfactory, as far as the products were concerned, but were not established on a profitable economic basis in this country. There are two principal reasons for this failure: (*a*) The climatic conditions in America are different from those in Europe, and as a result, casein plastic material must be restricted to buttons, buckles, and other small objects. (*b*) The process of manufacture is long and expensive, the material itself is not adapted to fabrication on automatic machines, and there is no profitable outlet for the large proportion of waste. Accordingly, Karolith, the Erinoid Company of America, and Pan-Plastics merged in 1931 to form the American Plastics Corporation. Their product, Ameroid, is the only casein plastic material of domestic origin available today.

The dry process for the manufacture of casein plastic material, as previously indicated, is based upon the plasticization of casein powder, containing about 40 per cent total moisture, by the simultaneous action of heat and pressure (*20*). These are usually applied in screw cylinder presses, such as are used in the rubber industry for the extrusion of rods. The soft plastic is extruded as rods or tubes, depending on the mandrel used. If sheets are required, the rods are flattened out in hydraulic presses to fill frames of the required size. Button blanks may be sliced from the rods or punched from the sheets. Dyestuff or fillers, as desired, are introduced with the water before plasticization. Mottled or streaked effects are produced by mixing small pieces or "buttons" of previously formed soft plastic (*16*) of the desired color into the powder before extrusion. The rods and sheets of soft plastic must be hardened by immersion in a bath of aqueous formaldehyde solution of about 4 per cent concentration for a period of about 3 weeks to 6 months, depending upon the thickness of the material. After hardening, the material must be dried to the normal moisture content of 8 to 12 per cent. The drying process requires about the same length of time as the hardening. Obviously such a course of manufac-

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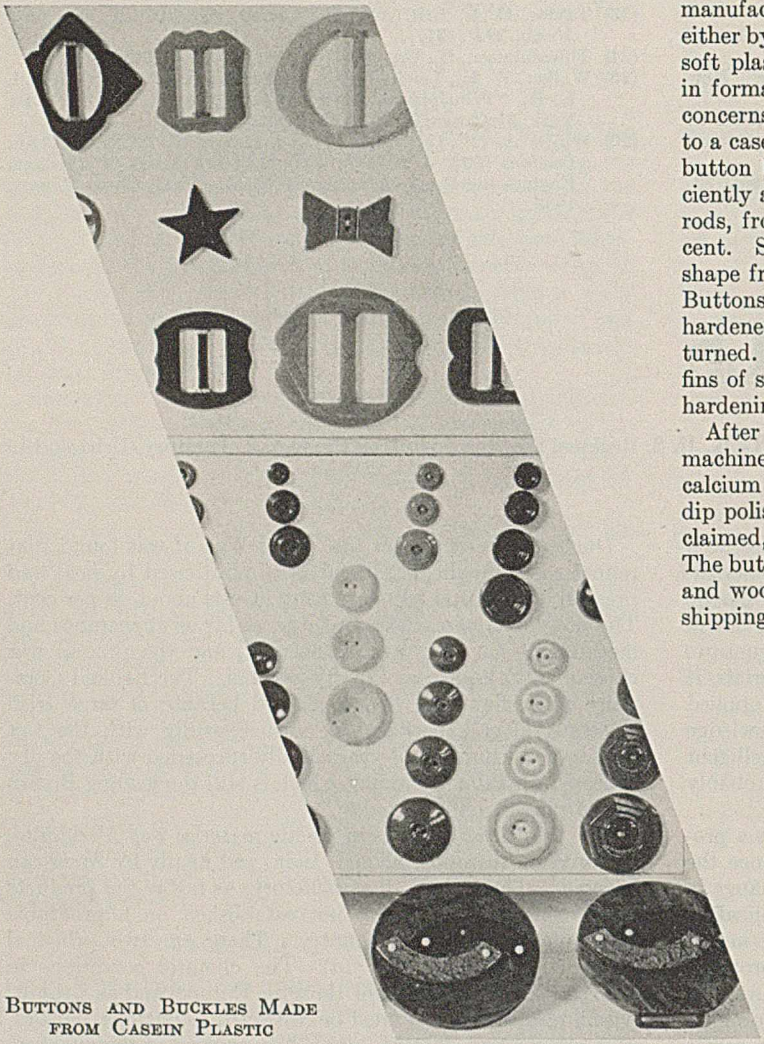
[1] A cooperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and of Plant Industry of the United States Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.



Buttons and Buckles Made from Casein Plastic

ture ties up an inordinate amount of material in process, and hence in capital, and is expensive without counting the amount of material lost as a result of spontaneous fractures.

Buttons from Plastics

The American button manufacturers have found a way to overcome most of these difficulties, and they must be given credit for building up a business which produces about 4000 tons of casein plastic buttons and buckles annually. They have accomplished this by the simple, nontechnical, commonsense move of combining the button factory and the casein plastics plant, with the result that waste is largely eliminated, and the partially fabricated button is thin enough to harden and season so rapidly that the cycle of production has been reduced to about a week. The annual domestic production of casein plastics finished as sheets and rods has dropped to about 50 tons, with a negligible amount imported.

George Morrell, a button manufacturer, bought the struggling Kyloid plant in 1928 and joined it directly to his button factory. The following year, Christensen, who had developed Aladdinite, found that alum (*8*) mixed directly with the water before extrusion, partially hardened the casein so that rods extruded from this mixture could be turned in automatic screw machines much more satisfactorily than either the soft plastic or the formaldehyde-hardened casein plastic. He formed the Button Corporation of America about 1931 to produce buttons by this process and discontinued the manufacture of Aladdinite. The buttons turned to shape, either by automatic machines from blanks sliced from the cold soft plastic (*17*) or directly from alum casein rods, harden in formaldehyde in a few days. Although these and other concerns follow the plan of uniting the button factory directly to a casein plastics plant, the smaller operators buy hardened button blanks of Ameroid. These cannot be used as efficiently as the soft plastic but are much better than sheets or rods, from which the waste is sometimes as high as 50 per cent. Some mention has been made of buttons molded to shape from soft plastic in sheets connected by thin fins (*2*). Buttons which have been molded can be punched out and hardened in formaldehyde in the same manner as those turned. In either case there is no waste, as the turnings or fins of soft or alum casein can be reworked, and the time of hardening is a matter of a few days.

After hardening, the buttons are drilled in automatic machines and polished by treatment with a hot sodium or calcium hypochlorite solution. This so-called chemical or dip polish (*8*, *24*) really produces a surface glaze which, it is claimed, also renders the material more water resistant. The buttons are usually given a final short tumbling with wax and wooden pegs, and they are then ready for grading and shipping.

Technical Improvements

Technically, the attempts to improve the process of manufacture of casein plastic material have followed two lines—namely, shortening the time of hardening by the incorporation of a salt such as ammonium chloride (*12*) or thiocyanate (*11*) in the powder before extrusion, and substitution of a dormant hardening agent for the formaldehyde bath. These latter agents have usually taken the form of trioxymethylene (*15*), hexamethylenetetramine (*3*), or repressing agents such as formamide (*9*), dicyandiamide (*19*), hydroaromatic alcohols or ketones (*22*) with formaldehyde. The object of all of these attempts was to permit the plastic to flow to shape and then have the hardening agent become active and harden the protein material. So far as can be determined, none of these experiments was sufficiently successful to warrant a commercial development.

Recently it has been found possible to produce a thermoplastic formaldehyde-hardened protein material (*5*) that may be formed to shape under the influence of heat and pressure and come finished from the die. The protein powder is treated with 40 per cent formaldehyde solution so adjusted with alkali that the pH of the equilibrium solution over the protein will be that of the isoelectric point of the protein. The excess formaldehyde is washed out with water and the formaldehyde-protein powder dried to normal moisture content or less. The moisture content may be reduced to 5 per cent or less, and a plasticizer, such as ethylene glycol (*6*), ethylene cyanohydrin, glycerol, etc., added.

Acid casein rather than rennet casein was found to give the best products by this treatment, the degree of hydrolysis appearing to affect the water absorption inversely (*4*). In every case, even when up to 20 per cent ethylene glycol was used as a plasticizer, the water absorption of this thermoplastic formaldehyde-hardened protein material was found to be less than the water absorption of casein plastic material prepared by the usual dry process which was 18 to 25 per cent. Acid casein hardened with formaldehyde and molded with 15 per cent moisture present gave a water absorption of approximately 10 per cent, while that with a moisture content of about 5 per cent and ethylene glycol content of 15 per cent gave about 15 per cent water absorption. The length of all tests was 24 hours.

This development is not of as great commercial importance as it would have been ten years or so ago. As the plastics industry is operated today, the only thermoplastic material of any interest or importance must lend itself to application of injection molding. In this process the plastic is heated considerably above its yield point and then forced into comparatively cool dies where it sets almost immediately and can be discharged. A cycle of two discharges per minute is not at all unusual for injection molding machines. Thermoplastic formaldehyde-hardened casein material is not sufficiently fluid to work in an injection machine, and to date a plasticizer has not been found that will render it applicable. Here is a field of worth while research and one that promises an ample reward for successful efforts. The material principally used in injection dies at the present time is cellulose acetate plastic, selling at about 80 cents per pound. Casein plastics could compete very favorably as far as color range is concerned. In case a plasticizer could be discovered that would also improve the water resistance, casein plastics might well be brought to a practical comparative basis for most applications, and applications not as yet considered would be possible because of the cheaper material.

Thermosetting Compounds

The other type of plastic material of commercial importance is the thermosetting, such as molding compounds with phenolic or urea resin bases. Pieces molded from thermosetting powders may be removed from the hot die without chilling. Many attempts have been made to combine casein with phenolic (*13*, *23*) or urea (*18*) resinous molding compounds, largely in the capacity of filler material. There is, however, only one well-known instance of such a combination having a successful commercial application—namely, that of an automobile manufacturer who uses soybean meal (*14*) in a phenolic molding mixture primarily for gearshift knobs and horn buttons. Recent experiments, the results of which have not yet been published, indicate, however, that the thermoplastic formaldehyde-hardened protein may be modified advantageously with either phenolic or urea resins to produce thermosetting molding powders of considerable potential commercial interest. Mixtures of 50 per cent formaldehyde-hardened protein (*7*) with a moisture content of 3 per cent or less, compounded with 25 per cent phenolic resin and 25 per cent wood flour may be pressed at 330° F. and 2000 pounds per square inch into unit pieces having good strength and closely resembling the regular phenolic material in appearance, except that they are more translucent. A good range of colors is possible, but they have not as yet been tested for light fastness. The water absorption which is about 3 per cent in 48 hours of immersion is higher than that of the regular phenolic plastics but much less than that of any protein plastic material.

This hardened protein material mixed with an equal portion of urea resin in place of alpha-cellulose, commonly used as filler, produces a good molding powder which is also thermosetting. The molded pieces are translucent, may be produced in any color or shade except pure white, and have a water absorption of about 5 per cent. The pieces do not soften or swell in water, nor do they fracture on drying. A difficult chemical problem will have to be solved, however, before this application can have any commercial importance. The problem arises from the fact that the formaldehyde-hardened protein gives a definite acid reaction when suspended in water. Methylol ureas in water dispersion are set up by acid, so that when they are mixed with protein-formaldehyde, the urea resin sets up. It has not been possible up to this time to neutralize the acid reaction of the hardened protein without the addition of so much alkali that the nature of the hardened protein has been adversely affected. A fundamental study of the protein-formaldehyde complex may be necessary before this problem can be solved.

This is only one of the problems whose solution awaits the fundamental investigation of casein itself and of casein complexes such as casein-formaldehyde. The industry has been seriously handicapped by the lack of fundamental information without which it is practically impossible to make intelligent application. Industry itself can do little to remedy this condition since industrial research must show a tangible return on money invested and, although fundamental research almost invariably pays a big dividend in the long run, there are few industrial concerns willing to support adequately the long-term and uncertain program that will be necessary to make even a good start in solving these problems.

However, the time appears to be ripe to undertake this work seriously. As mentioned before, the new tools available, such as the x-ray, infrared ray, ultracentrifuge, and monomolecular film technique, have stimulated interest in the investigation of protein structure probably to the greatest extent in history. If the industrial chemists will bring their problems to research workers in the universities, government laboratories, and independent agencies, if they will watch carefully the results of the investigations underway at these laboratories, and if they will apply the knowledge gained to their own practical problems, some of these problems will soon be solved.

To summarize, the casein plastic industry has been seriously handicapped by the lack of fundamental information in the past. This is no longer necessary. Interest in the fundamental structure and properties of proteins has been aroused and much work has been and will be done along this line. The fundamental research worker and the practical industrial chemist or chemical engineer have their work cut out. If they will coordinate their work and ideas, casein plastic material may yet earn a place among the major plastic materials.

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Aldehyde-Nitroparaffin Condensation[1]

B. M. VANDERBILT[2] AND H. B. HASS
Purdue University and Purdue Research Foundation, Lafayette, Ind.

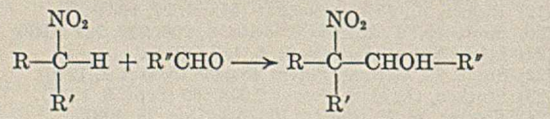
Although the aldehyde-nitroparaffin condensation to give nitroalcohols has been known for over forty years, many of the simple aliphatic nitroalcohols had not been prepared until this investigation was undertaken. Recent developments in vapor-phase nitration have made the lower aliphatic nitroparaffins available (*3*). By means of condensations of nitroethane, the nitropropanes, and the nitrobutanes with formaldehyde, acetaldehyde, and butyraldehyde, respectively, a number of monohydric and dihydric alcohols have been prepared. Typical acetates of these alcohols have been synthesized. Reduction of the nitroalcohols gives the corresponding aminoalcohols. The physical and chemical properties of the various compounds prepared are given. Certain theoretical aspects of their preparation are discussed. Some possible commercial uses are suggested.

VICTOR MEYER, the discoverer of the nitroparaffins, recognized that the hydrogen atoms attached to the nitro-bound carbon atom of primary or secondary nitroparaffins had properties different from those attached to other carbon atoms in the nitroparaffin molecule. However, it was not until twenty-three years later that Henry (*4*) discovered that nitroalcohols could be prepared from nitroparaffins by condensation with aliphatic aldehydes. From 1895 to 1902 Henry and his co-workers—Maas, Mousset, Pauwels, and Shaw—prepared a number of nitroalcohols by condensing aldehydes with nitroparaffins. They studied some of the properties and prepared a few derivatives. However, the literature is incomplete and in some cases conflicting relative to the preparation and properties of the nitroalcohols which may be obtained from the lower nitroparaffins and the more common aliphatic aldehydes.

In order to make a systematic study of this condensation reaction, nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, 2-nitrobutane, and 2-methyl-1-nitropropane were condensed with formaldehyde, acetaldehyde, and butyraldehyde, respectively. Nitromethane was omitted because it had previously been studied thoroughly (*4, 7*). The six nitroparaffins employed can readily be obtained by vapor-phase nitration of the corresponding hydrocarbons (*3*). The three aldehydes used are inexpensive articles of commerce.

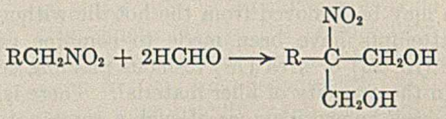
Methods of Preparing Nitroalcohols

The general reaction for the aldehyde-nitroparaffin condensation is as follows:



$$R\text{—}\underset{R'}{\overset{NO_2}{C}}\text{—}H + R''CHO \longrightarrow R\text{—}\underset{R'}{\overset{NO_2}{C}}\text{—}CHOH\text{—}R''$$

In case the nitroparaffin is primary and the aldehyde is formaldehyde, two molecules of aldehyde react:



$$RCH_2NO_2 + 2HCHO \longrightarrow R\text{—}\underset{CH_2OH}{\overset{NO_2}{C}}\text{—}CH_2OH$$

Unlike most aldehyde condensations, the aldehyde-nitroparaffin reaction does not occur unless the mixture is definitely alkaline. In order to obtain good yields of the nitroalcohols, aldol and polymer formation from the aldehydes employed had to be kept to a minimum. Since alkaline reagents are also catalysts for the formation of these latter substances, it was necessary to adopt experimental conditions unfavorable to their formation. Another undesirable reaction which may occur during the aldehyde-nitroparaffin reaction and recovery of the product, is the formation of nitroölefins and their polymers. A nitroalcohol derived from a primary nitroparaffin may split off water to form the corresponding nitroölefin:

$$RCHNO_2CHOHR' \longrightarrow RCNO_2{=}CHR' + H_2O$$

When nitroalcohols are prepared from aromatic aldehydes, this type of reaction is difficult to avoid (*8*). When nitroalcohols are prepared from aliphatic aldehydes and primary nitroparaffins, the formation of nitroölefins may be avoided completely by not using elevated temperatures until the reaction mixture has been neutralized. Nitroölefins are particularly undesirable since they are strong lachrymators and polymerize to highly colored products. By following the rules of procedure listed, the formation of aldols, nitroölefins, and polymers is kept to a minimum:

1. Use the minimum concentration of catalyst to obtain a reasonable reaction velocity.
2. Keep the reaction mixture homogeneous at all times, preferably by maintaining one phase.

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[1] This is the ninth in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY: **23**, 352 (1931); **27**, 1190 (1935); **28**, 333, 339, 1178 (1936); **29**, 1335 (1937); **30**, 67 (1938); **31**, 118 (1939).

[2] Present address, Standard Oil Development Company, Elizabeth, N. J.

3. Regulate the temperature to a practical minimum.
4. Maintain a molal excess of the nitroparaffin at all times.
5. Remove the alkaline catalyst quantitatively before working up the reaction mixture.

The pure nitroparaffins used in the various syntheses were obtained by careful rectification of the crude nitration products of propane or one of the butanes. 1-Nitropropane, 1-nitrobutane, 2-nitrobutane, and 2-methyl-1-nitropropane were obtained from the nitration products of the corresponding hydrocarbons. In the nitration of propane, both nitroethane and 2-nitropropane are formed along with nitromethane and 1-nitropropane (*3*). However, as nitroethane and 2-nitropropane distill so closely (113° and 118° C., respectively), it was not practical to try to obtain either of these two nitroparaffins in a pure state from this mixture. Nitromethane, nitroethane, 1-nitropropane, 2-nitrobutane, and 1-nitrobutane are formed when nitrating *n*-butane. Pure nitroethane was easily obtained from this mixture. In the nitration of isobutane, 2-nitropropane is formed with no nitroethane so that the nitration product from this hydrocarbon was used for the isolation of pure 2-nitropropane.

The formaldehyde employed was Mallinckrodt's U. S. P. grade. The acetaldehyde and butyraldehyde were commercial products which were carefully rectified. Each was freshly distilled prior to use in order to free the aldehyde from any aldol and/or oxidation products.

The following examples illustrate the technique employed in the preparation of the mono- and dihydric nitroalcohols:

5-NITRO-4-OCTANOL. Into a 500-cc. three-neck flask were placed 206 grams of 1-nitrobutane (2 moles), 100 cc. of 95 per cent alcohol, and 4 cc. of 10 *N* sodium hydroxide solution. One hundred and forty-four grams of freshly distilled butyraldehyde (2 moles) were added slowly to the well-agitated solution. Reaction temperature was maintained at 30–35° C. by external cooling. When approximately two thirds of the butyraldehyde had been added, an additional 4 cc. of 10 *N* sodium hydroxide and 15 cc. of water were added. After addition of the aldehyde was complete, the solution was allowed to stand at 35–38° for 4 days. The alkali was neutralized with an equivalent amount of hydrochloric acid and the mixture distilled under slightly reduced pressure. A small amount of unreacted butyraldehyde distilled with the ethyl alcohol followed by a little 1-nitrobutane and higher boiling impurities. The pressure was finally reduced to 5 mm. and the 5-nitro-4-octanol distilled. It was obtained as a pale yellow liquid. The yield was 310 grams (88.5 per cent of theory, based upon the 1-nitrobutane and the butyraldehyde employed).

2-ETHYL-2-NITRO-1,3-PROPANEDIOL. Into a 500-cc. three-neck flask were placed 35.6 grams of 1-nitropropane (0.4 mole) and 0.1 gram of hydrated lime. Sixty-four grams of 37.5 per cent formalin solution (0.8 mole of formaldehyde) were added dropwise to the well-stirred mixture. During the addition the temperature rose to 30° C. and was prevented from going higher by external cooling with tap water. On addition of approximately half of the formalin, the contents of the flask became one phase. After addition was complete and the exothermic reaction had subsided, the solution was allowed to stand at room temperature for 43 hours. Carbon dioxide in very slight excess was added and the calcium carbonate removed by means of a Filter-Cel suction filter. The precipitate was washed with 5 cc. of water, and the combined filtrate and washings were evaporated at 200 mm. The residue was finally heated to 90° at 20 mm. in a water bath. The molten product which remained in the distilling flask solidified on cooling. Yield was 59.4 grams of 2-ethyl-2-nitro-1,3-propanediol, of 98–99 per cent purity, practically a theoretical yield.

Purification and Properties of Nitroalcohols

The four nitroglycols (from the four primary nitroparaffins employed), 2-methyl-2-nitro-1-propanol, and 2-methyl-3-nitro-4-heptanol are solids at room temperature. The nitroglycols were obtained as solid residues on evaporation of their mother liquors and subsequent cooling. They were 95–99 per cent pure as obtained. Their chief impurities were paraformaldehyde and the corresponding monohydric nitroalcohols. They were purified by crystallization from a hot benzene-butanol solution and from water. The two solid monohydric alcohols may be purified by vacuum distillation and/or crystallization. A naphtha and benzene solution was used for crystallizing 2-methyl-2-nitro-1-propanol, and naphtha for 2-methyl-3-nitro-4-heptanol.

All the liquid nitroalcohols were colored yellow when obtained by vacuum distillation of the reaction mixture. They were aerated at 75–100° C. for about half an hour in order to hasten the polymerization of any unsaturates and then were washed with saturated sodium bisulfite solution to remove any aldehydes. Subsequent fractionation through a modified Podbielniak column at 10 mm. sufficed to convert them to colorless or nearly colorless products.

The solids are all white crystalline substances whose crystals suggest those of inorganic salts. The liquids are somewhat viscous and have a faint but rather sharp odor. All the dihydric nitroalcohols and those monohydric nitroalcohols containing less than seven carbon atoms are quite soluble in water. The former are insoluble in nonbenzenoid hydrocarbons as are the monohydric nitroalcohols containing less than six carbon atoms. All of these nitroalcohols are stable up to 100° C. but unstable at temperatures of 150° or above. They have chemical properties characteristic of aliphatic alcohols and nitroparaffins. Their chemical activity varies with the individual compounds. Table I summarizes some of their physical constants.

Aminoalcohols from Nitroalcohols

Nitroalcohols may be reduced to the corresponding aminoalcohols. Piloty and Ruff (*12*) reduced 2-methyl-2-nitro-1,3-propanediol with tin and hydrochloric acid to obtain impure 2-amino-2-methyl-1,3-propanediol. Their product melted at 60–95° C. Henry (*6*) used iron and acetic acid for reducing some of the nitroalcohols which he had prepared to the corresponding amino compounds. In all cases yields were low when metals were used in acids for such reductions. Montmollin and Achermann (*9*) state that this is due to the "fragility" of the aminoalcohols. They obtained a 50 per cent yield of 1-amino-2-butanol when 1-nitro-2-butanol was reduced with aluminum amalgam in alcohol.

It is believed that Schmidt and Wilkendorf (*13*) are the only investigators who previously had used catalytic hydrogenation for preparing aminoalcohols from nitroalcohols. They employed palladium as catalyst in an oxalic acid solution. They state that poor results are obtained when using neutral or alkaline solution.

The four nitroglycols cited in Table I were catalytically hydrogenated over Raney nickel (*1*) in collaboration with K. Johnson.[3] When pure, these dihydric aminoalcohols are solids at room temperature and cannot be distilled at atmospheric pressure without decomposition. They were obtained as viscous yellow sirups or gray-yellow solids. 2-Amino-2-methyl-1,3-propanediol was purified by crystallization from acetone. It was very difficult to get 2-amino-2-ethyl-1,3-propanediol as a solid. The crude reduction product was distilled at 1 mm. with slight decomposition. The distillate was placed in a refrigerator, and 23 days passed be-

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[3] This process will be described in detail in a later paper to be published from this laboratory

Table I. Physical Constants of Nitroalcohols

Nitroalcohol	Prepared from: Nitroparaffin	Prepared from: Aldehyde	B. P. at 10 Mm., ° C.	Specific Gravity, d_4^{25}	Refractive Index, n_D^{20}	% Nitrogen: Theoretical	% Nitrogen: Found
2-Nitro-1-propanol	$EtNO_2$	HCHO	99	1.1841	1.4379	...	....
3-Nitro-2-butanol	$EtNO_2$	CH_3CHO	92	1.1296	1.4420	...	....
2-Nitro-3-hexanol	$EtNO_2$	C_3H_7CHO	108	1.0575	1.4480	9.52	9.42, 9.45
2-Nitro-1-butanol	$1\text{-}PrNO_2$	HCHO	105	1.1332	1.4390	...	....
3-Nitro-2-pentanol	$1\text{-}PrNO_2$	CH_3CHO	100	1.0818	1.4419	...	....
3-Nitro-4-heptanol	$1\text{-}PrNO_2$	C_3H_7CHO	115	1.0275	1.4460	8.70	8.65, 8.72
2-Methyl-2-nitro-1-propanol	$2\text{-}PrNO_2$	HCHO	89.5–90[a]	....	....	...	....
3-Methyl-3-nitro-2-butanol	$2\text{-}PrNO_2$	CH_3CHO	90	1.1021	1.4469	10.53	10.58, 10.72
2-Methyl-2-nitro-3-hexanol	$2\text{-}PrNO_2$	C_3H_7CHO	109	1.0405	1.4499	8.70	8.55, 8.69
2-Nitro-1-pentanol	$1\text{-}BuNO_2$	HCHO	117	1.0818	1.4405	...	....
3-Nitro-2-hexanol	$1\text{-}BuNO_2$	CH_3CHO	112	1.0487	1.4438	...	....
5-Nitro-4-octanol	$1\text{-}BuNO_2$	C_3H_7CHO	124	1.0394	1.4463	8.00	7.81, 7.94
2-Methyl-2-nitro-1-butanol	$2\text{-}BuNO_2$	HCHO	98	1.1047	1.4468	10.53	10.51, 10.53
3-Methyl-3-nitro-2-pentanol	$2\text{-}BuNO_2$	CH_3CHO	100	1.1157	1.4518	9.52	9.39, 9.42
3-Methyl-3-nitro-4-heptanol	$2\text{-}BuNO_2$	C_3H_7CHO	119	1.0281	1.4532	8.00	7.81, 7.93
3-Methyl-2-nitro-1-butanol	$1\text{-}Iso\text{-}BuNO_2$	HCHO	111	1.0886	1.4430	...	....
4-Methyl-3-nitro-2-pentanol	$1\text{-}Iso\text{-}BuNO_2$	CH_3CHO	96–98	1.0599	1.4477	...	....
2-Methyl-3-nitro-4-heptanol	$1\text{-}Iso\text{-}BuNO_2$	C_3H_7CHO	111	1.0140	1.4485	8.00	7.98, 8.11
2-Methyl-3-nitro-4-heptanol (stereoisomer)	$1\text{-}Iso\text{-}BuNO_2$	C_3H_7CHO	121 (53[a])	....	....	8.00	7.91, 8.12
2-Methyl-2-nitro-1,3-propanediol	$EtNO_2$	2HCHO	149–150[a]	....	....	...	....
2-Ethyl-2-nitro-1,3-propanediol	$1\text{-}PrNO_2$	2HCHO	56[a]	....	....	...	....
2-Nitro-2-propyl-1,3-propanediol	$1\text{-}BuNO_2$	2HCHO	81–81.5[a]	....	....	...	....
2-Nitro-2-isopropyl-1,2-propanediol	$1\text{-}Iso\text{-}BuNO_2$	2HCHO	87–88[a]	....	....	...	....
2-Amino-2-ethyl-1,3-propanediol	....	......	.....	....	....	11.76	11.56, 11.69
2-Amino-2-propyl-1,3-propanediol	....	......	.....	....	....	10.52	10.25, 10.32
2-Amino-2-isopropyl-1,3-propanediol	....	......	.....	....	....	10.52	10.35, 10.38

[a] Melting point.

fore it solidified to a waxlike solid. A portion of this was then crystallized from butanol-toluene solution several times. It was necessary to cool to 0° C. and seed in order to obtain crystallization. Due to the amorphous nature of this product the last of the solvents could not be expelled by drying so that the recrystallized material was again distilled under vacuum to remove the last of the solvents. The liquid distillate was solidified by seeding and was used as such for analysis and determination of melting point. 2-Amino-2-propyl-1,3-propanediol was obtained pure by distillation at 1 mm. 2-Amino-2-isopropyl-1,3-propanediol crystallized nicely from benzene-butanol solution.

The dihydric aminoalcohols are all solids at room temperature and have a mild amine odor. They are much more stable thermally than are the corresponding nitroalcohols. They are stable toward strong alkalies at ordinary temperatures and form salts with acids.

The melting points of these aminoalcohols (in ° C.) are as follows:

2-Amino-2-methyl-1,3-propanediol	108–109
2-Amino-2-ethyl-1,3-propanediol	37.5–38.5
2-Amino-2-propyl-1,3-propanediol	58
2-Amino-2-isopropyl-1,3-propanediol	74

Acetates of Nitroalcohols

The only organic esters of these nitroalcohols which had been prepared previous to this investigation were the acetates of 2-nitro-1-butanol and 3-methyl-2-nitro-1-butanol. The former was prepared by Pauwels (*11*) from acetic anhydride and the corresponding alcohol and is described as a yellow liquid having a penetrating odor, as being easy to saponify, and as having a boiling point of 130° C. at 35 mm. The latter was prepared by Shaw (*15*), and its boiling point is given as 159–168° C. (38 mm.).

In order to observe the general properties of such compounds, the acetates of four typical nitroalcohols were prepared. Those esterified were:

2-Nitro-1-butanol, a primary alcohol whose nitro group is attached to a secondary carbon atom.

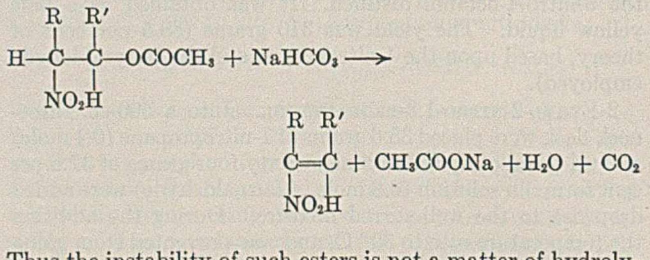
2-Methyl-2-nitro-1-butanol, a primary alcohol whose nitro group is attached to a tertiary carbon atom.

3-Nitro-2-butanol, a secondary nitroalcohol.

2-Ethyl-2-nitro-1,3-propanediol, a typical nitroglycol.

The standard procedure for preparing acetates from acetic anhydride was followed in the preparation of these esters. They were washed only with water prior to distillation. Nearly theoretical yields were obtained. The esters were further purified by rectification at 10 mm.

These acetates are all clear, colorless liquids with a faint, slightly mustardlike odor. Those from the monohydric alcohols are less viscous than the alcohols from which they are derived. All are less than one per cent soluble in water. They are thermally stable at 95° C., but at 150° the acetates of 2-nitro-1-butanol and 3-nitro-2-butanol became discolored within 5 hours; those of 2-methyl-2-nitro-1-butanol and 2-ethyl-2-nitro-1,3-propanediol showed no change after being heated at 150° C. for 16 hours. Similarly, the two esters in which the nitro group is attached to a tertiary carbon atom—i. e., the acetates of 2-methyl-2-nitro-1-butanol and 2-ethyl-2-nitro-1,3-propanediol—are very stable toward mild hydrolytic agents. However, the two acetates in which the nitro group is attached to a secondary carbon atom are very reactive toward all hydrolytic agents. It was found that boiling water rapidly decomposed the acetates of 2-nitro-1-butanol and 3-nitro-2-butanol. Sodium bicarbonate (0.1 *N*) decomposes such compounds and liberates the corresponding nitroolefin and sodium acetate:



$$\mathrm{H{-}\overset{R}{\underset{NO_2}{C}}{-}\overset{R'}{\underset{H}{C}}{-}OCOCH_3 + NaHCO_3 \longrightarrow \overset{R}{\underset{NO_2}{C}}{=}\overset{R'}{\underset{H}{C}} + CH_3COONa + H_2O + CO_2}$$

Thus the instability of such esters is not a matter of hydrolysis but is rather a cleavage of the ester molecule. The common physical constants of these esters are as follows:

	B. P. at 10 Mm., ° C.	Specific Gravity, d_4^{25}	Refractive Index, n_D^{20}
Acetate of 2-nitro-1-butanol	103	1.1164	1.4287
Acetate of 3-nitro-2-butanol	103	1.1089	1.4281
Acetate of 2-methyl-2-nitro-1-butanol	109	1.0932	1.4350
Diacetate of 2-ethyl-2-nitro-1,3-propanediol	157	1.1718	1.4444

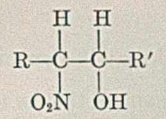
Identification of New Compounds

In all of the aldehyde-nitroparaffin condensations carried out, the normal course of reaction as reported by Henry and others evidently occurred. In no case did rearrangement take place. Those compounds described above which had not previously been reported were identified by analyses.

The monohydric nitroalcohols were analyzed for nitrogen by the method of Dumas. Some difficulty was encountered owing to the tendency of the sample to oxidize too rapidly in the combustion furnace and thus to give results which were too high. This difficulty was overcome by mixing the sample with a fifty-fifty mixture of copper oxide and calcium carbonate rather than with pure copper oxide. The dihydric nitroalcohols were analyzed for nitrogen by reducing to amino compounds, followed by regular Kjeldahl analysis. A 0.35-gram sample of nitroalcohol, 0.75 gram of aluminum dust, and 8 mg. of mercuric chloride were heated in dilute sulfuric acid in a Kjeldahl flask on the steam bath. After reduction was complete, the acid was concentrated by boiling, and the regular Kjeldahl digestion and analysis were carried out. The monohydric nitroalcohols gave low results by this method. The aminoalcohols were analyzed for nitrogen by the Kjeldahl method. The acetates were analyzed for nitrogen by the Dumas method. Table I summarizes the analyses of new compounds.

Stereoisomerism

Optical stereoisomers are possible for all the monohydric nitroalcohols prepared with the exception of 2-methyl-2-nitro-1-propanol. Any nitroalcohol obtained from an aldehyde higher than formaldehyde and a primary nitroparaffin other than nitromethane, gives a compound of the following type formula:



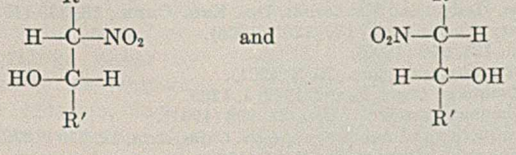
$$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ & | & & | & \\ \text{R}- & \text{C} & - & \text{C} & -\text{R}' \\ & | & & | & \\ & \text{O}_2\text{N} & & \text{OH} & \end{array}$$

Regardless of whether R and R′ are alike or not, such a molecule contains two asymmetric carbon atoms. Furthermore, the molecule is unsymmetrical. By means of the formula

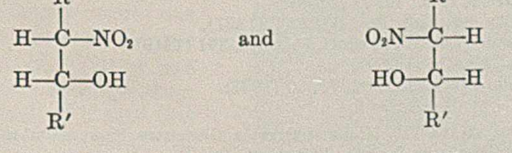
$$N = 2^n$$

where N = number of stereoisomers
n = number of asymmetric carbon atoms

one can predict two dextro and two levo forms—i. e., two racemic isomers. They are represented by the following projection formulas:



$$\begin{array}{c} \text{R} \\ | \\ \text{H}-\text{C}-\text{NO}_2 \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{R}' \end{array} \quad \text{and} \quad \begin{array}{c} \text{R} \\ | \\ \text{O}_2\text{N}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{R}' \end{array} \qquad (1)$$



$$\begin{array}{c} \text{R} \\ | \\ \text{H}-\text{C}-\text{NO}_2 \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{R}' \end{array} \quad \text{and} \quad \begin{array}{c} \text{R} \\ | \\ \text{O}_2\text{N}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{R}' \end{array} \qquad (2)$$

These racemic forms should possess somewhat different physical properties. They would be optically inactive, but each could be divided into its respective dextro and levo forms by the known methods. Likewise a nitroalcohol derived from an unsymmetrical secondary nitroparaffin and an aldehyde other than formaldehyde can exist as two optically inactive isomers—e. g., 3-methyl-3-nitro-2-pentanol.

From the properties of most of the nitroalcohols prepared which contain two asymmetric carbon atoms, it was apparent that only one of the racemic isomers was formed or that the two had nearly identical boiling points. However, the two nitroalcohols derived from 2-methyl-1-nitropropane and acetaldehyde and butyraldehyde, respectively, were exceptions. Both of these compounds distilled over a definite boiling range. That from butyraldehyde and 2-methyl-1-nitropropane had a sufficiently wide boiling range so that the two isomers could be separated to a large degree by careful rectification. One of these proved to be a solid at ordinary temperature which greatly facilitated further separation.

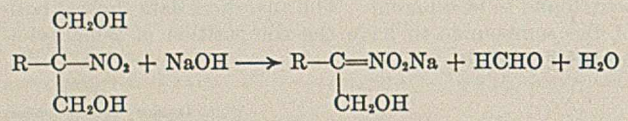
The condensation product of two moles of 2-methyl-1-nitropropane and two moles of butyraldehyde was carefully fractionated at 10 mm. Approximately 60 per cent of the 2-methyl-3-nitro-4-heptanol was obtained at about 111° C., and 40 per cent distilled close to 121°. The former was further purified by refractionation and the latter by crystallization from pentane. A portion of each was reduced to the corresponding aminoalcohols, and they were found to have different physical constants. The acetates were also prepared and were found to be different. The analytical data showed both of the compounds to have the composition of 2-methyl-3-nitro-4-heptanol:

	Solid Isomer	Liquid Isomer
Nitrogen by Dumas method (theory 8.00), %	7.91, 8.12	7.98, 8.11
Nitrogen of acetate by Dumas (theory 6.45), %	6.41, 6.51	6.39, 6.45
Nitrogen of aminoalcohol by titration (theory 9.65), %	9.26	9.36
Molecular weight (theory 175.1)	177.3	175.1
Boiling point at 10 mm., ° C.	121	111
Melting point, ° C.	53	....
Boiling point of acetate at 10 mm., ° C.	122.5	128

Discussion

Aliphatic aldehydes undergo several condensation reactions other than those with nitroparaffins. The addition compounds with sodium bisulfite, ammonia, and hydrogen cyanide are well known. As previously stated, the nitroparaffins, unlike the compounds mentioned above, do not spontaneously condense with aldehydes, but the reaction must be promoted by a definite type of catalyst. Previous investigators used a variety of alkaline catalysts, including alkali carbonates and hydroxides, sodium methylate and ethylate, methylamine, ethylamine, amylamine, piperidine, sodium sulfite, sodium acetate, and borax. We have used similar catalysts but not ammonia, primary amines, or secondary amines because of their reactivity toward aldehydes. In addition we have used alkaline earth hydroxides because of their ease of removal at the end of the reaction by precipitation and filtration.

The activity of the alkaline catalyst appeared to be determined to a greater degree by its pH value than by its concentration. For example, nitroethane or 1-nitropropane condensed readily with formaldehyde when catalyzed by sodium carbonate or sodium bicarbonate. 2-Nitropropane and formaldehyde condensed hardly at all in the presence of sodium bicarbonate and only very slowly with 3 per cent sodium carbonate at 30° C. On the other hand, a solution of the two reactants condenses readily when 0.1 per cent of sodium hydroxide is added. The exact action of the catalyst in this reaction is not known. It was found that pyridine, which has an ionization constant of 2.3×10^{-9}, does not catalyze the reaction of nitroethane and acetaldehyde, whereas trimethylamine ($K_i = 7.4 \times 10^{-5}$) rapidly promotes this condensation at 30–35° C. On the other hand, the condensation of 2-nitrobutane and acetaldehyde proceeds slowly in the presence of trimethylamine, and sodium hydroxide rapidly catalyzes this reaction at the temperatures employed. Nitromethane has an ionization constant of 1×10^{-11}. The rest of the nitroparaffins are considerably less acidic, carbonic acid being capable of liberating them from their salts. It is believed that the secondary nitroparaffins are considerably less acidic than the corresponding primary compounds. Judging from the yields of nitroalcohols obtained from these two types of nitroparaffins, it is indicated that the reactivity of the nitroparaffins toward aldehydes varies directly with their pH. Alkalies convert the primary and secondary nitroparaffins to their corresponding nitronic salts. The fact that several of the catalysts employed will not convert the nitroparaffins to their salts but will catalyze their condensation with aldehydes indicates that salt formation of the nitroparaffin is not essential for the condensation reaction to proceed. In fact, it has been established that the sodium salt of a nitroparaffin will not condense with an aldehyde unless the former is primary—i. e., unless there is a free hydrogen atom attached to the alpha carbon atom. It was found that when a dihydric nitroalcohol is treated with a molecular equivalent of sodium hydroxide, it is converted to the salt of a monohydric nitroalcohol containing one less carbon atom:



$$R-\underset{CH_2OH}{\overset{CH_2OH}{C}}-NO_2 + NaOH \longrightarrow R-\underset{CH_2OH}{C}=NO_2Na + HCHO + H_2O$$

On further treatment with sodium hydroxide at moderate temperatures, the monohydric alcohol does not decompose, and if the formaldehyde is removed and the sodium hydroxide neutralized, the free monohydric alcohol can be recovered. In a similar manner, nitroalcohols from secondary nitroparaffins are decomposed to the original nitroparaffin and aldehyde by sodium hydroxide. Thus it is apparent that a strong alkali will reverse the aldehyde-nitroparaffin condensation reaction and form the salt of the monohydric nitroalcohol or of the secondary nitroparaffin. Since a primary nitroparaffin is monobasic and is apparently not a stronger acid than the monohydric nitroalcohols derived from it, there is no tendency for such nitroalcohols to decompose further. This is exactly true only with nitroalcohols derived from formaldehyde, since the sodium salts of nitroalcohols derived from primary nitroparaffins and acetaldehyde were found to give cleavage products in aqueous solution. This is probably due to the fact that the aldehydes which would be liberated in case of the reversal of the condensation reaction are partially destroyed by the alkali and thus shift the equilibrium in this direction.

Previous investigators have been able to condense two molecules of a given aldehyde with the primary nitroparaffins above nitromethane only when they employed formaldehyde (*11*). However, they could apparently condense one molecule of any aldehyde and one molecule of formaldehyde with such nitroparaffins (*10*). Nitromethane has been condensed, respectively, with three molecules of formaldehyde (*5*), two molecules of aldehydes higher than formaldehyde (*14*), and two molecules of formaldehyde and one molecule of a higher aldehyde (*2*).

Early in the course of this investigation it was ascertained that nitroethane, 1-nitropropane, 1-nitrobutane, and 2-methyl-1-nitropropane will readily condense with two molecules of formaldehyde. However, in the case of acetaldehyde or butyraldehyde only one molecule of the aldehyde condenses with these nitroparaffins. Use of great excesses of the aldehydes, high concentrations of catalysts, and elevated temperatures did not suffice to cause any nitroglycols to form when using either of these two aldehydes.

When formaldehyde is condensed with any of the four mentioned primary nitroparaffins, the first molecule of the formaldehyde apparently condenses more easily than the second, but only very slightly. We thought that it might be possible to find a catalyst which would facilitate the addition of one molecule of formaldehyde to primary nitroparaffins, but would not be alkaline enough to cause the second molecule to condense to form the nitroglycol. In an attempt to form 2-nitro-1-butanol from equimolar quantities of 1-nitropropane and formaldehyde, various concentrations of sodium carbonate, sodium bicarbonate, trimethylamine, and pyridine were used as catalysts. However, in all cases considerable amounts of 2-ethyl-2-nitro-1,3-propanediol were formed, leaving a corresponding quantity of nitropropane unreacted. The use of various temperatures and times of reaction appeared to be of no avail. In order to obtain a monohydric alcohol in good yield from a primary nitroparaffin and formaldehyde, it was found necessary to use approximately a 100 per cent excess of the nitroparaffin and to use a strong base as catalyst. Any nitroglycol formed could be added to the next batch. In the presence of an alkaline material there is evidently an equilibrium between the two nitroalcohols and the primary nitroparaffin.

Conclusions

The primary and secondary nitroparaffins offer a convenient means of preparing aliphatic nitroalcohols. Owing to the presence of both the nitro and the hydroxy groups in the molecule, these compounds show promise as solvents. Their reduction to the corresponding aminoalcohols offers a means of preparing a huge number of compounds suitable for the synthesis of wetting agents, emulsifiers, and detergents. A large number of esters, ethers, and other organic chemicals can be prepared from these nitroalcohols. It is probable that some of these compounds will find their place as valuable articles of commerce.

Acknowledgment

The authors wish to express thanks to the Commercial Solvents Corporation and the Purdue Research Foundation for financing this research as a part of Fellowship No. 38. The former also kindly supplied the nitroparaffins used in this investigation and performed some of the analyses. The following United States patents assigned to the Purdue Research Foundation, are based upon this work: 2,132,352; 2,132,353; 2,139,120; 2,139,121; 2,139,122; 2,139,123; and 2,139,124, all of December 6, 1938.

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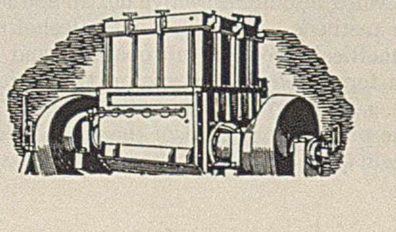


Cracking Tars and Distillates from Coal

GUSTAV EGLOFF, JACQUE C. MORRELL G. B. ZIMMERMAN, W. E. LEMEN

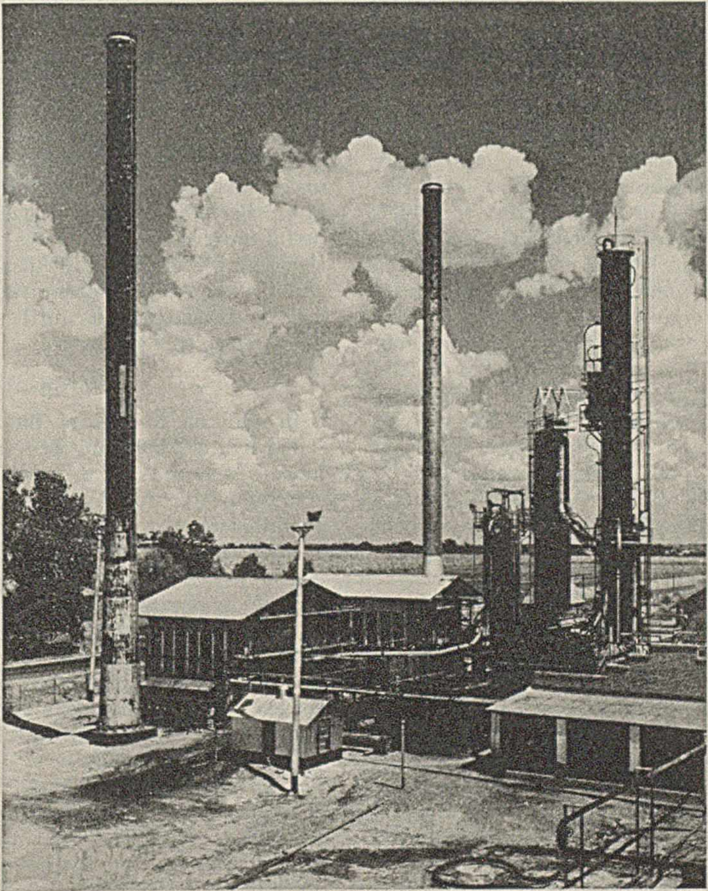
Universal Oil Products Company, Chicago, Ill.

Coal tars and distillates from them may be cracked by the modern process under proper conditions to produce gasoline, gas, and coke or fuel oil residues. Low-boiling phenols may be simultaneously produced from higher boiling tar acids. Commercial products include finished gasoline, cresylic acid, fuel oil, domestic coke, electrode carbon, and polymer gasoline. The quantity of tar acids produced from any coal tar fraction may be varied within limits by changing the boiling range of the whole distillate from the cracking unit.

In comparison with petroleum cracking, greater corrosion is encountered and lower plant capacities are obtained. Somewhat greater gasoline and gas yields are obtained than would be expected, based on the specific gravity of the cracking stocks. The finished gasoline has a greater heating value per unit volume and is satisfactory in other respects, with particularly good antiknock quality. The gas is lower in molecular weight and heating value than that from petroleum cracking, but by fractionation useful concentrations of higher olefins may be produced for chemical derivative use or for the production of polymer gasoline.

IN RECENT years national self-sufficiency has increased the importance of methods of producing motor fuel from native materials. Because of its low cost, tremendous quantity, and wide distribution, coal has been a raw material for several processes in the production of motor fuel. In addition to the motor benzene obtained from the light oil fraction in coal carbonization, either by high- or low-temperature operation, production of motor fuel as a major product on a commercial scale has been obtained by two methods. These are direct hydrogenation of coal (*3*) and the catalytic conversion of water gas obtained from coal to hydrocarbons by the method of Fischer and Tropsch (*8*).

As a source of light motor fuel the hydrocarbons in the tars resulting from coal carbonization have received relatively little attention, although they represent 4 to 5 per cent of the coal charged to high-temperature retorts or about twice this proportion in the low-temperature processes (*9*, *13*). Since most hydrocarbons may, under proper conditions, be decomposed to yield lighter hydrocarbons by thermal treatment, light motor fuels may be produced from coal tars and allied material by a cracking process similar to that used commercially to crack petroleum.



THERMAL CRACKING UNIT WITH A CAPACITY OF 2500 BARRELS OF CHARGING STOCK A DAY

To evaluate this type of material as a cracking stock, a number of tests were made charging coal tars, creosote oils, lignite tar fractions, and distillates from the low-temperature carbonization of coal-oil mixtures. These tests were carried out in a pilot cracking plant with a combined

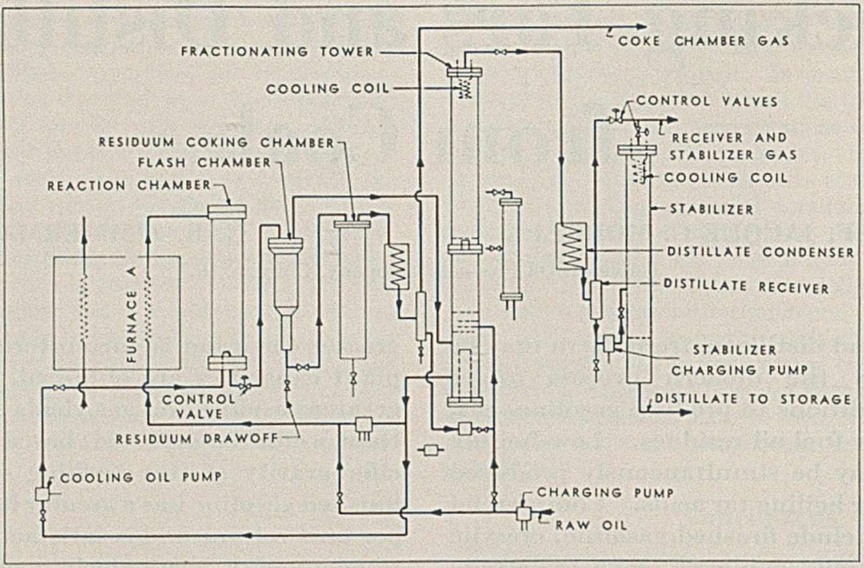


Figure 1. Single-Coil Cracking Pilot Plant for Residuum or Coking Operations

feed capacity of 5 to 7 gallons per hour. Both single-coil and two-coil operations were used, as illustrated in Figures 1 and 2. In each test the desired boiling range of the distillate produced and the quality of the liquid residue were established by the temperature conditions under operating pressure in the fractionating column and flash chamber, respectively. In producing coke, the liquid residue was withdrawn to the chamber and reduced to coke; the distillate was returned to the system for further cracking. The conditions of pressure and temperature in the heating coil and reaction chamber were adjusted to give maximum distillate yield.

The original tars and distillates were inspected to determine the A. P. I. gravity, sulfur content, viscosity, Engler distillation, and other characteristics which are customarily determined on petroleum cracking stocks. All cracked distillates produced were inspected for A. P. I. gravity, distillation, and antiknock quality (as octane number), in addition to other tests of general interest. Liquid residues were tested for A. P. I. gravity, viscosity, and sediment, and proximate analyses were made on coke residues. A. S. T. M. methods (*1*) were employed in these tests. Specific gravities were obtained by conversion from A. P. I. gravities when not directly determined. Engler viscosities were converted from determinations in the Universal or Furol instruments. Gas analyses were made by absorption and low-temperature fractionation methods (*12*). Tar acids and bases were determined by the reduction in volume of the oil layers on agitation with a 23.5 per cent solution of sodium hydroxide and 10 per cent sulfuric acid, respectively (*12*).

Vertical-Retort Tar

Tar recovered as a by-product in gas manufacture by carbonization of coal was obtained from Chile. The properties of this tar are shown in column 1, Table I; it is representative of those produced in vertical-retort carbonization processes. The acids and bases in this tar were necessarily determined on an 80 per cent overhead distillate. It is estimated that the tar acid content of the whole tar is of the order of 30 per cent. Acids in the original tar falling within the boiling range of phenol and cresylic acid represent approximately 3 per cent by volume of the tar.

During preliminary tests, indications were obtained that in cracking this tar the quantity of tar acids in the lower boiling range increased, probably through partial decomposition of the higher boiling phenolic compounds. Cracking tests, summarized in the first column of Table II, were therefore conducted to produce a maximum yield of the valuable tar acids in the cresylic acid boiling range, together with gasoline, coke, and gas. The fractionating column was controlled to produce a distillate of approximately 430° F. (220° C.) end point in order to include fractions in the gasoline and cresylic acid boiling range. The operating conditions of 250 pounds per square inch with temperatures of 889° F. (476° C.) at the furnace transfer and 835° F. (446° C.) in the reaction chamber are illustrative of the temperatures and pressures used in cracking coal tars.

The 164 pounds of coke produced per barrel of tar from this operation may be considered as a finished product (solid domestic fuel) after screening to size. The low ash content makes this material suitable for reduction to electrode carbon by further processing. The gas is a high B. t. u. value fuel, useful for enriching lean gases or the heavier components of the gas; for example, the pentanes, may be recovered as gasoline whereas the higher olefins (e. g., propene and butenes) may be concentrated for further processing to polymer gasoline or chemical derivatives.

Creosote Oils

In addition to the tar produced in coal carbonization, liquid hydrocarbons are recovered in the creosote oil distillates. Columns 2 and 3, Table I, show the properties of two creosote oils produced by high-temperature carbonization of English coal.

These two creosote oils were separately cracked in single-coil operation to produce gasoline and heavy liquid residue suitable for use as a road oil. In this operation the fractionating column was controlled to produce a distillate of 385–395° F. (196–202° C.) end point. In this manner raw gasoline having the desired boiling range was obtained, and naphthalene, which might crystallize and plug the condenser, was retained in the system for further cracking. In addition, the tar acids which usually occur in high concentrations in the distillate boiling from 390–430° F. (199–221° C.) were also eliminated from the raw gasoline. Detailed results of these tests are shown in Table II. A substantial yield of raw gasoline is obtained from either stock, and the volume of tar acids in the gasoline is much less than that in the original creosote oil.

In the absence of appreciable amounts of water in the products, this apparent loss of phenols may be largely accounted for by polymerization to higher boiling material appearing in the residuum. The residua, while considerably heavier than the original creosote oils, are only slightly more viscous. In addition to use as road oils, these residua are suitable medium-viscosity fuel oils. For this purpose the low sediment (bottoms, settlings, and water) content and low cold test are particularly advantageous.

Low-Temperature Tar

Low-temperature coal carbonization, while less extensively used than high-temperature carbonization, possesses a decided advantage in the yield of liquid hydrocarbons. The production of tar in the low-temperature process is roughly double that obtained in high-temperature operations.

In this study of coal tar cracking, low-temperature tar was represented by a product from Moundsville, W. Va. Because of the poor cracking characteristics of the whole tar as indicated by analysis, it was distilled to remove 54.2 per cent by volume as distillate cracking stock, and a briquetting pitch residue was left. The results of laboratory inspection of both the original tar as well as the distillate cracking stock are shown in Table I.

The distillate from the low-temperature tar was cracked in single-coil operation to produce 410° F. (210° C.) end point raw gasoline with a fuel oil residue. In a second operation 395° F. (202° C.) end point raw gasoline with a coke residue was produced. Columns 4 and 5, Table II, present the results of these tests. Yields in the residuum operation were 38.1 per cent raw gasoline with 50.0 per cent fuel oil residue. In the coking operation the gasoline yield was 51.6 per cent with 139 pounds of coke per barrel of charge. Based on the original low-temperature tar, the gasoline yield in the residuum operation was 20.6 per cent and in the coking run, 27.9 per cent. The high octane ratings shown for the gasolines were calculated from tests on a blend of the coal tar cracked gasoline and a reference fuel of 41 octane number. The residue has the requisite properties of a medium-viscosity fuel oil. The coke is high in volatile content as a result of moderate temperatures in the coke chamber.

Lignite Tar and Its Components

In Europe, particularly in Germany, lignite coal is extensively used through low-temperature carbonization. The relatively large tar yield in this operation lends particular interest to further processing of this product. The properties of two raw lignite tars produced in Germany by low-temperature carbonization of brown coal are shown in columns 6 and 7, Table I. Each of the lignite tars was cracked in a single-coil operation to produce 390–400° F. (199–204° C.) end point gasoline and heavy liquid residues. A detailed summary of the results obtained is given in Table II. The yield of gasoline produced in cracking the 17.5° A. P. I. gravity tar was equivalent to 42.6 per cent by volume of the charge; a 51.4 per cent yield was obtained from the lighter, 19.0° A. P. I. gravity tar. The properties of the gasolines are comparable. However, the liquid residue was considerably heavier in the latter case, which would account for a part of the yield increase, the remainder being attributed to the lighter gravity of the charging stock. As in the case when other coal tar fractions were processed, a portion of original tar acids present in the raw lignite tar are converted to lower boiling tar acids which can be recovered from the gasoline.

In order to investigate further the cracking of German lignite tar, the 19.0° A. P. I. gravity tar was separated into its tar acid and neutral oil components by extraction with an excess of 25 per cent sodium hydroxide solution, followed by treatment with 10 per cent sulfuric acid. In carrying out this treatment, agitation with the reagents was at 150–160° F. (66–71° C.), and a settling time of 8 hours was allowed before withdrawal of the extract. Each treatment was followed by a water wash. The tar acids were recovered from the sodium phenolate solution by neutralization with dilute sulfuric acid and settling.

The neutral tar and the tar acids were separately cracked to produce 390–400° F. (199–204° C.) end point gasoline and heavy liquid residuum. Properties of the neutral tar and tar acids are shown in Table I following the properties of the original 19° A. P. I. gravity tar. Representative yields and analyses of the products are reported in Table II. From examination of the boiling range of the tar acids removed from the 19.0° A. P. I. gravity raw lignite tar, it is evident that the original tar contained less than 1 per cent of tar acids boiling below 400° F. (204° C.). By cracking the whole tar, a 51.4 per cent yield of gasoline distillate was obtained which contained 11.9 per cent tar acids. Thus the yield of tar acids boiling below 400° F. (204° C.) was increased to 6.1 per cent

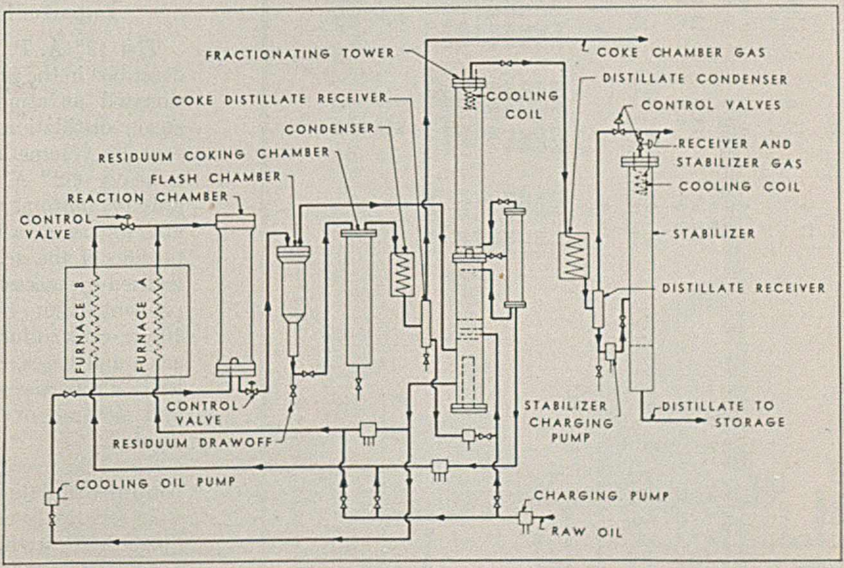


FIGURE 2. TWO-COIL SELECTIVE CRACKING PILOT PLANT FOR RESIDUUM OR COKING OPERATIONS

Table I. Properties of Tars and Distillates from Coals

	Vertical-Retort Coal Tar	Creosote Oil		Low-Temp. Tar		Lignite Tar Components				Lignite Tar Fractions		Coal-Oil Dist.		
		No. 1	No. 2	Original	Overhead dist.	Raw tar		Neutral tar	Tar acids	Acid overhead dist.	Neutral overhead dist.	Untreated	Dephenolated	Untreated
Gravity, ° A. P. I.	2.9	10.1	6.7	−5.9	7.2	17.5	19.0	21.4	9.0	21.6	25.2	14.4	16.8	3.8
Sp. gr., 60° F. (15.6° C.)	1.053	0.999	1.024	1.127	1.020	0.950	0.940	0.925	1.007	0.924	0.903	0.970	0.954	1.046
Viscosity														
Universal, 100° F. (37.8° C.), sec.	601	...	...	...	...	...	...	...	...	...	...	41	39.2	43
Furol, sec.														
77° F. (25° C.)	...	12	10	...	...	...	20	...	...	11	11	...	...	...
122° F. (50° C.)	...	...	...	...	...	13	...	13	27	...	...	...	...	...
Engler, degrees														
100° F.	17.6	...	...	...	...	...	...	...	...	...	...	1.30	1.24	1.34
77° F.	...	1.9	1.34	...	...	...	4.6	...	...	1.61	1.61	...	...	...
122° F.	...	...	...	...	...	2.21	...	2.21	7	...	...	...	...	...
Sulfur, wt. %	0.54	0.92	0.89	2.37	1.99	0.43	0.49	0.47	0.53	0.42	0.41	0.94	0.93	...
Bottoms, settlings, and water, vol. %	1.7	0.2	0.6	...	...	2.2	2.2	0.6	4.8	1.0	0.2	1.2	0.15	1.8
Water, A. S. T. M., vol. %	0.8	...	...	...	...	1.3	Trace	...	1.8	Trace	...	...	...	...
Tar acids, vol. %	35.0[a]	13.0	13.9	...	45.8	22.0	22.5	...	...	27.7	0.0	24.0	<1	35
Tar bases, vol. %	2.0[a]	4.6	6.7	...	1.5	1.6	3.0	...	...	3.0	0.0	3.0	<1	...
Flash point, Pensky Martens, ° F. (° C.)	180 (82.2)	190 (88)	...	...	...	145 (63)	70 (21)	210 (99)	190 (88)	...	...	...	205 (96)	...
Cold test, ° F. (° C.)	80 (26.7)	<0 (<−18)	<0 (<−18)	...	...	80 (27)	70 (21)	85 (29)	90 (32)	70 (21)	60 (16)	<0 (<−18)	<−20 (<−29)	<0 (<−18)
Characterization factor	10.2	...	...	...	...	11.04	...	11.35	10.60	...	...	10.3	10.3	...
100-cc. distillation, ° F. (° C.)														
Initial b. p.	217 (103)	370 (188)	220 (104)	224 (107)	205 (96)	208 (98)	190 (88)	400 (204)	386 (197)	192 (89)	236 (113)	386 (197)	407 (208)	252 (122)
5% over	410 (210)	425 (218)	396 (202)	350 (177)	229 (109)	366 (186)	227 (108)	447 (231)	400 (204)	288 (142)	301 (149)	407 (208)	429 (221)	395 (202)
10	437 (225)	437 (225)	423 (217)	426 (219)	360 (182)	403 (206)	324 (162)	471 (244)	432 (222)	336 (169)	345 (174)	416 (213)	437 (225)	405 (207)
30	544 (284)	481 (249)	458 (237)	570 (299)	448 (231)	507 (264)	458 (237)	572 (300)	530 (277)	447 (231)	510 (266)	439 (226)	461 (238)	424 (218)
50	630 (332)	536 (280)	496 (258)	690 (366)	518 (270)	607 (319)	578 (303)	650 (343)	630 (332)	548 (287)	610 (321)	474 (246)	490 (254)	452 (233)
70	707 (375)	603 (317)	559 (293)	...	614 (323)	662 (350)	670 (354)	693 (367)	680 (360)	659 (348)	702 (372)	528 (276)	544 (284)	505 (263)
90	...	694 (368)	664 (351)	...	750 (399)	724 (384)	698 (370)	...	...	735 (391)	...	659 (348)	643 (339)	667 (353)
End point	756 (402)	715+ (379)	715 (379)	730 (388)	750 (399)	724 (384)	704 (373)	713 (378)	694 (368)	735 (391)	737 (392)	714 (379)	704 (373)	698 (370)
% over	86.0	97.5	99.0	74.0	99.0	95.5	97.5	96.5	90.4	99.5	98.5	97.5	98.0	96.5
% coke by weight	14.1	2.7	1.2	25.9	1.0	4.6	2.6	3.8	9.2	0.7	1.5	2.4	2.3	3.3
% water	0.5	...	...	1.0	3.0	...	...	...	...	...	...	Trace	Trace	...
% at 400° F.	3.0	0.5	5.5	6.5	14.0	8.5	19.5	Trace	2.5	20.0	16.0	6.0	0.5	12.5
% at 572° F.	33.0	61.0	74.0	29.5	59.0	41.0	49.0	30.0	34.5	55.0	42.5	78.5	77.0	79.0

[a] Determined on 80 per cent overhead fraction.

of the original raw lignite tar, and the yield of tar-acid-free gasoline amounted to 45.3 per cent.

The neutral oil is similar in properties to a highly aromatic or naphthenic petroleum stock, and the 52.5 per cent yield of gasoline is approximately the yield that would be expected in cracking a petroleum stock of the same gravity and characterization factor. In cracking the tar acid fraction, a 44.8 per cent yield of distillate containing 21.0 per cent tar acids was obtained. Although the tar acids contained 1.8 per cent water as they entered the cracking plant, water amounting to 5.7 per cent of the charging stock was recovered with the distillate. This particular test indicates that the higher boiling phenolic molecules, of which the tar acid charging stock is chiefly composed, are cracked or partially decomposed to produce hydrocarbons in the gasoline boiling range, together with the production of a considerable amount of lower boiling tar acids and water. The yield of tar acids boiling below 400° F. (204° C.) is equivalent to only 2.1 per cent by volume of the original lignite tar as compared to the 6.1 per cent yield from cracking the whole tar. The combined yield of tar-acid-free gasoline produced in cracking the neutral oil and the tar acid fraction amounts to 46.6 per cent by volume of the original lignite tar as compared to the 45.3 per cent obtained in cracking the whole tar.

The bottoms, settlings, and water precipitate by the regular A. S. T. M. test on the liquid residues was not the same type of material that is precipitated on residues from petroleum stocks, but rather represents a resinouslike component which is insoluble in benzene.

Lignite Tar Fractions

The 19° A. P. I. gravity lignite tar described in the previous tests was fractionated at atmospheric pressure by steam distillation to remove 90.0 per cent by volume as overhead distillate; a heavy 6.3° A. P. I. (1.027 specific gravity) bottoms was left which is suitable for use as a briquetting pitch. A portion of the acid overhead was neutralized by successive treatment with 25 per cent sodium hydroxide solution and 10 per cent sulfuric acid to remove tar acids and bases, and a neutral oil was left. Properties of the acid overhead and neutral overhead are shown in Table I.

The acid overhead distillate and the neutral distillate from the lignite tar were separately cracked in a single-coil operation to produce a high yield of high-antiknock gasoline and liquid residue. Table II presents the results of the cracking tests. When the acid overhead is cracked, an appreciable yield of lower boiling tar acids is produced along with the gasoline.

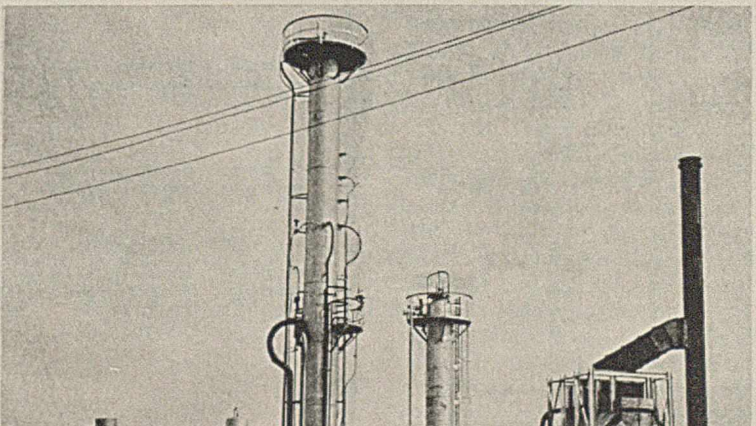
A number of advantages are evident when cracking the neutral overhead in comparison with the distillate containing tar acids. In addition to the reduction in corrosion, a gasoline is obtained which contains less sulfur and requires less treatment, a fuel oil of lower cold test and lower bottoms, settlings, and water content is produced, and greater capacity is obtained when products of similar quality are made. However, the yield of gasoline based on the whole tar is reduced and a negligible yield of tar acid is obtained.

Coal-Oil Distillates

In addition to the well known high- and low-temperature coal carbonization processes, a number of modifications have been proposed and used in commercial-scale operation. Among these are processes for the treatment and conversion of a suspension of pulverized coal in oil. Column 12, Table I, presents the properties of a distillate produced from a coal–petroleum oil blend treated in a special retorting process (*2*). A portion of this distillate was agitated with sodium hydroxide and separated from the alkali by a centrifuge to produce a dephenolated oil. The properties of this oil are shown in Table I.

The original and the dephenolated coal-oil distillates were separately cracked in two-coil operation to produce raw gasoline of 410° F. (210° C.) end point and heavy residuum suitable for mixing with pulverized coal to be charged to carbonization retorts. Typical results are shown in Table II. Comparison of the results on these two oils shows that the dephenolated oil produced practically the same yield of raw gasoline as the original oil. However, the quantity of tar acids present in the raw gasoline is much lower when processing the dephenolated stock, and hence the yield of finished gasoline will be considerably higher. The presence of large quantities of tar acids in the raw gasoline accounts for the high octane rating.

A considerably heavier distillate produced by coking coal in creosote oil rather than petroleum oil was also cracked. The properties of such a coal-oil distillate are given in the last column of Table I. The cracking tests were similar to those discussed in connection with processing the light coal oil distillate. Its high specific gravity made dephenolation difficult, and tests were confined to cracking the original oil only. As would be expected from its greater specific gravity, a smaller raw gasoline yield (39.2 per cent) was obtained. The gasoline contains 27.8 per cent tar acids, equivalent to 10.9 per cent of the charge. Detailed results are shown in Table II. The high percentage bottoms, settlings, and water shown in the residuum is not water or granular sediment such as often occurs with petroleum, but rather a resinous material insoluble in benzene.



Cracking Unit with Capacity of 500 Barrels a Day; Equiflux-Type Furnace to the Right

In order to obtain data on the operation of coal in oil coking processes in connection with cracking where the cracked residue is returned to the retort as a coal suspending medium, the following test was made: Equal parts of pulverized coal and residuum from cracking the heavy coal–creosote oil distillate in the foregoing test were mixed and charged to a small aluminum retort. On heating to 950° F. (510° C.) until no further distillate came over, a yield of distillate amounting to 49.2 per cent by weight of charge was obtained having properties similar to the original heavy coal-oil distillate before cracking. The 47.8 per cent residue was a hard porous coke.

Recovery of Tar Acids and Bases

Although the presence of tar acids in the cracked gasolines in concentrations of 1 per cent and more results in a higher octane product, these acids must be removed during the treating process to obtain a finished gasoline. By chemical treatment these low-boiling tar acids may be recovered as by-products of considerably higher value than the gasoline itself.

Since the raw gasoline produced in cracking the vertical-retort tar contained 30 per cent tar acids, the following procedure was followed in recovering these fractions: The whole cracked distillate was treated in the laboratory to remove the tar acids by successive washes with sodium hydroxide. The resulting sludge was separated and neutralized with sulfuric acid to liberate the tar acids which were then water-washed. The tar-acid-free distillate was subsequently washed with sulfuric acid and the sludge neutralized with sodium hydroxide to recover tar bases.

Table III presents the yields and properties of the tar acids and bases thus recovered. The specific gravity of the gasoline fraction is high and indicates a highly aromatic composition. The boiling range of the tar acid fraction is largely above 360° F. (182° C.), as would be expected from the known boiling points of individual phenols. The tar acids recovered were subsequently distilled to remove a light fraction; a heavier residue remained which had a specific gravity and boiling range corresponding to a commercial cresylic acid used in the flotation refining of copper ores. This fraction represents 12.9 per cent of the vertical-retort tar, an increase of approximately 10 per cent in cresylic acid yield by cracking as expressed on the basis of the original tar. Detailed yields and properties of the tar acid fractions are also shown in the second section of Table III. Approximately 70 per cent of the crude cresylic acid fraction is within the boiling range, 374–403° F. (190–206° C.), which corresponds to the cresols.

By similar treatment the tar acid fractions may be recovered from the gasolines produced in cracking the various tars and distillates from coal.

Additional Treatment of Cracked Gasolines

After removal of the tar acids and bases, additional treatment of the distillates is required in order to produce a marketable gasoline. An outline of the method used in treating the gasoline produced by cracking the vertical-retort tar follows: After removal of the tar acids and bases, the cracked gasoline was agitated with 93 per cent sulfuric acid in the proportion of 5 pounds of acid per barrel of gasoline while the temperature was maintained at 30° to 40° F. (−1.1° to +4.4° C.). The gasoline was then separated from the acid sludge, neutralized with sodium hydroxide, rerun using a fire and steam distillation, and sweetened with sodium plumbite solution. An inspection of the gasoline free from tar acids and bases and of the acid-treated product are reported in columns 1 and 2 of Table IV. In order to investigate the blending characteristics the treated gasoline was blended with a commercial regular-grade gasoline, the blend containing 8 per cent by volume of the coal tar product. Inspections of the commercial gasoline and the blend shown in Table IV indicate that the copper-dish gums, sulfur content, and specific gravity of the commercial gasoline were increased while the storage stability as indicated by the induction period was improved by the addition of the cracked coal tar gasoline.

The treated gasoline was also blended with an 82-octane-number commercial polymer gasoline; the proportions were used which would be produced in cracking the vertical-retort tar, and the gases were polymerized by the catalytic process. The blend consisting of 97 per cent cracked coal tar gasoline and 3 per cent poly-

TABLE II. PILOT-PLANT CRACKING RESULTS

						Lignite Tar Components				Lignite Tar Fractions		Coal Oil Dist.		
	Vertical-Retort Tar	Creosote Oils		Low Temp. Tar		Raw tar								
		No. 1	No. 2	Overhead	Dist.	17.5°	19.0°	Neutral tar	Tar acids	Acid overhead	Neutral overhead	Untreated	Dephenolated	Untreated
Type of residue produced	Coke	Liquid	Liquid	Liquid	Coke	Liquid residuum								
Operating conditions														
Pressure, lb./sq. in.														
Heavy oil cracking coil	250	250	250	200	200	250	200	200	200	200	200	250	250	205
Light oil cracking coil	...	...	...	...	...	...	...	...	...	...	...	300	350	350
Reaction chamber	208	250	250	200	200	250	200	200	200	200	200	250	250	204
Flash chamber	50	53	25	51	51	50	50	50	50	50	50	50	50	50
Temperature, ° F. (° C.)														
Heavy oil transfer	889 (476)	885 (474)	875 (468)	904 (484)	890 (477)	900 (482)	900 (482)	900 (482)	900 (482)	900 (482)	925 (496)	880 (471)	890 (477)	858 (459)
Light oil transfer	...	...	...	...	...	...	...	...	...	...	...	950 (510)	969 (521)	951 (511)
Reaction chamber	835 (446)	836 (447)	825 (441)	853 (456)	840 (449)	850 (454)	850 (454)	850 (454)	850 (454)	850 (454)	876 (469)	865 (463)	885 (474)	875 (468)
Raw oil charge rate, gal. (liters)/hr.	0.96 (3.63)	0.41 (1.52)	0.26 (0.98)	0.27 (1.02)	0.11 (0.42)	1.11 (4.20)	0.94 (3.55)	0.59 (2.23)	0.77 (2.91)	0.73 (2.76)	0.66 (2.50)	0.27 (1.02)	0.31 (1.17)	0.23 (0.87)
Yield, vol. % of charge														
Gasoline	53.1	29.9	21.5	38.1	51.6	42.6	51.4	52.5	44.8	55.7	58.8	49.2	49.7	39.2
Liquid residuum	0.0	64.7	75.5	50.0	0.0	51.9	41.1	39.7	41.4	34.1	29.4	43.9	38.8	52.0
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0	0.0	0.8	0.0	Trace
Recovery	53.1	94.6	97.0	88.1	51.6	94.5	92.5	92.2	91.9	89.8	88.2	93.9	88.5	91.2
Liquid vol. loss	46.9	5.4	3.0	11.9	48.4	5.5	7.5	7.8	8.1	10.2	11.8	6.1	11.5	8.8
Yield, wt. % of charge														
Gasoline	45.3	23.7	18.5	33.1	42.9	35.1	43.8	43.2	36.4	47.0	49.3	42.0	41.5	34.8
Liquid residuum	0.0	68.5	77.8	53.7	0.0	56.8	46.5	44.3	44.3	38.2	35.0	49.6	45.0	54.4
Coke	44.6	0.0	0.0	0.0	39.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Receiver and stabilizer gas	2.9	4.0	1.0	5.9	9.8	7.4	7.8	10.9	11.4	7.9	13.1	9.8	13.0	8.0
Coke chamber gas	4.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0	0.0	0.8	0.0	Trace
Recovery	96.9	96.2	97.3	92.7	92.5	99.3	98.1	98.4	97.8	93.1	97.4	102.2	99.5	97.2
Exptl. error	−3.1	−3.8	−2.7	−7.3	−7.5	−0.7	−1.9	−1.6	−2.2	−6.9	−2.6	+2.2	−0.5	−2.8
Gas, cu. ft./lb. of charge	1.18	0.586	0.154	0.859	1.85	0.930	1.17	1.60	1.67	1.16	1.76	1.20	1.63	1.17
Analysis of products														
Untreated gasoline														
Gravity, ° A. P. I.	25.8	47.0	29.0	28.2	35.6	44.6	44.9	54.4	41.8	47.1	55.3	39.6	46.6	21.0
Sp. gr., 60° F. (15.6° C.)	0.900	0.793	0.882	0.886	0.847	0.803	0.802	0.761	0.816	0.792	0.757	0.827	0.795	0.928
Sulfur, % by wt.	...	0.59	0.46	1.43	...	...	0.41	0.23	0.36	0.39	0.25	...	...	0.34
Tar acids, % by vol.	30.0	5.8	11.4	23.5	18.0	13.1	11.9	1.6	21.0	10.8	1.3	19.1	4.4	27.8
Tar bases, % by vol.	2.7	1.3	1.8	1.0	1.3	2.8	0.4	Trace	0.0	0.4	Trace	1.0	1.9	1.4
Reid vapor pressure, lb./sq. in.	4.8	...	...	...	...	...	...	...	...	...	...	9.3	9.2	...
Octane No.														
Research method	...	...	...	126	114	88	87	77	90	85	84	...	...	...
Motor method	...	76	85	108	...	...	...	...	...	...	...	86	76	85
100-cc. A. S. T. M. distn., ° F. (° C.)														
Initial b. p.	157 (69)	104 (40)	145 (63)	156 (69)	135 (57)	98 (37)	108 (42)	100 (38)	122 (50)	112 (44)	113 (45)	120 (49)	104 (40)	94 (34)
10% over	213 (101)	167 (75)	278 (137)	207 (97)	218 (103)	164 (73)	170 (77)	158 (70)	167 (75)	171 (77)	161 (72)	173 (78)	168 (76)	172 (78)
20	348 (176)	215 (102)	301 (149)	290 (143)	267 (131)	216 (102)	216 (102)	202 (94)	231 (111)	210 (99)	194 (90)	225 (107)	206 (97)	256 (124)
50	369 (187)	293 (145)	330 (166)	340 (171)	316 (158)	304 (151)	296 (147)	293 (145)	323 (162)	286 (141)	263 (128)	317 (158)	292 (144)	353 (178)
90	400 (204)	354 (179)	366 (186)	380 (193)	364 (184)	365 (185)	380 (193)	370 (188)	377 (192)	364 (184)	335 (168)	389 (198)	385 (196)	392 (200)
End point	432 (222)	386 (197)	395 (202)	409 (209)	395 (202)	394 (201)	403 (206)	392 (200)	392 (200)	391 (199)	361 (183)	416 (213)	413 (212)	425 (218)

Residuum														
Gravity, ° A. P. I.	...		1.5	2.6	−2.5	...	4.8	1.5	5.7	−0.1	2.9	0.4	−2.5	−3.8	−2.2
Sp. gr., 60° F. (15.6° C.)	...		1.064	1.055	1.097	...	1.038	1.064	1.031	1.077	1.053	1.073	1.097	1.108	1.094
Viscosity															
Furol, 122° F., sec.	...		18	13	74	...	63	602	206	1430	262	157	64	38	30
Engler, 50° C., degrees	...		4.0	2.2	21	...	18	171	59	410	73	43	18	11	8
Bottoms, settlings, water, %	...		0.4	0.2	...	...	2.0	10.0	12.0	20.0	4.2	0.4	1.6	0.3	33.3
Sediment benzene ext., %	...		...	...	...	...	...	...	...	...	...	...	1.08	1.31	...
Carbon residue, %	...		...	...	...	...	...	...	...	...	...	...	16.5	16.5	15.7
Cold test, ° F. (° C.)	...		<0 (<−18)	<0 (<−18)	35 (1.7)	...	65 (18)	70 (21)	60 (16)	95 (35)	65 (18)	45 (7)	30 (−1.1)	50 (10)	
Flash, Pensky Martens, ° F. (° C.)	...		205 (96)	200 (93)	200 (93)	...	260 (127)	300 (149)	170 (77)	170 (77)	155 (68)	220 (104)	176 (80)	...	
100-cc. distillation															
Initial b. p., ° F. (° C.)	...		439 (226)	424 (218)	456 (236)	...	455 (235)	490 (254)	438 (226)	461 (238)	453 (234)	428 (220)	410 (210)	...	
% at 572° F. (300° C.)	...		30.0	57.0	30.0	...	13.0	7.0	13.0	17.0	16.5	16.0	35.0	...	
Coke, proximate analysis, wt. %															
Moisture	0.40		...	...	...	0.60	...	...	...	...	...	...	...	...	...
Volatile matter	7.74		...	...	...	27.19	...	...	...	...	...	...	...	...	...
Ash	0.44		...	...	...	1.05	...	...	...	...	...	...	...	...	...
Fixed carbon (by diff.)	91.42		...	...	...	71.16	...	...	...	...	...	...	...	...	...
Gas compn., mole %															
Noncondensables and methane	59.2[a]	77.2[b]	...	...	...	...	...	56.6	50.5	61.4	60.7	63.0	43.5	41.7	...
Ethylene	1.7	0.8	...	...	...	...	...	10.3	10.2	5.8	3.2	2.3	4.9	5.2	...
Ethane	14.5	10.8	...	...	...	...	...	6.5	7.8	10.5	6.9	10.7	13.4	15.6	...
Propylene	3.8	1.6	...	...	...	...	...	3.3	13.6	7.0	13.9	7.0	9.1	9.3	...
Propane	11.1	3.9	...	...	...	...	...	14.4	8.9	9.5	7.8	7.7	14.2	16.0	...
Butylenes	2.5	2.2	...	...	...	...	...	...	...	...	...	...	6.1	4.6	...
Butanes	3.7	1.6	...	...	...	...	...	6.1[c]	7.5[c]	4.5[c]	5.6[c]	6.3[c]	4.6	3.6	...
Pentanes and heavier	3.5	1.9	...	...	...	...	...	2.8	1.5	1.3	1.9	3.0	4.2	4.0	...
Total	100.0	100.0	...	...	...	...	...	100.0	100.0	100.0	100.0	100.0	100.0	100.0	...
Sp. gr. (air = 1.00)	0.90	0.72	...	...	...	...	...	...	...	...	...	0.98	1.07	1.05	...
Calorific value															...
B. t. u./cu. ft.	1440	1120	...	...	...	...	...	...	...	...	...	1740	1725	1710	...
Kg.-cal./cu. meter	160	124	...	...	...	...	...	...	...	...	...	193	192	190	...

[a] Receiver and stabilizer gas. [b] Coke chamber gas. [c] Total C_4 fractions.

Table III. Recovery of Tar Acids and Bases

Yield, vol. % of cracked dist.		
Gasoline	67.3	
Tar acids	30.0	
Tar bases	2.7	
Total	100.0	
Yield, vol. % of coal tar		
Gasoline	35.7	
Tar acids	15.9	
Tar bases	1.5	
Total	53.1	
Properties of gasoline free of tar acids and bases		
Gravity, ° A. P. I.	35.5	
Specific gravity, 60° F. (15.6° C.)	0.8473	
Sulfur, % by weight	0.50	
Octane No., A. S. T. M. motor method	69	
100-cc. A. S. T. M. distillation, ° F. (° C.)		
Initial b. p.	139 (59)	
10% over	254 (123)	
50	370 (188)	
90	412 (211)	
End point	440 (227)	
% over	98.0	
% bottoms	1.0	
% loss	1.0	
Properties of tar acids and bases	Acids	Bases
Gravity, ° A. P. I.	9.0	24.2
Specific gravity, 60° F. (15.6° C.)	1.0071	0.9088
Preparation of Cresylic Acid Fraction		
Yield, vol. % of tar acids		
Light tar acids	15.7	
Cresylic acid fraction	81.3	
Water	3.0	
Total	100.0	
Yield, vol. % of coal tar		
Light tar acids	2.5	
Cresylic acid fraction	12.9	
Water	0.5	
Total	15.9	
Properties of tar acid fractions	Light tar acids	Cresylic acid fraction
Gravity, ° A. P. I.	23.4	6.5
Specific gravity, 60° F. (15.6° C.)	0.9135	1.0253
100-cc. distillation, ° F. (° C.)		
Initial b. p.	....	372 (189)
5% over	....	382 (194)
10	....	384 (196)
30	....	390 (199)
50	....	395 (202)
70	....	403 (206)
90	....	416 (213)
End point	Below 374 (190)	437 (225)
% over	....	99.0
% coke by weight	....	1.0

mer had an octane rating one point higher than the straight-cracked coal tar gasoline.

During the acid treatment at reduced temperatures, naphthalene crystallized out on the sides of the treating vessel. In rerunning the acid-treated gasoline, it was necessary to operate with a warm condenser toward the end of the distillation in order to prevent solidification of the naphthalene. In anticipation of difficulties from this source in the commercial production of a high end point gasoline from cracking coal tars, the untreated distillate free from tar acids and bases was rerun to yield 75 per cent by volume of 410° F. (210° C.) end point gasoline; it was thus separated from the material in the naphthalene boiling range. The 25 per cent bottoms from rerunning the cracked distillate were composed of approximately 33 per cent of crude naphthalene; the remainder was a dark reddish liquid at room temperature, which became solid at reduced temperatures.

Similar treatment of the gasolines produced in cracking the creosote oils with larger proportions of sulfuric acid resulted in finished products of better than water-white (22+° Saybolt) color, which contained only 0.21 per cent sulfur and had a low gum content with satisfactory storage stability. The high motor-method octane rating of the treated gasoline from creosote oil 2 makes this fuel particularly valuable as a blending agent with lower octane gasolines. Complete treating results are shown in Table IV.

The properties of the acid-treated cracked gasoline produced from the low-temperature tar show excellent antiknock value, good color, and fair gum, and the sulfur content is considerably above that usually accepted. It appears that the sulfur compounds present in this gasoline are particularly resistant to removal by sulfuric acid. In view of the high antiknock value of the final gasoline, it could be most advantageously used as a blending agent with a gasoline of lower sulfur content and antiknock rating.

After removal of the tar acids and bases, the cracked gasoline produced from the 17.5° A. P. I. gravity raw lignite tar was treated by two methods: (*a*) by agitation with 6 pounds of 93 per cent sulfuric acid per barrel of gasoline and (*b*) treatment in the vapor phase with brass turnings in the presence of hydrochloric acid. The latter method is known as the U. O. P. treating process. The acid-treated gasolines in each case were rerun in a fire and steam distillation to remove polymers and were sweetened with sodium plumbite solution. Results are shown in Table IV. The treated gasolines are better than 22° Saybolt color and have reasonable sulfur content and good octane rating. The addition of a small quantity of inhibitor ensures good stability.

Table IV also gives the results of additional treatment on the gasolines free from tar acids and bases, from each of the various lignite tar cracking stocks; 93 per cent sulfuric acid was used in the proportions indicated.

Treating tests were conducted on the gasolines produced in cracking both the 14.4° A. P. I. gravity untreated and the dephenolated coal-oil distillate. The properties of the cracked gasolines after removal of tar acids and bases, together with the properties of the treated products, are reported in the last four columns of Table IV. The treating results show final yields of acid-treated gasoline from the original and dephenolated oils of 36.1 and 43.2 per cent, respectively, with octane ratings of 72 and 73. In spite of the large differences in density and other properties between the raw gasolines from the two types of charge, the final treated gasolines have similar characteristics. They are satisfactory motor fuels, although the sulfur content is greater than is permitted by some specifications.

To demonstrate the value of the acid-treated gasoline from coal-oil distillate in a blend with one of inferior octane number, a 43-octane-number mid-continent straight-run gasoline was blended with each of the cracked gasolines in the proportion of four parts of straight-run gasoline to one part of cracked gasoline. The octane number of the resulting blend

TABLE IV. TREATMENT OF CRACKED GASOLINES FROM COAL TARS AND DISTILLATES

Cracking stock	Vertical-Retort Tar				Creosote Oil No. 1	Creosote Oil No. 2	Low-Temp. Tar, Overhead and Dist.	Lignite Tar Components					Lignite Tar Fractions		Coal-Oil Dist.			
			Commercial regular grades	Blend 8% coal tar gasolines				Raw lignite tar			Neutral tar	Tar acids	Acid overhead dist.	Neutral overhead dist.	Un-treated	14.4° A. P. I.	Dephenolated	
								17.5		19.0								
Preliminary treatment	Tar acids and bases removed				Tar acids and bases removed													
Additional treatment	None	Acid	...	...	Acid	Acid	Acid	Acid	U. O. P.	Acid	Acid	Acid	Acid	Acid	None	Acid	None	Acid
Acid																		
Lb./bbl. gasoline	...	5	...	...	15	15	8	6	...	14	8	14	10	8	...	1	...	1
Wt. % gasoline	...	1.7	...	...	5.4	4.9	2.6	2.1	...	5.0	3.0	4.9	3.6	2.9	...	0.35	...	0.36
Treating losses, vol. %																		
Tar acids removed	30.0	30.0	...	...	5.8	11.4	23.5	13.1	13.1	11.9	1.6	21.0	10.8	1.3	19.1	19.1	4.4	4.4
Tar bases removed	2.7	2.7	...	...	1.3	1.8	1.0	2.8	2.8	0.4	0.0	0.0	0.4	0.0	1.0	1.0	1.9	1.9
Acid soln. loss	...	1.4	...	...	3.8	4.3	2.6	2.4	...	4.1	2.6	4.8	3.3	2.3	...	1.6	...	1.5
Polymerization loss	...	1.2	...	...	2.8	2.9	4.8	1.0	...	2.2	1.3	2.5	0.9	2.4	...	1.9	...	2.0
Distn. loss	...	0.0	...	...	0.0	0.9	0.5	2.0	...	3.6	4.0	3.1	3.5	4.2	...	3.0	...	3.2
Total loss	32.7	35.3	...	...	13.7	21.3	32.4	21.3	...	22.2	9.5	31.4	18.9	10.2	20.1	26.6	6.3	13.0
Treated gasoline yield, vol. % of cracking stock	35.7	34.4	...	...	25.8	16.9	25.8	33.6	...	39.9	47.5	30.7	45.2	52.7	39.3	36.1	46.6	43.2
Properties of treated gasoline																		
Gravity, ° A. P. I.	35.5	37.6	59.6	57.5	50.3	36.2	41.8	52.8	52.7	46.4	55.4	52.0	51.3	55.9	47.5	50.3	46.9	49.4
Sp. gr., 60° F.	0.847	0.836	0.740	0.749	0.778	0.844	0.816	0.768	0.768	0.795	0.757	0.771	0.774	0.755	0.790	0.778	0.793	0.782
Color, ° Saybolt	Black	15	Red	Red	30+	26	24	23	25	22	23	27	23	28	Red	25	Yellow	25
Color stability[a]	...	...	...	...	20	20	...	22	18	16	21	10	18	26	...	15	...	15
Sulfur, % by wt.	0.50	0.44	0.05	0.09	0.21	0.21	1.20	0.35	0.31	0.39	0.19	0.29	0.36	0.26	0.47	0.41	0.39	0.36
Doctor test	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Pos.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Corrosion, 122° F.	...	...	Neg.	Neg.	...	...	...	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	...	...	...	...
Gums, A. S. T. M.	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	4	...	3
Gums, Cu dish, mg./100 cc.																		
Without inhibitor	...	242	11	18	5	5	50	530	56	125	157	23	80	252	...	32	...	78
With inhibitor	...	...	...	...	...	...	...	12	...	14	5	8	12	19	...	...	...	...
Oxygen-bomb induction period, min.	...	1020	420	570	490	800+	...	...	...	...	...	...	...	...	...	865	...	430
Octane No.																		
Research method	...	...	...	...	...	...	97	75	77	79	73	65	73	76	...	...	...	...
Motor method	69	67	70	69.5	73	81	85	...	...	...	...	...	...	...	74	72	74	73
100-cc. A. S. T. M. distn., ° F. (° C.)																		
Initial b. p.	139 (59)	149 (65)	110 (43)	118 (48)	120 (49)	155 (68)	141 (61)	100 (43)	108 (42)	127 (53)	114 (46)	128 (53)	123 (51)	116 (47)	104 (40)	116 (47)	100 (38)	104 (40)
10% over	254 (123)	251 (122)	166 (74)	170 (77)	180 (82)	281 (138)	230 (110)	177 (81)	176 (80)	182 (83)	163 (73)	182 (83)	178 (81)	160 (71)	168 (76)	174 (79)	155 (68)	157 (69)
20	...	...	...	...	219 (104)	303 (151)	260 (127)	210 (99)	214 (101)	223 (106)	199 (93)	220 (104)	212 (100)	188 (87)	...	...	...	...
50	370 (188)	357 (181)	259 (126)	266 (130)	287 (142)	327 (164)	310 (154)	292 (144)	288 (142)	302 (150)	277 (136)	296 (147)	280 (138)	245 (118)	292 (144)	280 (138)	288 (142)	278 (137)
90	412 (211)	402 (206)	355 (179)	368 (187)	342 (172)	351 (177)	364 (184)	356 (180)	360 (182)	376 (191)	356 (180)	372 (189)	360 (182)	308 (153)	372 (189)	375 (191)	383 (195)	378 (192)
End point	440 (227)	424 (218)	399 (204)	405 (207)	371 (188)	379 (193)	398 (203)	389 (198)	390 (199)	402 (206)	390 (199)	400 (204)	394 (201)	362 (183)	440 (227)	408 (209)	426 (219)	414 (212)

[a] Color after exposure equivalent to 2 hours midday June sunlight.

was 53 in each case, and the calculated blending octane value of the cracked gasolines in these blends was 93 octane number. Since the straight-run gasoline contained only 0.04 per cent sulfur, the sulfur content of the blends was as low as 0.11 per cent and the gums were only 4 mg.

Corrosion

It was anticipated and confirmed by experience during the foregoing tests that corrosion would be a problem in cracking coal tars and distillates containing tar acids and bases. Following preliminary trials, to minimize corrosion, all equipment in which cracking temperatures were maintained was made of 18–8 stainless steel, including tubes and headers of the cracking furnace and the entire reaction chamber. Some tests were conducted using tubes of 4–6 per cent chromium with 0.5 per cent molybdenum. Because of intermittent operation and relatively short test periods (20–30 hours), interspersed with operation on petroleum oils, no definite conclusions may be drawn from the service record of this equipment. Excessive corrosion of the alloy parts was not experienced, however.

TABLE V. CORROSION BY COAL TARS AND DISTILLATES

	Neutral Lignite Tar	Raw Lignite Tar	High-Temp. Coal Tar	Dephenolated Coal Oil Dist.
Tar acid content, vol. %	Trace	22.5	28+	Below 1
Sulfur, wt. %	0.47	0.49	0.54	0.93
Reaction chamber conditions				
Temp., ° F.	850	850	835	885
Temp., ° C.	454	454	446	474
Pressure, lb./sq. in.	200	200	208	250
Pressure, atm.	13.6	13.6	14.1	17.0
Test metal penetration rate, inch/month				
Mild steel	0.02684	0.0295	0.0127	0.009
18–8 (18% Cr, 8% Ni, 0.2% C)	0.00814	0.00882	0.00125	
No. 2825 (28% Cr, 0.25% C)	0.00476	0.00075		
Cyclops 17 B (7.25% Cr, 19.3% Ni, 0.15% C)	0.00659	0.01249		
No. 1809 (17.25% Cr, 0.09% C)	0.00173	0.00789		
Excelloy (12% Cr)	0.00343	0.0051		
24–11 (24% Cr, 11% Ni)	0.00595	0.00224		
Cyclops 17A (7.25% Cr, 19.3% Ni, 0.41% C)	0.00419	0.01003		

To obtain information on the relative corrosion rates of various coal tars and distillates, the corrosion test procedure proposed by Calcott (*4*) was applied. Weighed test strips of mild steel and various alloys were suspended in the reaction chamber during a test run. After the run, the surfaces of the test strips were ground to the level of the deepest pit and the strips reweighed. From the duration of cracking temperatures during the test and the area and loss in weight of the test strip, corrosion was calculated to inches penetration per month. Results of a number of tests on various alloys with several of the coal tars are shown in Table V. Because of differences between pilot-plant and commercial operation with respect to temperature and duration of runs, these results must be considered as relative only. Although the high-chromium steels appear to best advantage, their hardness makes fabrication difficult. The availability and workability of 18–8 stainless steel and its excellent physical properties when properly stabilized tend to favor this alloy for service in equipment for cracking coal tars.

Behavior of Tar Acids in Cracking

The wide utility and high market value of the lower boiling phenols make the behavior of these materials in cracking of particular interest. The lower boiling phenols, in order of their boiling points, are as follows:

	° F.	*° C.*		*° F.*	*° C.*
Phenol	360	182	Guaiacol	401	205
o-Cresol	376	191	Ethylphenols	406–426	208–219
m-Cresol	397	203	Xylenols	414–437	212–225
p-Cresol	397	203	Cresol	432	222

These compounds find many uses; among them are solvent refining of lubricating oils and inhibiting cracked gasolines (*7*), production of synthetic resins (*5*, *10*), as an absorbent in benzene recovery (*6*), as a disinfectant, and in the production of synthetic tannins (*10*), and for the manufacture of synthetic dyes, perfumes, and explosives (*11*).

Reviewing the results of cracking the various coal tars and distillates, the following will be noted: The concentration of tar acids in the distillate varies with the proportion of distillate in the boiling range of about 390–430° F. (199–221° C.), or the range of most of the lower boiling phenols. The concentration of these compounds may be increased to exceed that in the charging stock, which indicates that the higher boiling phenols are decomposed to lower boiling phenols, as well as hydrocarbon fractions in the gasoline boiling range.

Comparison of Coal Tar and Petroleum Cracking

Direct comparison of cracking coal tars and distillates with petroleum fractions is not practicable because of the wide variation in results between individual samples of either type. For petroleum cracking, gasoline, residue, and gas yields may be roughly related to density of the charge for normal stocks in any particular type of operation. Extrapolating a mean plot of such a relationship to the range of density of coal tars and distillates indicates that finished gasoline yields and gas production from the coal tars are somewhat greater than would be anticipated from the plot. Plant capacity is from one half to one tenth that obtained with petroleum stocks, and operating conditions, limited by coke deposition, are milder. The raw cracked gasolines are of high specific gravity and high octane number. On treatment the specific gravity decreases and the octane number falls to a varying degree. The final gasoline from coal tars in comparison with a petroleum cracked gasoline, is higher in density, and usually higher in antiknock quality, and has a very high oxygen bomb stability, apparently because of naturally occurring inhibitors. Sulfur reduction in treatment is difficult with these gasolines, and gum reduction requires attention.

The gas, although somewhat greater than in petroleum cracking, is lower in density and heating value; it lies intermediate between dry natural gas and normal cracking plant gas. This difference is mainly due to a larger proportion of hydrogen and methane. By fractionation, useful concentrations of the higher olefin and paraffin constituents may be obtained for further processing to motor fuel by catalytic polymerization.

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High-Pressure Vapor-Liquid Equilibrium

For the Systems Propylene-Isobutane and Propane–Hydrogen Sulfide

E. R. GILLILAND AND H. W. SCHEELINE[1]
Massachusetts Institute of Technology, Cambridge, Mass.

By means of an apparatus and experimental technique described in a previous article (*13*), *P-T-x-y* data have been obtained on the propylene-isobutane and hydrogen sulfide–propane systems. A comparison between experimental values and those calculated from the *K*-charts indicate that the latter are in considerable error in the critical region. A general empirical correlation is presented for predicting phase equilibrium data for two-component hydrocarbon systems in the critical region.

A PREVIOUS paper (*13*) described an apparatus and experimental technique for obtaining high-pressure phase equilibrium data, and reported data on the propane-isobutylene system. The present article includes a presentation of the results of experimental work on two more systems, propylene-isobutane and hydrogen sulfide–propane, as well as a general correlation which has been developed for predicting phase equilibrium data for two-component hydrocarbon systems in the critical region. The apparatus and experimental technique were the same as described in the previous article.

Materials and Analytical Procedure

The isobutane was C. P. grade (Phillips Petroleum Company) and was reported to contain 99.5 per cent isobutane and 0.5 per cent *n*-butane. It showed no absorption in strong bromine water. Propylene was prepared by the dehydration of isopropyl alcohol over activated alumina. It was liquefied and stored in cylinders. The propylene was absorbed to the extent of 99.5 per cent in strong bromine water. The propane was C. P. grade (Phillips Petroleum Company) and was reported to contain 99.9 per cent propane. It showed no absorption in bromine water, sulfuric acid, or caustic. The hydrogen sulfide was also C. P. grade (Matheson Company).

For all three of the hydrocarbons, vapor pressure data were obtained from room temperature up to their respective critical points. In all cases these data were in excellent agreement with values recommended in the literature (*2*, *5*).

Mixtures of propylene and isobutane were analyzed by absorbing the olefin in bromine water. A strong solution of bromine in 5 per cent potassium bromide was adopted and used in a standard type Orsat apparatus. The gas was bubbled rapidly three times through the bromine solution, then four times through 40 per cent sodium hydroxide to remove bromine fumes. Care was taken not to expose the apparatus to direct sunlight or to allow the gas to remain in contact with bromine for too long a time, as some absorption of isobutane could be detected under these conditions. A small correction, based on the data of Jessen and Lightfoot (*6*) was made for deviations of the gas mixtures from the perfect gas laws. Duplicate samples were run in all cases.

For mixtures of hydrogen sulfide and propane, the analytical technique recommended in the U. S. Steel Handbook (*15*) was adopted. It consisted of absorbing the hydrogen sulfide in a caustic solution and measuring the volume of the unabsorbed propane. The absorbed hydrogen sulfide was determined by titration with standard iodine and sodium thiosulfate.

Experimental Results

Table I gives the experimental vapor pressure data on the three pure hydrocarbons studied. The first five columns of Tables II give the results of the original measurements on propylene-isobutane and hydrogen sulfide–propane. Data on these mixtures were obtained at pressures sometimes deviating slightly from even multiples of 100 pounds per square inch. For convenience in using the data, small adjustments were made in the following manner: From the experimental points large-scale plots of *x vs. y* and *x vs.* temperature were constructed, with the average pressure of a series of runs as a parameter. At a given value of *x*, increments in *y* and temperature between two successive pressure curves were measured, and fractional parts of these increments were added to or subtracted from the experimental values, to correspond to a pressure correction to an even multiple of 100 pounds per square inch. The adjusted points so obtained are given in the last four columns of Table II.

TABLE I. VAPOR PRESSURE DATA[a] ON INDIVIDUAL HYDROCARBONS

Propane						
Temp.	107	135	162	184	210[b]	
Pressure	204	294	398	494	636[b]	
Propylene						
Temp.	93	125	151	172	192	203[b]
Pressure	205	297	401	494	604	675[b]
Isobutane						
Temp.	174	211	241	266	274[b]	
Pressure	198	290	395	493	535[b]	

[a] Temperature in ° F., pressure in lb./sq. in. abs.
[b] Critical point.

In all cases the corrections were small, so that practically any method of making the adjustments would yield identical results. The best smooth curves were finally drawn through the adjusted points. These curves are presented in Figures 1 to 4; values read from them are given in Table III.

The data on the propylene-isobutane system cover all ranges of liquid composition at pressures from 200 to 600 pounds per square inch. It is believed that values given in Table III*A* conform to the following limits of accuracy:

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[1] Present address, Standard Oil Development Company, Elizabeth, N. J.

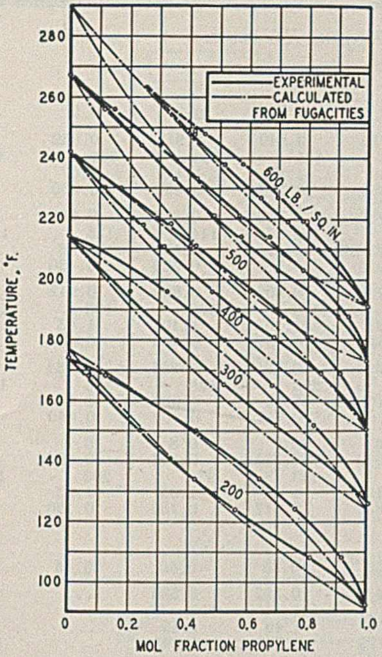

Figure 1. Temperature-Composition Diagrams at Constant Pressure for Propylene-Isobutane

Table II. Original and Adjusted Experimental Data

Exptl. Points				Adjusted Points			
Abs. Pressure Lb./sq. in.	Temp. ° F.	x_{C_3}	y_C	Abs. Pressure Lb./sq. in.	Temp. ° F.	x_{C_3}	y_{C_3}
			Propylene-Isobutane				
197	167	0.065	0.118	200	168	0.065	0.118
199	155	0.206	0.337	200	155	0.206	0.337
200	150	0.238	0.423	200	150	0.238	0.423
198	134	0.419	0.637	200	134	0.419	0.636
200	124	0.555	0.747	200	124	0.555	0.747
199	108	0.810	0.916	200	108	0.810	0.916
293	194	0.200	0.323	300	196	0.200	0.321
297	179	0.353	0.516	300	180	0.353	0.515
296	164	0.515	0.678	300	165	0.515	0.677
297	151	0.691	0.817	300	152	0.691	0.816
298	139	0.848	0.927	300	140	0.848	0.927
395	229	0.113	0.169	400	230	0.113	0.168
395	219	0.204	0.290	400	220	0.204	0.289
394	217	0.242	0.340	400	218	0.242	0.338
399	211	0.297	0.398	400	211	0.297	0.398
394	210	0.313	0.421	400	211	0.313	0.419
390	194	0.475	0.604	400	196	0.475	0.600
396	189	0.562	0.692	400	190	0.562	0.691
393	179	0.681	0.796	400	181	0.681	0.794
396	168	0.846	0.910	400	169	0.846	0.909
490	254	0.111	0.148	500	256	0.111	0.146
493	242	0.234	0.302	500	244	0.234	0.298
496	232	0.348	0.421	500	233	0.348	0.419
494	220	0.476	0.568	500	221	0.476	0.566
492	212	0.570	0.668	500	214	0.570	0.665
496	202	0.694	0.780	500	203	0.694	0.779
491	186	0.899	0.935	500	188	0.899	0.935
600	249	0.385	0.412	600	249	0.385	0.412
591	246	0.410	0.452	600	248	0.410	0.446
592	236	0.515	0.577	600	238	0.515	0.572
594	226	0.633	0.696	600	227	0.633	0.692
594	218	0.723	0.780	600	219	0.723	0.777
595	209	0.828	0.870	600	210	0.828	0.868
			Hydrogen Sulfide–Propane				
		x_{H_2S}	y_{H_2S}			x_{H_2S}	y_{H_2S}
401	154	0.037	0.122	400	154	0.037	0.123
400	149	0.054	0.159	400	149	0.054	0.159
400	129	0.241	0.379	400	129	0.241	0.379
400	124	0.332	0.499	400	124	0.332	0.499
501	180	0.014	0.021	500	180	0.014	0.021
500	170	0.081	0.130	500	170	0.081	0.130
500	145	0.395	0.547	500	145	0.395	0.547
601	201	0.055	0.076	600	201	0.055	0.077
601	197	0.078	0.101	600	197	0.078	0.102
600	173	0.342	0.451	600	173	0.342	0.451
600	158	0.465	0.592	600	158	0.465	0.592

liquid and vapor compositions, ±0.5 mole per cent; temperatures, ±1° F.; pressures, ±2 pounds per square inch. An exception to this generalization exists in the case of the critical point of the mixture in Table III*A*. Since it was not practical experimentally to attempt to find the exact mixture which had a critical pressure of 600 pounds per square inch, the point in Table III*A* represents the result of a calculation by Smith and Watson's method (*14*).

In the case of the hydrogen sulfide–propane system, measurements were made only on mixtures containing low percentages of hydrogen sulfide. The data show larger deviations from the smoothed curves than do the results on the propylene-isobutane system. These deviations can be explained in two ways. Duplicate analyses were not made, on account of the inconvenience of storing gas samples containing hydrogen sulfide, and analytical errors may account for some of the scattering of the data. Secondly, it was found at the conclusion of the experimental runs on the system that there had been an appreciable attack of the copper parts of the apparatus by the hydrogen sulfide. This had the effect of plugging the small tubes with products of corrosion and thus of making operation of the apparatus less satisfactory. The smoothed data in Table III*B* should be of sufficient accuracy for most engineering purposes, but must be considered subject to somewhat larger limits of error than those mentioned above.

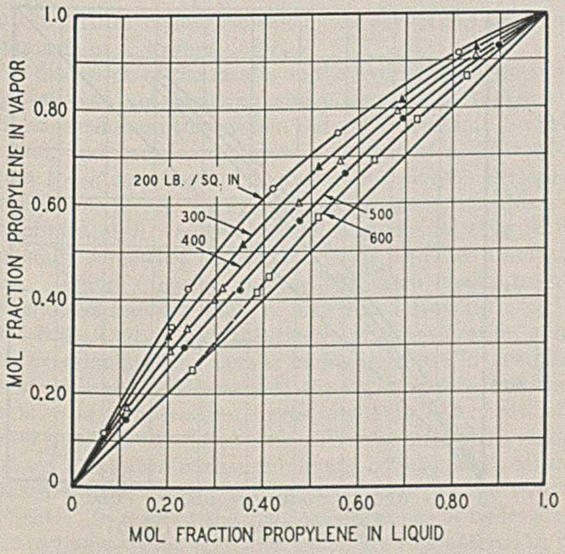

Figure 2. Vapor *vs.* Liquid Composition at Constant Pressure for Propylene-Isobutane

A general correlation of phase equilibrium data for hydrocarbon mixtures at high pressure has been proposed (*8, 9*), in which the ratio of the mole fraction in the vapor to that in the liquid for any component of a hydrocarbon mixture is expressed by the equation,

$$y/x = f_P/f_\pi = K$$

where f_P is the fugacity of the component in liquid under its own vapor pressure and at the temperature of the mixture, and f_π is the fugacity of the same component in the vapor at the total pressure and the temperature of the mixture. A generalized fugacity chart for hydrocarbons (*10*) has been published in which fugacity is given as a unique function of reduced temperature and reduced pressure. By using this

Table III. Smoothed Data on Mixtures, with Corresponding *K* Values

A. Propylene-Isobutane

Abs. Pressure, Lb./Sq. In.	x_{C_3}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
200	y_{C_3}	0.000	0.177	0.354	0.504	0.617	0.704	0.780	0.849	0.910	0.962	1.000
	t, ° F.	174	165	154	144	136	128	121	115	109	102	92
	K_{C_3}	...	1.77	1.77	1.68	1.54	1.41	1.30	1.21	1.14	1.07	1.00
	K_{C_4}	1.000	0.914	0.808	0.709	0.638	0.592	0.550	0.503	0.450	0.380	...
300	y_{C_3}	0.000	0.161	0.318	0.450	0.567	0.664	0.750	0.826	0.896	0.951	1.000
	t, ° F.	214	203	194	185	176	167	159	152	144	136	126
	K_{C_3}	...	1.61	1.59	1.50	1.42	1.33	1.25	1.17	1.12	1.06	1.00
	K_{C_4}	1.000	0.932	0.853	0.786	0.722	0.672	0.625	0.580	0.520	0.490	...
400	y_{C_3}	0.000	0.149	0.285	0.407	0.524	0.629	0.726	0.809	0.880	0.942	1.000
	t, ° F.	242	231	221	212	203	194	187	180	172	163	150
	K_{C_3}	...	1.49	1.43	1.36	1.31	1.26	1.21	1.16	1.10	1.05	1.00
	K_{C_4}	1.000	0.946	0.894	0.847	0.793	0.742	0.685	0.637	0.600	0.580	...
500	y_{C_3}	0.000	0.132	0.255	0.368	0.483	0.592	0.695	0.785	0.864	0.934	1.000
	t, ° F.	267	257	247	238	228	219	211	203	196	188	173
	K_{C_3}	...	1.32	1.28	1.23	1.21	1.18	1.16	1.12	1.08	1.04	1.00
	K_{C_4}	1.000	0.964	0.931	0.903	0.862	0.816	0.763	0.717	0.680	0.640	...
600	x_{C_3}	...	...	...	0.250[a]	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	y_{C_3}	...	...	...	0.250[a]	0.433	0.555	0.660	0.755	0.844	0.924	1.000
	t, ° F.	...	...	...	264[a]	248	238	230	221	212	203	191
	K_{C_3}	...	...	...	1.000	1.08	1.11	1.10	1.08	1.05	1.03	1.00
	K_{C_4}	...	...	...	1.000	0.945	0.890	0.850	0.817	0.780	0.760	...

B. Hydrogen Sulfide–Propane (*1*)

Abs. Pressure, Lb./Sq. In.	x_{H_2S}	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
400	y_{H_2S}	0.000	0.102	0.182	0.255	0.326	0.393	0.458	0.522	0.583	...	...
	t, ° F.	163	150	141	135	131	128	126	124	122	...	...
	K_{H_2S}	...	2.04	1.82	1.70	1.63	1.57	1.53	1.49	1.46	...	...
	K_{C_3}	1.000	0.945	0.909	0.876	0.842	0.809	0.776	0.735	0.695	...	...
500	y_{H_2S}	0.000	0.083	0.156	0.227	0.296	0.362	0.427	0.491	0.550	0.609	...
	t, ° F.	189	176	168	162	159	156	153	151	148	145	...
	K_{H_2S}	...	1.66	1.56	1.51	1.48	1.45	1.42	1.40	1.38	1.36	...
	K_{C_3}	1.000	0.966	0.938	0.909	0.880	0.851	0.819	0.784	0.750	0.712	...
600	y_{H_2S}	0.000	0.067	0.135	0.203	0.269	0.335	0.398	0.460	0.520	0.577	0.631
	t, ° F.	205	203	195	188	182	177	173	169	166	163	160
	K_{H_2S}	...	1.34	1.35	1.35	1.34	1.34	1.33	1.31	1.30	1.28	1.26
	K_{C_3}	1.000	0.983	0.961	0.938	0.914	0.887	0.860	0.831	0.800	0.769	0.738

[a] Critical point of mixture.

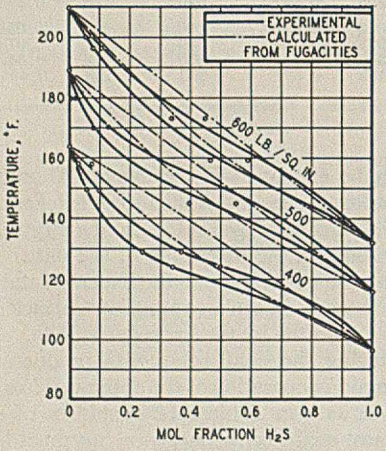

Figure 3. Temperature-Composition Diagrams at Constant Pressure for the System Hydrogen Sulfide–Propane

generalized fugacity chart and the above equation, values of *K* for various hydrocarbons can be calculated as unique functions of temperature and pressure. Such sets of *K* values, or *K*-charts, have recently been developed (*11*) and are in use at present for predicting high-pressure phase equilibrium data.

A comparison between the experimental data and those calculated from the fugacity equation for the propylene-isobutane system is given in Figures 1 and 5. At the lower pressures agreement is fairly good; this is the case for all hydrocarbon systems on which data are available. As critical conditions are approached, however, the calculated curves deviate considerably from the experimental ones. At 500 and 600 pounds per square inch the experimental relative volatility is lower than that predicted from fugacities. There is, furthermore, a discontinuity in the experimental *x*-*y* curve at 600 pounds per square inch (Figure 5) which is not predicted by the *K*-charts.

The values of *K* given by f_P/f_π are shown as dotted lines in Figures 6 and 7. Agreement with the experimental curves is fairly good in regions of low temperature and pressure, but

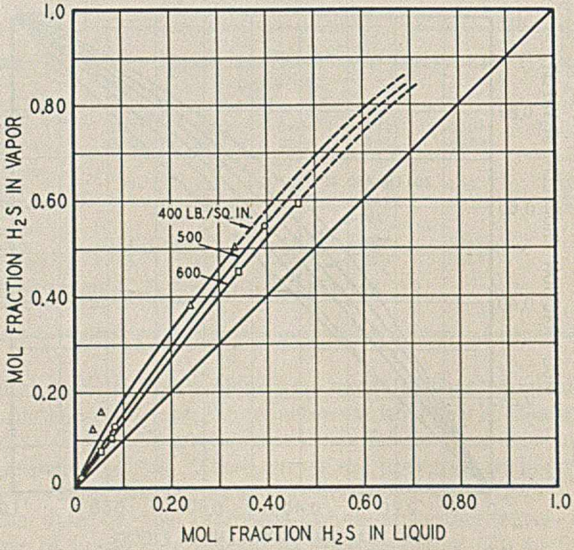

Figure 4. Vapor *vs.* Liquid Composition at Constant Pressure for Hydrogen Sulfide–Propane

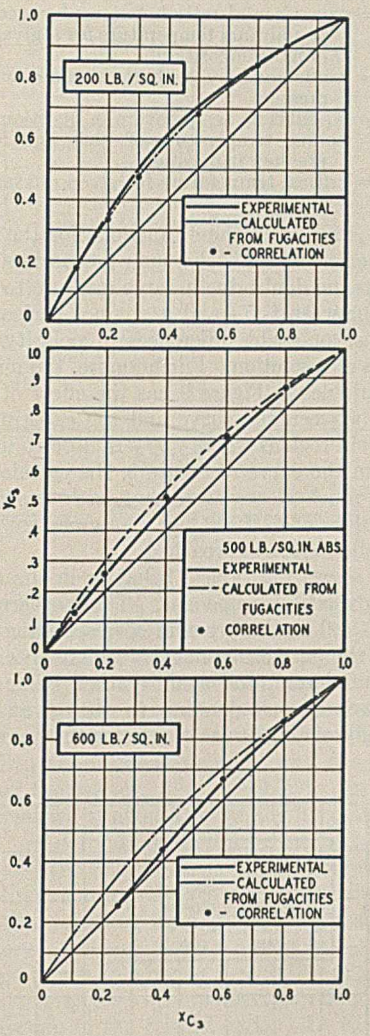

Figure 5. Comparison of Calculated and Experimental Vapor *vs.* Liquid Compositions for the System Propylene-Isobutane

in the critical region the calculated curves fail to show the approach of K toward unity.

A discussion of the results on the hydrogen sulfide–propane system was not included above because of the fact that measurements on this system did not extend into the critical region, and because the system itself is of a different type from those composed of hydrocarbons alone. Certain generalizations about the system can be made, however. The experimental K values for both components (Figure 8) lie generally somewhat higher than those predicted from fugacities. These fugacity calculations were made from the generalized fugacity plots of Lewis and Kay (*9*) and Lewis and Luke (*10*). Over the ranges of concentration studied, the experimental x-y curves in Figure 4 are in good agreement with the predictions of the fugacity rule, but the experimental temperature curves in Figure 3 lie considerably lower than the calculated ones. There seems to be a tendency toward a mixture with a minimum boiling point, no doubt caused by the difference in polarity between the two components. In view of the low concentrations of hydrogen sulfide in hydrocarbon mixtures which are encountered in practice, however, it may be said that the fugacity equation gives a satisfactory picture of the behavior of this compound.

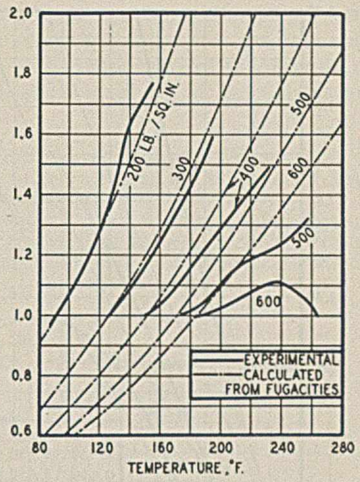

Figure 6. Calculated and Experimental K Values for Propylene in the System Propylene-Isobutane

Correlation of Two-Component Hydrocarbon Phase Equilibrium Data in the Critical Region

There is an increasing tendency in present-day industrial practice to subject hydrocarbon mixtures to conditions of temperature and pressure approaching or exceeding the critical values. Since the K-charts break down completely in the critical region, the development of some new method of correlating equilibrium data under these conditions would appear to be particularly desirable. Data on a wide variety of two-component hydrocarbon systems are now available (*3, 4, 7, 12, 13*); one approach to the problem would therefore be the correlation of the data on these two-component systems, in the hope that such a correlation can be made to apply to more complex mixtures when more complete data on them become available.

The present K-charts (*11*) and the Smith and Watson correlation of critical constants for mixtures (*14*) suggested

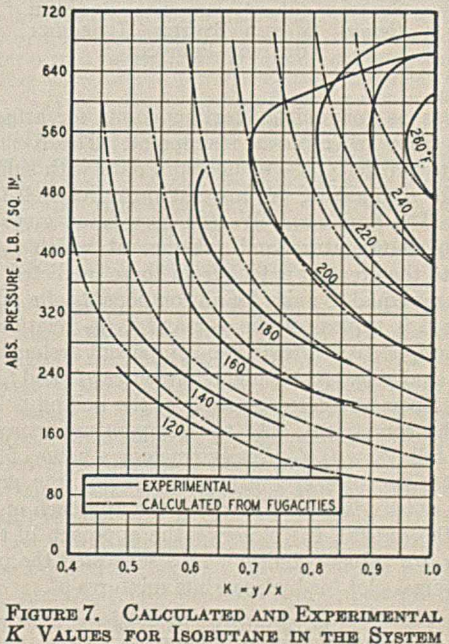

Figure 7. Calculated and Experimental K Values for Isobutane in the System Propylene-Isobutane

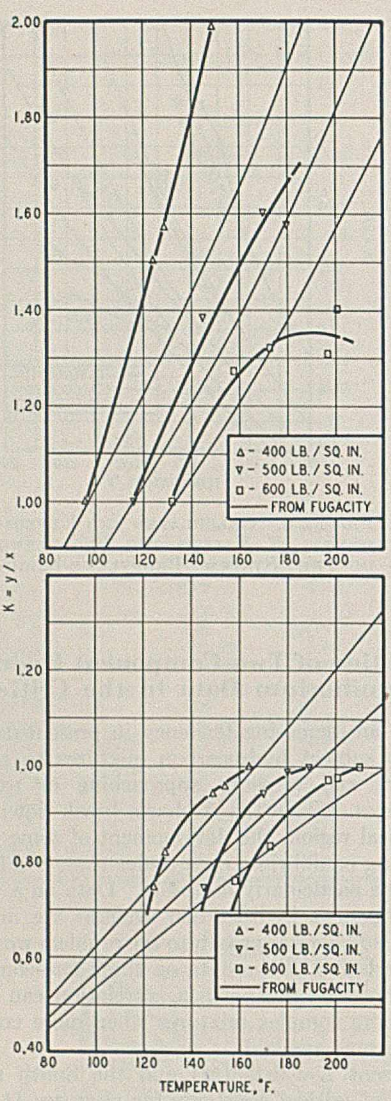

FIGURE 8. CALCULATED AND EXPERIMENTAL K VALUES FOR HYDROGEN SULFIDE (*above*) AND FOR PROPANE (*below*) IN THE SYSTEM HYDROGEN SULFIDE–PROPANE

themselves as convenient starting points for attacking the problem from an empirical standpoint. The K-charts may be said to predict phase equilibrium data with sufficient accuracy for engineering purposes at pressures well below the critical. The Smith and Watson correlation gives the conditions of temperature and pressure at which y/x values deviate to the greatest extent from those predicted by f_P/f_π, and become equal to unity for all components of a mixture.

Figure 6 is typical of the y/x and f_P/f_π relations for the lighter component of the six two-component systems on which data are available. At the higher pressures y/x and f_P/f_π agree at the temperature corresponding to the boiling point of the pure light component. As the temperature increases, y/x tends to fall below f_P/f_π, finally reaching a value of 1.0 at the critical temperature of the mixture having the pressure in question as its critical. The closer the approach of temperature to the critical, the closer is the approach of the corresponding y/x value to unity. This suggested the possibility of a universal plot for hydrocarbon mixtures of

$$\frac{f_P/f_\pi - y/x}{f_P/f_\pi - 1} \ vs. \ \frac{t - t_B}{t_c - t_B}$$

where y/x = experimental ratio between phase compositions at equilibrium temperature for a given pressure and liquid composition
f_P/f_π = value given by K-charts at same temperature and pressure
t = equilibrium temperature in question
t_B = boiling temperature of pure light component at pressure in question
t_c = critical temperature for given mixture

Figure 9 is a plot of these functions for the six two-component systems. There is obviously a considerable scattering of the points, no doubt due in large measure to the fact that agreement between f_P/f_π and y/x is not perfect at low pressures because of slight differences in polarity between the components of a solution. Furthermore, the method of plotting the variables in Figure 9 has the effect of exaggerating deviations between the curve and the experimental points, particularly in regions where f_P/f_π is close to unity. Nevertheless, from the curve in Figure 9, the calculated values of y/x are in much closer agreement with experimental data than are values of f_P/f_π alone, the agreement improving as critical conditions are approached.

Figure 7 shows the typical behavior in the critical region of the less volatile component. The isothermal curves of y/x start at 1.0 at the pressure corresponding to the vapor pressure of the pure component at the given temperature, go through a minimum, and again reach a value of 1.0 at the critical pressure corresponding to the given temperature. From a study of the curves of y/x for the heavy component in all six two-component systems on which data are available, it was found that in all cases: (*a*) the curves started out from 1.0 at the lower pressure with the same slope as the corresponding f_P/f_π lines, (*b*) the minimum value of y/x in all cases occurred at pressures corresponding approximately to the arithmetic average of the vapor pressure of the component and the critical pressure, and (*c*) at the critical pressures the respective y/x curves approached 1.0 with a slope of zero. Having thus fixed the general shape of all the curves, the chief remaining problem was to predict the minimum value of y/x in any given case.

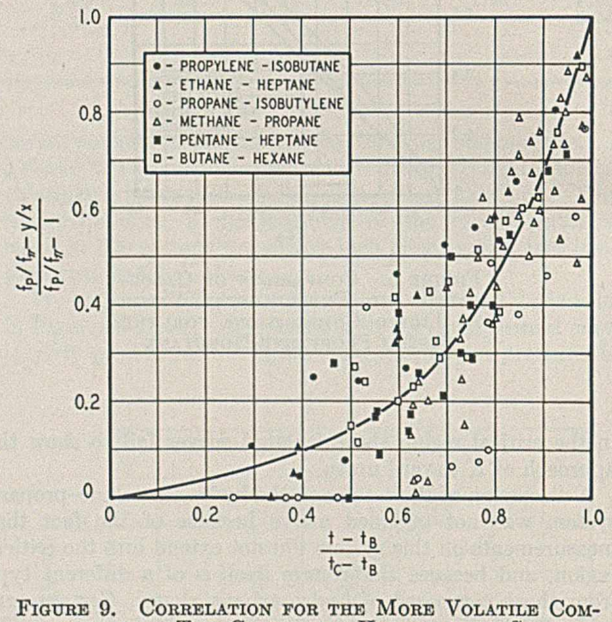

FIGURE 9. CORRELATION FOR THE MORE VOLATILE COMPONENT OF A TWO-COMPONENT HYDROCARBON SYSTEM

In Figure 10 the minimum value of y/x on any isothermal curve in the critical region is plotted against P_c/P_B, where

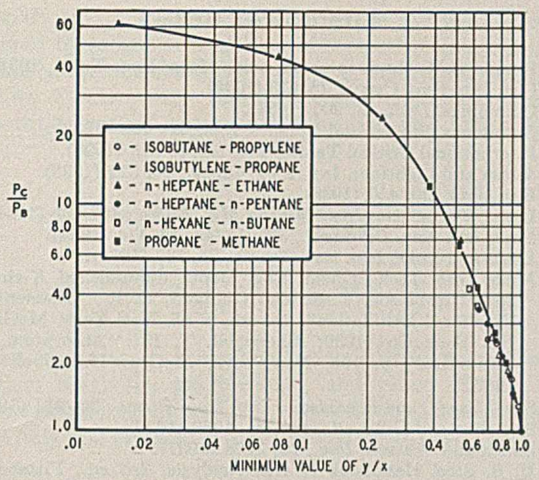

FIGURE 10. CORRELATION FOR THE LESS VOLATILE COMPONENT OF A TWO-COMPONENT HYDROCARBON SYSTEM

P_c is the critical pressure of the mixture having the temperature in question as its critical, and P_B is the vapor pressure of the pure heavy component at the same temperature. All the points lie nearly on a single smooth curve, despite the wide variation in the nature of the systems involved.

When we know the coordinates of the minima in the various isothermal curves of y/x *vs.* pressure, as well as the slopes at each end of the curves, it is possible to sketch in the curves themselves with sufficient accuracy for most engineering purposes. A derivation of the equation relating the known slopes and the minimum for any given curve was attempted, but the resulting mathematical expressions were so complex that the sketching in of the curves was considered more satisfactory.

If the curves shown in Figures 9 and 10 are accepted as being applicable to any two-component paraffinic or olefinic hydrocarbon system in the critical region, the calculation of phase equilibrium data can be accomplished very simply. It is assumed that complete vapor pressure data and K-charts are available for both components of the mixture under consideration. The steps involved in the calculations are as follows:

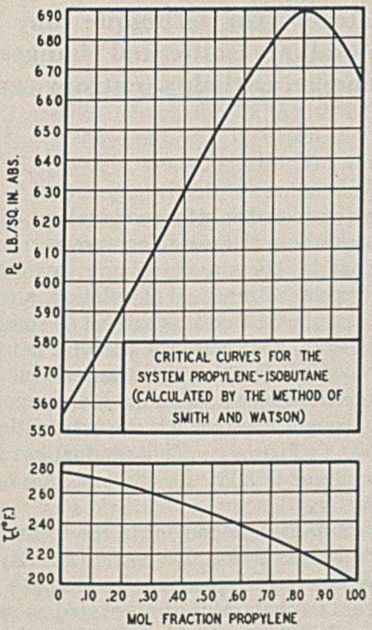

FIGURE 11. CRITICAL CURVES FOR PROPYLENE-ISOBUTANE (CALCULATED BY THE METHOD OF SMITH AND WATSON)

1. Using the method of Smith and Watson (*14*), the critical temperature and pressure curves for mixtures of the two components are obtained (Figure 11).
2. From these curves, at a series of temperatures in the critical region, corresponding values of critical pressure, P_c, are found; at the same temperatures corresponding vapor pressures of the pure heavy component, P_B, are also obtained. From the ratios of these pressures, the minimum value of y/x for the less volatile component at each temperature can be read from Figure 10. The complete isothermal curves of y/x for the heavy component are then sketched in, remembering the following: At P_B, $y/x = 1.0$, and the slope of the curve is the same as that of the corresponding f_P/f_π line; at $0.5\ (P_B + P_c)$, y/x goes through the minimum value; and at P_c, y/x is again equal to 1.0, and the slope $dP/d(y/x)$ is equal to zero.
3. Assume now that pressure and liquid composition are specified, and it is desired to find the corresponding equilibrium temperature and vapor composition. The critical temperature, t_c, of the given liquid mixture is read from the critical curve. The boiling temperature, t_B, for the pure light component at the given pressure is obtained either from vapor pressure data on the component or from an extrapolation of the data on a Cox chart. If we assume a trial value, t, for the equilibrium temperature, the corresponding value of y/x for the lighter component is calculated from f_P/f_π and the correction factor given by Figure 9. From the curves constructed in step 2, y/x is found for the heavier component at the trial temperature and the pressure in question.
4. The test of the validity of the assumed temperature, t, is made by finding the sum of the products $x(y/x)$ for the two components. At the correct temperature, this sum must equal unity. Successive values of t are assumed until this condition is satisfied, at which time $x(y/x)$ should give the true mol fraction of the component in the vapor phase.

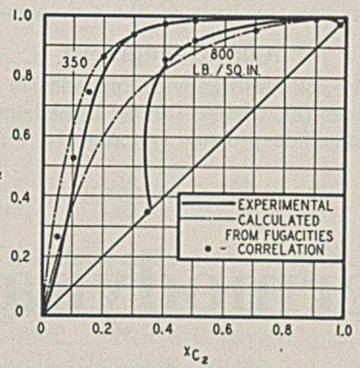

FIGURE 12. COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR *vs.* LIQUID COMPOSITIONS FOR THE SYSTEM ETHANE–*n*-HEPTANE

Data calculated by the above method for the propylene-isobutane and ethane-heptane systems are compared in Figures 5 and 12 with corresponding values obtained experimentally and by the use of the K-charts alone. The correlation gives values of y which are in general lower than those predicted from the K-charts, though at the lower pressures the methods give almost identical results. In the critical region, the correlation is in very good agreement with experimental data, whereas the K-charts are in considerable error. It should be noted particularly that discontinuities at the ends of the x-y curves (Figure 5, at 600 pounds pressure and Figure 12) are accurately predicted, an important improvement over the fugacity equation which gives continuous x-y: curves in all cases.

The correlation, then, represents an improvement over the present *K*-charts for predicting phase equilibrium data for two-component hydrocarbon systems at pressures near the critical. At lower pressures there is agreement between the correlation and the *K*-charts, and the use of the latter alone is recommended. It is possible that the correlation may apply, without any modification, to systems containing more than two components. In such a case the method of correlation for the more volatile component would be used for all components having, in a particular case, y/x values greater than unity, and the less volatile component correlation used for all components having y/x less than unity. No data are available in the critical region for more complex mixtures, in which complete analyses of the two phases are given.

Acknowledgment

The authors acknowledge with appreciation the assistance of R. J. Brauer (*1*), who performed the laboratory work on the hydrogen sulfide–propane system.

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Thermodynamic Properties from *P-V-T* Data

ROBERT YORK, Jr.[1]

Department of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, Mass.

A method of residuals is proposed which is especially useful for evaluating isothermal changes in thermodynamic properties from *P-V-T* data. Unlike many other methods using residuals previously proposed, here advantage is taken of the fact that, along the isometric of a gas, approximately a linear relation exists between pressure and temperature. The technique may be applied to evaluate isothermal changes in internal energy, enthalpy, entropy, and free energy.

WHERE the *P-V-T* relations of a fluid can be expressed in terms of an algebraic equation of state, it is possible to calculate various thermodynamic properties. Unfortunately none of the equations of state thus far proposed are valid throughout the experimentally measured range of pressures. Consequently resource must be had to other methods. For practical purposes graphical methods must be used; of these, that of Deming and Shupe (*2*) appears to be the best hitherto suggested.

To illustrate the utility of residual functions, suppose a curve resembles in character a parabola of the type $y = kx^2$. Were it desirable to determine the slope dy/dx, a residual function Δ could be employed:

$$\Delta = y_{\text{actual}} - kx^2$$

$$\text{or } y = kx^2 + \Delta$$

$$\text{hence} \quad dy/dx = 2\,kx + d\Delta/dx$$

in which all values are determined algebraically, except $d\Delta/dx$ which must be found graphically. Generally the Δ term will be only a small fraction of y. Consequently, using a residual will improve the accuracy of graphically handling functions which resemble but do not fit a simple curve. In the event that one residual does not yield the desired precision, then a second residual may be employed.

Deming and Shupe used residuals from a physical property of a perfect gas, such as pressure or volume—that is, differences between the calculated volume for a perfect gas and the measured volume for the actual gas. Both volumes and their residuals are subject to relatively large variations. In addition, they considered only first residuals which introduced large differences where the variables were numerically large. For example, at low pressures, volume residuals would be large. For purposes of practical calculation, a residual function should be so chosen that it is subject to small variations. Thus $(RT/P - V)/V$ at constant pressure is more suitable than $(RT/P - V)$. In this work the residual investigated is the difference between the pressure of the experimental isometric and a straight line through the extremities of the isometric as shown in Figure 1. This residual has been treated in such a manner as to allow for the precision of the *P-V-T* data available.

A recent important development in the technique of measuring *P-V-T* relations is that of Beattie (*1*). By his method changes in volume of the apparatus due to both temperature and pressure are mechanically compensated so as to measure the true isometric of the material under investigation. Such a technique suggests a method for computation for thermodynamic properties, because it eliminates necessity for interpolation with respect to volume. The purpose of this paper

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[1] Present address, Carnegie Institute of Technology, Pittsburgh, Penna.

is to show how P-V-T data measured in this manner can be utilized by means of a method of successive residuals to calculate isothermal changes in energy, enthalpy, and entropy.

Two fundamental thermodynamic equations involving quantities readily determinable by isometric measurements are:

$$(E_2 - E_1)_T = \int_{V_1}^{V_2} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \tag{1}$$

$$(S_2 - S_1)_T = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV \tag{2}$$

These formulas are limited to two independent variables and neglect magnetic, gravitational, and other effects. Their derivation may be found in any good text on thermodynamics. The only real problem is to determine $(\partial P/\partial T)_V$.

Determining Slope of Isometric

To determine the isometric slope, $(\partial P/\partial T)_V$, the pressure at constant gas density is plotted against temperature as shown in Figure 1. The points lie nearly in a straight line. By algebraically passing a straight line through the P-T extremities of the isometric and by plotting the "first residual", r, against temperature, the curvature is decidedly magnified as Figure 2 shows. Residual r is the distance, measured parallel to the temperature axis, between the measured isometric and the straight line connecting the terminals of the isometric. When the available data were plotted in this fashion, however, such smooth curves resulted from precise experimental measurements that it was apparent a second residual should also be employed. For this, several types of algebraic equations could be utilized to approximate the curves determined when, as shown in Figure 2, the first residual is plotted against temperature. After some study, an exponential type was adopted from the viewpoint of simplicity and adaptability to the range of numerical values involved. In fact, a 10-inch log-log slide rule is satisfactory as long as it gives the desired precision for r, which makes it usable in most cases.

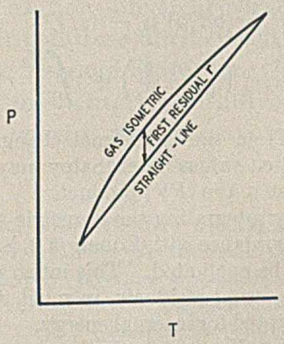

Figure 1. Isometric of Gas on Pressure-Temperature Plane Showing First Residual r

To express r as a function of temperature, axes were shifted to the maximum value of r, denoted by r_0, and to the corresponding temperature, t_0, as indicated in Figure 2. Two exponential equations were passed within one-thousandth atmosphere of r_0, t_0, and the other point at the lower left or lower right of the parabolic curve of Figure 2. Since an exponential or logarithmic equation cannot be made to pass through 0, 0, a point within 0.001 atm. is used without introducing appreciable error. Such equations are:

$$(r_0 - r)_{\text{left}} = k_1\,(t_0 - t)^n$$
$$(r_0 - r')_{\text{right}} = k_2\,(t - t_0)^m$$

Second residuals denoted by r' were determined as the difference between $(r_0 - r)_{\text{actual}}$ and $(r_0 - r)_{\text{calculated}}$.

When plotted against temperature, these second residuals showed pronounced wobbling of a saw-tooth nature, an indication that, except for minor trends, the precision of the experimental data has been reached. The use of residuals not only yields all the precision justified by the data but also discloses the points at which irregularities develop.

The equation for pressure as a function of temperature at constant density will be of the form:

$$P = a\,t + b - r' \pm \begin{cases} k_1(t_0 - t)^n \\ k_2(t - t_0)^m \end{cases} \tag{3}$$

where P and t are variables, r' the second residual, and all other terms constants. The isometric slope, $(\partial P/\partial T)_V$, is obtained by differentiating:

$$\left(\frac{\partial P}{\partial T}\right)_V = a - \left(\frac{dr'}{dt}\right) \pm \begin{cases} -nk_1\,(t_0 - t)^{n-1} \\ +mk_2\,(t - t_0)^{m-1} \end{cases} \tag{4}$$

All terms are calculable except (dr'/dt) which is obtained by graphical differentiation.

So far the general method for determining isometric slopes has been described. Often it is advisable to smooth these slopes graphically. For this purpose the (small) variable part (last two terms of Equation 4) was plotted against temperature and adjusted. Only in extreme cases need adjustment by auxiliary equation be used. Provided the data are sufficiently precise, only smoothed values should be used for further calculations of thermodynamic properties.

Advantages and Limitations. The proposed method of determining the isometric slope, $(\partial P/\partial T)_V$, has the following advantages: (*a*) An equation of state is not required. (*b*) The isometric slopes are determined with all the precision justified by the data and without undue labor. (*c*) The precision of the experimental data is revealed by noting the irregularities shown by second residuals. However, as a limitation it must be mentioned that this method cannot show the presence of constant or systematic errors.

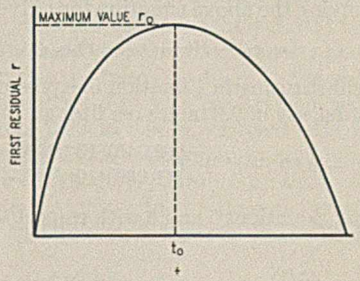

Figure 2. First Residual Plotted against Temperature, to Determine Maximum Value r_0

Although it may seem that some unnecessary plotting is recommended, it is believed that the construction of these simple graphs serves the useful purpose of showing any irregularities in data or errors in arithmetic.

Example of Values for Isometric Slopes. As an example, values for the isometric slope will be calculated and checked. Isometric data, as reported by Su (*3*), for gaseous ethane at a constant density of 9.0 moles per liter, are as follows:

t, ° C.	50	75	100	125	150	175	200
P, atm.	76.90	118.32	160.77	203.63	246.57	289.49	332.56

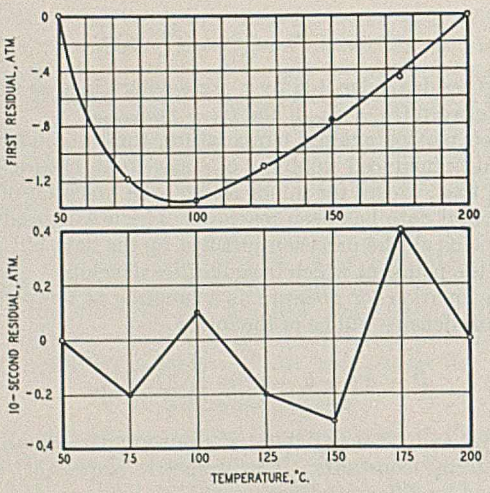

Figure 3. First Residual and Second Residual *vs.* Temperature, for Illustrative Examples

When applied to these data, the equation of the straight line for pressure through pressures at 50° and 200° C. is $1.7044t - 8.32$. To this the first residual r must be added to give the actual pressure, hence:

$$P = 1.7044t - 8.32 + r \tag{5}$$

Values of r are now calculated and plotted against temperature as shown in the upper half of Figure 3. From this the maximum value of r and the corresponding temperature is read, giving $r_0 = -1.37$ atmospheres and $t_0 = 93°$ C. Values of $(r_0 - r)_{\text{actual}}$ and $(t_0 - t)$ are calculated and plotted on logarithmic coordinate paper. The two equations for $(r_0 - r)$ will be

$$\text{For } t < 93°\text{: } (r - r)_{\text{calcd.}} = -(2.045)(10^{-4})(93 - t)^{2.342}$$
$$\text{For } t > 93°\text{: } (r_0 - r)_{\text{calcd.}} = -(1.930)(10^{-3})(t - 93)^{1.405}$$

Values of a second residual, r', are calculated by

$$r' = (r_0 - r)_{\text{actual}} - (r_0 - r)_{\text{calcd.}}$$

and plotted against temperature as shown in the lower half of Figure 3. Solving the above equation for r gives

$$r = r_0 - r' - (r_0 - r)_{\text{calcd.}}$$

which upon substituting in Equation 5 expresses the pressure at a constant density of 9.0 moles per liter as

$$P = 1.7044t - 9.69 - r' + \begin{cases}(2.045)(10^{-4})(93 - t)^{2.342} \\ (1.930)(10^{-3})(t - 93)^{1.405}\end{cases} \tag{6}$$

Differentiating Equations 5 and 6 with respect to temperature gives

$$\left(\frac{\partial P}{\partial T}\right)_V = 1.7044 + \left(\frac{dr}{dt}\right) \tag{7}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = 1.7044 - \left(\frac{dr'}{dt}\right) + \begin{cases}(-4.788)(10^{-4})(93 - t)^{1.342} \\ (2.712)(10^{-3})(t - 93)^{0.405}\end{cases} \tag{8}$$

Table I. Isometric Slope $(\partial P/\partial T)_V$ for Gaseous Ethane at 9.0 Moles per Liter

Temp., ° C.	$(\partial P/\partial T)_V$ by Equation 7	$(\partial P/\partial T)_V$ by Equation 8
50	1.6364	1.6305
75	1.6704	1.6812
100	1.7107	1.7104
125	1.7162	1.7165
150	1.7171	1.7184
175	1.7169	1.7206
200	1.7231	1.7225

Substituting numerical values for t in Equation 8 and getting (dr/dt) and (dr'/dt) graphically yields the results listed in Table I. The average agreement is in the neighborhood of 0.1 per cent, though the values of $(\partial P/\partial T)_V$ obtained by Equation 8 are more precise than those calculated by means of Equation 7.

Isothermal Changes in Thermodynamic Functions

Internal Energy. Having determined the isometric slopes, the change in internal energy is evaluated by solving

$$(E_2 - E_1)_T = \int_{V_1}^{V_2} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]_T dV \tag{9}$$

in which the term in brackets equals $(\partial E/\partial V)_T$. Integration is readily carried out by using residuals from van der Waals equation, the constants for which are obtained directly from $(\partial E/\partial V)_T$. This procedure is summarized by the following steps:

1. Calculate $(\partial E/\partial V)_T$ by the fundamental equation:

$$\left(\frac{\partial E}{\partial V}\right) T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

2. Integrate $(\partial E/\partial V)_T$ using residuals from the van der Waals equation, according to:

$$r'' = (\partial E/\partial V)_T - (a/V^2) \tag{10}$$

$$(E_2 - E_1)_T = \left(\frac{a}{V_1} - \frac{a}{V_2}\right) + \int_{V_1}^{V_2} r''\,dV \tag{11}$$

Enthalpy. From the isothermal change in internal energy, corresponding values for enthalpy may be computed by adding the change in the (PV) product.

Entropy. By integrating the isometric slope with respect to volume, in accordance with Equation 2, isothermal changes in entropy may be evaluated. This integration may be also accomplished by using residuals, in much the same manner as has been suggested for internal energy.

Free Energy. Knowing values for the preceding functions, the pressure correction for isothermal changes in free energy (in the absence of chemical reactions) may be calculated from the equation

$$(F_2 - F_1)_T = (H_2 - H_1)_T - T(S_2 - S_1)_T \tag{12}$$

Acknowledgment

Thanks are due W. K. Lewis for his valuable and helpful suggestions.

Nomenclature

E = internal energy
F = free energy $(H - TS)$
H = enthalpy $(E + PV)$
P = absolute pressure, normal atmospheres
R = gas law constant
r_0 = maximum value of r
r' = second residual
r'' = residual defined by Equation 10
r = first residual
S = entropy
t = temperature, ° C.
T = absolute temperature
V = volume

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Diameter Variation in Cellulose Fibrils

A. J. BAILEY[1] AND R. M. BROWN
University of Minnesota, St. Paul, Minn.

Various plant fibers were disintegrated by mechanical means alone and by beating after different chemical treatments. Measurements of fibril diameters were made and analyzed statistically. The analysis showed that cellulose fibrils exist as uniform and true morphological units. Diameters of these fibrils are in the range of 0.928 to 0.956 μ and are apparently independent of botanical origin, chemical treatment, or physical processing. The fact that cellulose fibrils fluctuate around a common average diameter, the amount of fluctuation being essentially the same for various species and treatments, has far-reaching industrial significance. Two physical materials were found in all fibers—a compact, dense, unit fibril and a substance forming a hydrogel upon comminution in water. The unit fibril was incapable of gelatinization in water by ordinary methods. The disintegration of fibers into a gel and an inert fraction indicates that freeness and similar tests have only limited and empirical significance. The observed course of fiber disintegration explains many of the complex physical and chemical changes accompanying commercial beating. Unit fibrils from various sources are illustrated by photomicrographs.

THE degree of subdivision of a solid is of extreme importance in relation to chemical and colloidal changes. Not infrequently physical appearance and properties are directly dependent upon particle size. Cellulose is markedly of this type. Changes in cellulose particle size by commercial beating processes are so complex that no means exists for accurately defining the change analytically or for exactly duplicating a given commercial beating operation. A tendency of cellulose to form particles of a definite size and resist further subdivision would be important in both physical and chemical processing. Cellulose esterification, for example, is often considered to be a micellar reaction in which some zones in a single micelle may be fully esterified or completely unchanged (*18*). Similarly, higher nitrates are known to exist on the fiber exterior, but lower nitrates persist in the interior (*8*). The present study had for its purpose the determination of the diameters of cellulose fibrils from different sources, of different chemical histories, and subjected to different mechanical processing, to learn the following: whether fibril diameters tend to be of an average size; how these sizes varied from the mean; how fibril diameters compared with diameters observed by other investigators; and what industrial importance might attach to fibrils which resisted further subdivision.

Experimental History

Different fibril diameters have been reported by independent investigators. Balls and Hancock (*5*) concluded that cotton fibrils were 0.4 μ in diameter, Jancke (*14*) in Herzog's laboratory observed a width of 0.3 to 0.5 μ, and Frey-Wyssling recorded 0.4 μ (*13*). In contrast, Freudenberg (*12*), Bailey and Kerr (*4*), Anderson and Moore (*2*), and Anderson and Kerr (*1*) expressed the opinion that fibrils have no consistent size and grade down to the limits of microscopic resolution. Seifriz and Hock (*16*) recognized "primary fibrils" of 1.4 μ diameter and "secondary fibrils" of 0.1–0.3 μ diameter. Farr and Eckerson (*10*) reported a diameter of approximately 1.1 μ for ellipsoidal particles and believed that they were a more or less constant building unit. Another investigator (*3*), who recorded a somewhat larger fibril diameter, believed that fibrils had a more or less uniform minimum diameter, or multiple of this diameter if grouped. As a result he proposed the term "unit fibril" to designate a fibril having this minimum uniform diameter and visually estimated the range to be from 3 to 4 μ. In the present investigation this diameter range was determined accurately and found to be from 0.93 to 0.96 μ. Because the cylindricoids (*3*) formed from fibrils are approximately equidimensional, the height is also in the range of 1.0 to 1.5 μ; the exact dimension requires statistical study. In the present investigation unit fibrils could not be differentiated from Farr's fibrils composed of ellipsoids.

Although most of these earlier studies included only cotton, a few dealt with wood fibers. In spite of marked difference in the type and development of fibers, there is no apparent reason why cellulose deposition cannot be identical in seed hairs and wood tracheids. A comparison of methods used to determine fibril diameters indicates that the fibril diameters actually found are correlated with the methods used. Generally speaking, the diameters obtained indirectly by inference from observations of zones in swollen sections of the walls have been smaller than those obtained by other methods. The larger diameters were usually obtained by simpler treatments, such as comminution in water. Because of the interference of Liesegang effects and pressure artifacts, there might be some danger in broadly inferring that zones or markings in drastically swollen material indicate fibril size. Little is known of the specificity of the gel involved. Varying

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[1] Present address, University of Washington, Seattle, Wash.

concentrations of reacting ions might bring about progressive peptization and coagulation with attendant reticulation and articulation. This might easily account for zones of varying density observed by some investigators. Only recently Farr (*9*) showed that some zones on transverse sections, believed by some workers to be growth rings, are in reality artifacts caused by pressure on the cover glass above swollen material. It is perhaps significant that many of the workers who separated and measured diameters of individual fibrils, rather than inferring diameter from wall markings or zones, have reported the higher diameters.

To define material in terms of analytical procedures is not new or unusual. Cellulose, for example, is designated as alpha, beta, gamma, Cross and Bevan, and holocellulose, depending on the method of preparation; yet an absolutely pure cellulose, giving theoretical yields of glucose, has yet to be prepared. It is entirely possible (*a*) that mild treatment might yield fibrils of a uniform size and (*b*) that more drastic swelling treatments might reduce these fibrils to fibrils of smaller diameter by overcoming intermicellar attraction, but would not decrease their length since this could be brought about only by hydrolysis (shortening of chains). It is therefore rational to define fibrils not only on the basis of botanical origin, but also by chemical and physical histories. It might easily be the case that all recorded diameters have some significance, that agreement merely necessitates exact analytical definitions. Obviously, any clarification of such an important but contradictory and confusing concept would be of value.

In the interests of clarity, the term "fibril" is used here, as it appears in the literature, to mean a threadlike filament of varying length and diameter. The term "unit fibril" is used to indicate fibrils of definite diameter (about 1.0 μ), whose length is still unknown. It is believed that fiber laminations are built up of unit fibrils, that fibrils of greater diameter than 1.0 μ are aggregates of unit fibrils, and that fibrils of diameters less than 1.0 μ are strips torn longitudinally from unit fibrils.

Preparative and Observational Technique

Some fibrous materials were obtained in various stages of industrial processing; others had no treatment. By processing these in the laboratory chemically or physically, or both, it was possible to eliminate the effects of a given beating apparatus or specific chemical treatment. A description and history of the various materials used follows:

1. Surgical cotton (*Gossypium* sp.), fiber length reduced with scissors to permit beating without roping and lumping, pebble-milled 2 hours (all beating was in distilled water only).
2. Commercial unbleached aspen soda pulp (*Populus tremuloides*), pebble-milled 1.5 hours.
3. Commercial unbleached aspen soda pulp, bleached overnight in a large excess of 5 per cent sodium hypochlorite solution, pebble-milled 1 hour.
4. Commercial unbleached aspen soda pulp, pebble-milled 2 hours, hydrolyzed 2 hours with boiling, 2 per cent sodium hydroxide.
5. Commercial strawboard, pebble-milled 2 hours.
6. Southern pine (*Pinus* sp.) commercial kraft paper, pebble-milled 2 hours.
7. Southern pine kraft paper, bleached (similarly to sample 3) in 5 per cent sodium hypochlorite, pebble-milled 2 hours. (Both samples 6 and 7 were unbleached kraft paper which had had the usual beating and sizing. The paper was disintegrated in water before beating in this study.)
8. Thin western white pine (*Pinus monticola*) shavings, pebble-milled 2 hours.
9. Western white pine shavings pulped with nitric acid and potassium chlorate, pebble-milled 2 hours.
10. Western white pine shavings pulped with nitric acid and potassium chlorate, bleached in 5 per cent sodium hypochlorite, (similarly to sample 3) pebble-milled 1 hour.
11. Commercial Fir-Tex (Douglas fir, *Pseudotsuga taxifolia*) pulp, pebble-milled 2 hours.
12. Commercial Fir-Tex pulp, bleached in 5 per cent sodium hypochlorite (similarly to sample 3), pebble-milled 2 hours.
13. Commercial Masonite (southern pine) pulp, pebble-milled 3 hours.
14. Commercial Masonite pulp, bleached in 5 per cent sodium hypochlorite (similarly to sample 3), pebble-milled 3 hours.
15. Western hemlock (*Tsuga heterophylla*) shavings, pulped with nitric acid and potassium chlorate, pebble-milled 2 hours.
16. Sitka spruce (*Picea sitchensis*) shavings, pulped with nitric acid and potassium chlorate, pebble-milled 2 hours.

Samples 2, 3, and 4 were from the same commercial pulp, and samples 6 and 7 were from the same paper. Lap pulp and paper were boiled a few minutes in dilute alkali, the water was squeezed out, and the mass was washed and kneaded in the hands to loosen the fibers. The pulp was then disintegrated with a motor-driven stirrer and thickened by filtering. The pebble mill consisted of an 800-ml. porcelain jar about half full of approximately half-inch pebbles and was driven by a synchronous motor at 130 r. p. m. The mill was furnished by adding 100 ml. of distilled water and 2 to 3 grams (air dry) of fibrous material. All of the beating periods produced effects greatly in excess of commercial beating. All pulps were neutralized (if necessitated by prior treatment), or washed with sulfurous acid if oxidized, and then washed to neutrality before beating. Slides were prepared from diluted suspensions, mounted in a nonaqueous medium of high index of refraction, and observed with an achromatic-aplanatic condenser of 1.40 N. A. (numerical aperture), an achromatic 1.9-mm. oil immersion objective of 1.30 N. A., and a filar micrometer with an achromatic eyepiece. The magnification was 930 diameters and the theoretical resolution slightly better than 0.2 μ. Measurements were made independently by an unprejudiced observer. Readings from the filar micrometer drum, calibrated by a stage micrometer, were rounded off to the nearest 0.1 μ, in spite of a resolution of 0.2 μ. Readings were made in different parts of the slide where individual fibrils were separated and therefore could be measured accurately so that a representive sample was obtained and the effects of selective deposition on the slide were eliminated.

The appearance of the beaten material on slides is shown in Figures 1 to 5.

The resolution in all of these illustrations is less than half that obtained in making the measurements, owing to the necessity of obtaining optical contrast by diffraction. Variations in diameter of a single unit fibril are due to clots of gel, or to lying in a different focal plane; the result is the well known exaggeration of size of near objects by all short-focus lenses. These photomicrographs were prepared from air-mounted fiber slides with no attempt to place all fibrils in one plane. The distortion caused by a lens of less than 2-mm. focal length is increased 640 to 1080 times by the magnification.

Bailey presented a complete description of the beaten material (*3*); he observed that the frayed fibers seemed to be composed of fibrils whose diameters were too uniform at various places in a single fibril and in different fibrils to be accidental. Figure 1 illustrates this condition. It was suspected that this uniformity indicated a morphological and fundamental unit of cellulose. These uniform fibrils are termed "unit fibrils" in the present discussion.

Statistical Analysis

To determine the number of diameter measurements necessary to obtain a reliable estimate of the average fibril diameter, a preliminary sample of fifty fibrils was obtained from each of the following sources—surgical cotton, unbleached aspen soda pulp, and hydrolyzed unbleached aspen soda pulp. The

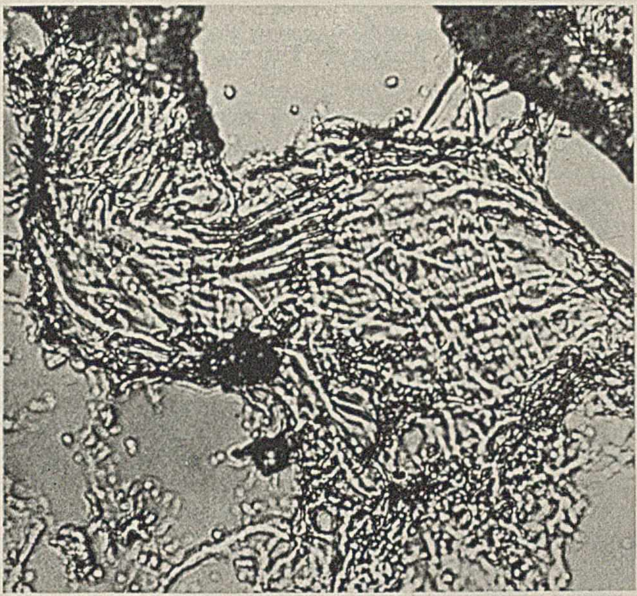

Figure 1 (*above*). Sample 2, Commercial Unbleached Aspen Soda Pulp

The fiber is just losing structural integrity, releasing unit fibrils and gel. Note the uniformity of fibril diameters, the separated unit fibrils, and the cylindricoids (× 640).

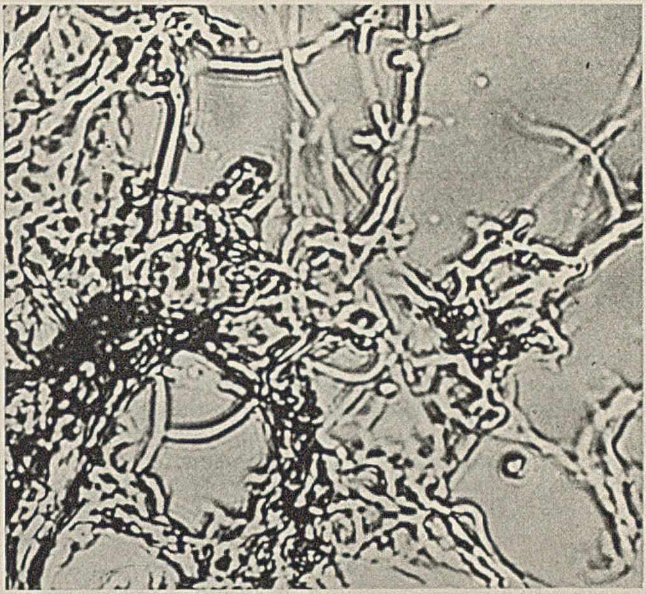

Figure 2 (*above*). Sample 8, White Pine Shavings Mechanically Disintegrated in Water with No Chemical Treatment (× 1080)

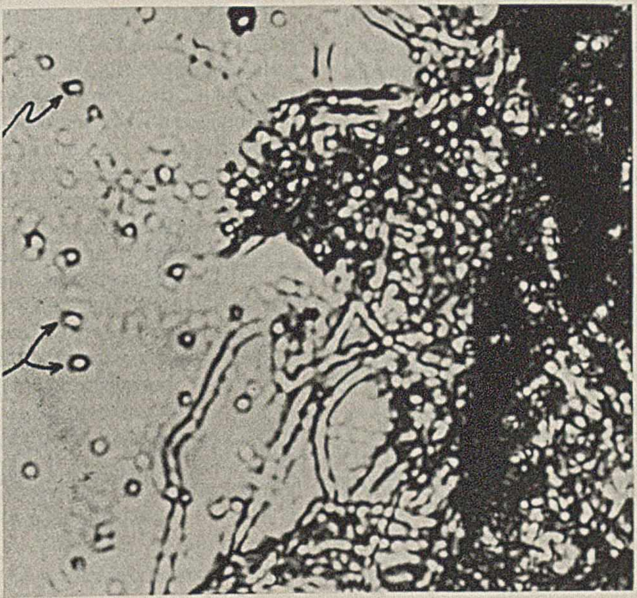

Figure 3 (*left*). Sample 1, Surgical Cotton Mechanically Disintegrated in Water with No Chemical Treatment

Note the prominent cylindricoids indicated by arrows (× 1080).

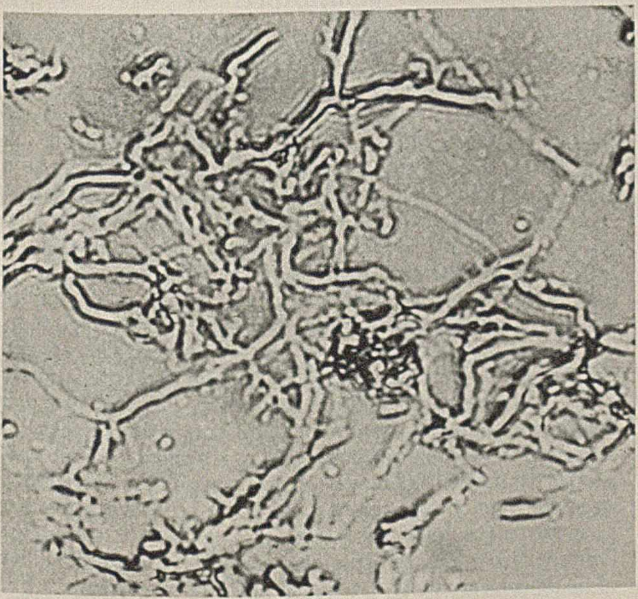

Figure 4 (*below*). Sample 16, Spruce Pulped with Nitric Acid and Potassium Chlorate (× 1080)

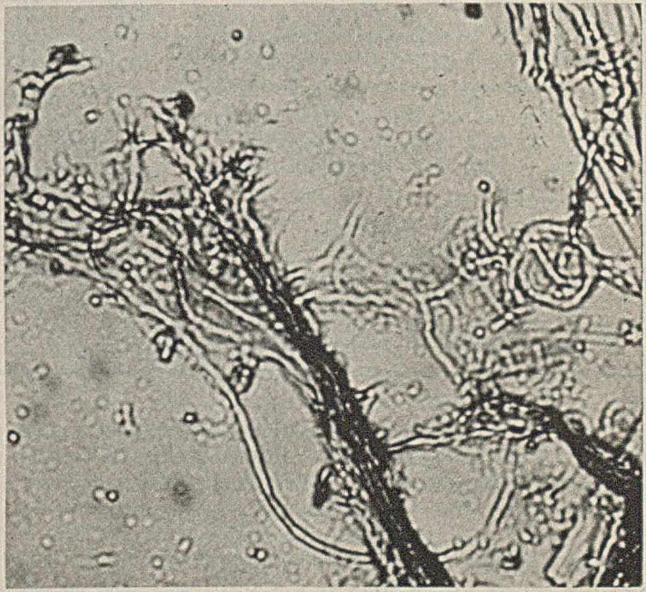

Figure 5 (*below*). Sample 5, Commercial Strawboard (× 1080).

averages, standard deviations, and standard errors of the averages are as follows:

Source of Fibril	Av. Diam.	Standard Deviation	Standard Error
	Microns		
Surgical cotton	0.92	0.059	0.008
Pebble-milled unbleached aspen soda pulp	1.08	0.110	0.015
Hydrolyzed unbleached aspen soda pulp	1.00	0.077	0.011

These standard errors (0.008, 0.015, and 0.011) show that a sample of fifty fibrils gave an average with a sampling error much less than the power of resolution, 0.2 μ, of the microscope. Even for the most variable of these sources—pebble-milled unbleached aspen—the sampling error is only one twentieth of this power of resolution. Because this high degree of precision is not necessary, the size of sample required to give a sampling error equal to one fifth of the power of resolution for the most variable source was computed by the formula for the standard error of the average as follows:

$$N = \left(\frac{SD}{0.04}\right)^2 = \left(\frac{0.11}{0.04}\right)^2 = 8$$

where N is the number of observations required to give an average with a precision equal to one fifth the power of resolution, and SD is the standard deviation of pebble-milled aspen soda pulp. Although a sample of eight would satisfy this arbitrary requirement, ten measurements were actually used in order to simplify computations.

The average diameters of the fibrils from sixteen samples drawn from nine different sources of cellulose treated, with one exception, by one or more of five different pulping processes are given in Table I.

TABLE I. AVERAGE DIAMETERS OF FIBRILS FROM CELLULOSES TREATED BY DIFFERENT PROCESSES

Source of Cellulose Fibrils	Av. Diam.	Standard Deviation	Standard Error of Av.
	Microns		
Not Significantly Different from Fundamental Group			
Western hemlock shavings, pulped with HNO_3 and $KClO_3$, pebble-milled 2 hr.	0.91	0.100	0.032
Commercial Fir-Tex pulp, bleached in 5% NaOCl, pebble-milled 2 hr.	0.92	0.082	0.026
Commercial strawboard, pebble-milled 2 hr.	0.92	0.094	0.030
Surgical cotton	0.92[a]	0.093	0.011
Western white pine shavings pulped with HNO_3 and $KClO_3$, pebble-milled 2 hr.	0.93	0.066	0.021
Southern pine kraft paper, bleached in 5% NaOCl, pebble-milled 2 hr.	0.94	0.047	0.015
Sitka spruce shavings, pulped with HNO_3 and $KClO_3$, pebble-milled 2 hr.	0.94	0.047	0.015
Thin western white pine shavings, pebble-milled 2 hr.	0.95	0.055	0.017
Southern pine kraft paper, pebble-milled 2 hr.	0.95	0.100	0.032
Commercial Masonite (southern pine) pulp, pebble-milled 3 hr.	0.96	0.047	0.015
Commercial unbleached aspen soda pulp, bleached in 5% NaOCl, pebble-milled 1 hr.	0.96	0.082	0.026
Western white pine shavings pulped with HNO_3 and $KClO_3$, bleached in 5% NaOCl, pebble-milled 1 hr.	0.96	0.066	0.021
Commercial Fir-Tex pulp, pebble-milled 2 hr.	0.97	0.082	0.026
Commercial Masonite pulp bleached in 5% NaOCl, pebble-milled 2 hr.	0.97	0.066	0.021
Av. (based on samples of ten)	0.942	0.077	0.007
Very Highly Significantly Different from Fundamental Group			
Commercial unbleached aspen soda pulp hydrolyzed 2 hr. with NaOH at 100° C., pebble-milled 2 hr.	1.01[b]	0.080	0.010
Commercial unbleached aspen soda pulp pebble-milled 1.5 hr.	1.07[b]	0.106	0.013

[a] Based on 70 observations.
[b] Based on 60 observations; all others based on 10 observations.

The primary question to be answered by these data is as follows: May these averages be considered estimates of the average fibril diameter of the same fundamental population of cellulose unit fibrils, or do they differ by more than could be expected if they had been drawn from such a population? To determine this, these data were analyzed by Fisher's variance method (*11*) and Snedecor's F test (*19*). The results (Table II) indicate that as a group the variation between the averages differs by more than could reasonably be expected if the sixteen samples had been drawn from the same fundamental population of unit fibrils. This general conclusion is indicated by the fact that the actual value of F, 1.9, is just a trifle larger than the value, 1.7, that occurs by chance five times out of one hundred trials (the level of significance arbitrarily chosen by statisticians as the dividing line between sampling and true differences). F is the number of times one measure of variation is larger than the accidental or chance variation.

TABLE II. ANALYSIS OF VARIANCE OF FIBRIL DIAMETER FROM CELLULOSES PULPED BY DIFFERENT PROCESSES

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F Test: Actual F	F Test: 5%	F Test: 1%
Between sources of cellulose	15	0.19	0.013	1.9[a]	1.7	2.1
Within sources (error)	144	0.99	0.007			
Total	159	1.18				

[a] Just significant.

To discover which of these averages might be grouped together and considered typical of a fundamental population of cellulose unit fibrils, or conversely, which averages could not be considered members of such a population, all the possible differences between pairs of averages were subjected to the t test (*11, 19*). The number of times an actual difference is greater than a sampling difference is designated as t. For the size of sample analyzed, the values of t that would occur five times in a hundred trials and only once in a hundred trials are 2.0 and 2.6. These figures multiplied by the standard error of a difference give the significant and highly significant differences with which the actual differences may be compared. The standard error of a difference between two means computed from samples of ten is computed from the mean square for error in Table II by the following formula:

$$\text{Standard error of a difference} = \sqrt{\frac{2\ (\text{mean square for error})}{10}} = \sqrt{\frac{2\ (0.007)}{10}} = 0.037\ \mu$$

Any difference equal to at least twice this standard error of a difference, or 0.074 μ, would be considered a significant difference (i. e., more than a sampling difference); and a difference 2.6 times this, or 0.096 μ, a highly significant difference (i. e., one still less likely to occur as a result of sampling). Therefore, all averages between 0.91 and 0.07 or 0.98 μ may be considered as belonging to the same population of fibrils. As Table I shows, this group includes all sources and treatments, except pebble-milled aspen soda pulp and hydrolyzed soda aspen pulp, with averages over 1 μ. This group may therefore be considered the fundamental population of typical cellulose unit fibrils. If this group is assumed to represent the fundamental population of cellulose unit fibrils, the limits within which the true average diameter of this population will fall may be computed from the average and standard error of this average. As Table I shows, the average diameter of the unit fibril is 0.942 μ ± 0.007. Therefore the limits within which the true average falls with a probability of being correct ninety-five out of one hundred trials are this average plus and minus twice this standard error, or 0.928 to 0.956 μ. Furthermore, not only because these treatments cover the range of severity of treatment of industrial conditions, but also because most of them are more severe, it is felt that these limits do represent the probable range of the average diameters of the cellulose unit fibril from most sources.

The variation of the individual fibrils from their averages is also shown in Table I by the standard deviations. For the fundamental group, the standard deviations range from 0.047 to 0.100 μ. A Chi-square test (*19*) of this variation indicates, however, that these values are not significantly different. Therefore it appears that cellulose fibrils from most of these sources not only fluctuate around a common average diameter but also that the amount of this fluctuation is the same. The standard deviation of the fundamental group (Table I) is 0.077 μ. Figure 6 gives the distribution of fibrils, based on the sixteen samples of ten each, from all the sources. If the two sets of significantly different aspen data are eliminated, the range will be reduced from 0.8–1.3 to 0.8–1.1 μ.

To determine whether or not the alkali-treated aspen soda pulp (No. 4) and the unbleached aspen soda pulp could be considered as extreme members of this family of unit fibrils, a supplementary *t* test was used to compare the averages from the larger samples of data available for this material with the average, 0.942 μ, of the group. For this test seventy measurements were available for unbleached pebble-milled aspen and sixty measurements for the alkali-treated aspen. The test was therefore more sensitive. The results of this analysis not only corroborated the original findings, but indicated that it was highly improbable that these two sets of aspen fibril diameters were members of the fundamental group.

A similar test was also made on the seventy measurements available for cotton. This more precise test indicated that the average diameter of the cotton fibrils was just significantly different from the average of the group. However, because a variation of this magnitude may occur five times in a hundred trials by chance alone, the cotton fibrils may be looked upon as smaller members of this fundamental group.

Although it has been demonstrated by these statistical tests that some of the differences and measures of variation are statistically different, from a practical industrial standpoint these differences are without significance.

Optical, Chemical, Mechanical, and Botanical Limitations

As noted above, optical resolution was 0.2 μ. Average vision would require a magnification of 350 to 700 diameters to distinguish this separation; actually 930 diameters was used. An additional allowance was made for resolution less than this amount in calculating the number of observations necessary for a given accuracy. No claim is made that any individual measurement is more accurate than 0.2 μ, although for mathematical reasons drum readings rounded off to the nearest 0.1 μ were retained.

Chemically, considerable diversity was obtained. Some fibers were wet only with water throughout the entire process from the block of wood to the slide. Others had alkaline or oxidative pulping and bleaching. Drastic nitric acid pulping and alkaline bleaching would presumably give nearly an ultimate oxycellulose product, visibly demonstrated by increased ease of disintegration in beating, shorter beating time, and friability of the pulp. The mildest treatment consisted only of agitation in water, whereas the most severe treatments were close to causing more or less complete degradation and disappearance of the cellulose as such; therefore we believe that not only was the range of severity of industrial conditions included, but that, for practical purposes, the extreme limits of chemical conditions were approached. It was not intended to include all industrial materials but rather the range of severity of industrial conditions. Because of this great diversity there is little possibility that the formation of unit fibrils was a result of specific chemical action.

The mechanical treatments used also varied greatly. From shavings to unit fibrils, some fibers were subjected only to pebble milling, of which Figure 2 is an example. The Masonite fibers had been defibered by steam explosion, the Fir-Tex had been hammer-milled, the straw had been rod-milled, the soda and kraft pulps had been through the macerating action of blowing the digester, and the kraft had been processed by standard beating tackle. The formation of unit fibrils by specific mechanical action is thus also remotely improbable.

Botanically, cotton, straw, one hardwood, and four coniferous woods were examined. Morphologically these include tracheids, true fibers, seed hairs, and the heterogeneous cellular system of the grasses. Although no claims are made beyond the sources studied, it is believed that these samples embrace sufficient plant species to indicate that the occurrence of cellulose in unit fibrils is more or less general.

Fundamental Significance and Practical Applications

The implications of uniform fibril diameter are extremely far-reaching. Probably the most important relate to industrial processing. It is obvious that a dense, resistant, morphological unit of cellulose (the unit fibril) is of immense importance in all physical processing of cellulose, such as beating. Resistant units (unit fibrils) are likewise important in the solution processes, such as cuprammonium and viscose, in that the unit fibril offers greater resistance to solution than the interfibril material, or, as Farr showed recently (*9*), in that fragments of unit fibrils resist cuprammonium solution entirely and form merely a microscopically visible part of a disperse system. The resistance of the dense unit fibrils is probably related to the relative amounts of the fibril fraction and gel fraction present, whereas the viscosity of the dispersion is also derived directly from these quantities and the specific viscosity of each. Similar considerations apply to the cellulose derivative processes such as nitrate and acetate. In addition, the unit fibril, which completely resists comminution in water and solution in cuprammonium alike, undoubtedly gives rise to heterogeneous fibrillar reactions and thus adds to the difficulty of obtaining the fully nitrated or otherwise completely reacted cellulose derivative (probably measured directly in the longer time of reaction to secure contact and the higher concentration of reagents necessary to accelerate diffusion into the unit fibril).

Comminution in water demonstrated that unit fibrils retained structural integrity after all other fiber characteristics had been demolished. Undoubtedly this indicates greater cohesion due to secondary valence between adjacent micelles or chain molecules. That these forces are high is shown by the resistance of fibrils to disintegration. Apparently water alone did not satisfy intermicellar or intermolecular attraction sufficiently to lower it below the mechanical forces. Conceivably, but not probably, other bonds between micelles (chemical bonds from micelle to micelle) might account for this high resistance. Chemically resistant fibrils undoubtedly give rise to heterogeneous fibrillar reactions in a manner similar to that depicted by Sisson for micellar reactions (*18*), which consist of reacted outer layers and progress inward through lower derivatives to the unreacted core. It is possible that unit fibrils represent cellulose crystals as Sisson (*17*) suggested of Farr's particles.

Interior walls of cellulose fibers show spiral striations when swollen and bruised; that further mechanical demolition separates such a structure into closely packed unit fibrils lying side by side is visually demonstrated by Figure 1. The appearance of a clear gel, simultaneously with the separation of unit fibrils, points rather definitely to the existence of two different materials in the cell wall—one the physically resistant and chemically less active unit fibril, and the other the gel-forming material apparently functioning as a cement between fibrils and laminations (*3*). This structure explains many of the changes occurring in beating, such as freeness, the development of strength, change in hydrolysis number, the impossibility of completely gelatinizing cellulose by only mechanical means, and other associated phenomena. These are substantially the same conclusions reached by Brauns and Lewis (*6*) on a highly purified pulp containing 99.1 per cent alpha-cellulose with practically no pentosan or uronic acid present. Beating failed to hydrate this pulp, freeness did not change, and sheet-forming properties failed to appear, although the viscosity was fairly high. Also, fibers of this pulp treated with cuprammonium solution separated easily into individual lamellae, as though the original cementing material had been removed. In view of wall striations, the isolation of unit fibrils is direct evidence of strong and weak spots in the wall, in contrast to the homogeneous-lamella concept of some investigators. The presence of a gel-forming material and another substance, which does not gelatinize in beating, demonstrated by two independent investigations (*3*, *6*), is highly important in the development and control of beating operations. Both of these materials would affect the viscosity of the material. Brauns and Lewis showed that the resistant cellulose may have high viscosity, yet no sheeting properties at all. Further, it is apparent that viscosity may err widely if used to follow beating or predict strength properties.

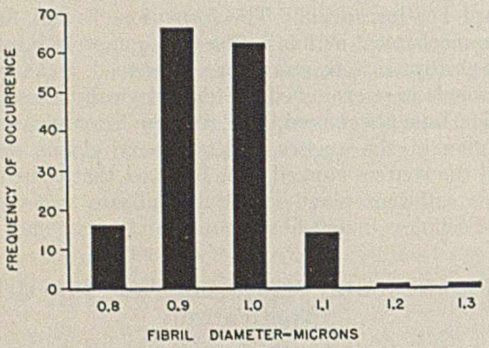

Figure 6. Distribution of Cellulose Fibril Diameter Measurements from Sixteen Samples of Ten Each, Taken from Nine Different Sources and Treated, with One Exception, by One or More of Five Different Pulping Processes

On slides prepared in this study, some fibers were covered by clots of a clear gel illustrated earlier (*3*). This was removed by immersing uncovered slides in sulfuric acid and hydrolyzing for several hours. The hydrolysis was so successful that the cement (gel) holding the fiber fragments to the slide was dissolved and the glass emerged clean. Partial hydrolysis was obtained by placing a few drops of the dilute acid on the slide and heating over a flame. Because the acid concentrated by evaporation, the threshold conditions to hydrolyze the gel without dissolving the unit fibrils were not apparent. After this hydrolysis many fibrils were still fastened to the slide in spots. It appeared that the gel had clotted the fibers and cemented them during drying, and that the gel was later hydrolyzed by the acid without apparent change to the unit fibrils except a sharpening and clarifying of the microscopic image. Similar results were obtained by alkaline hydrolysis with sodium hydroxide. Further work on the character, quantity, and location of this gel is contemplated.

Farr's observations of ellipsoidal particles forming a fibril are undoubtedly significant. Following the course of carbohydrate condensation on the cell wall, it would appear tenable that production of cellulose from the cytoplasm would soon cause saturation. According to Campbell's theory of cellulose hydration (*7*), longer chains would precipitate first and would be deposited preferentially on the growing particle due to their greater surface and difficulty of retaining a "hydrated atmosphere". It is not difficult to understand how fibrils might be laid down with smaller particles or shorter chains filling the gaps and forming the matrix. It is possible that matrix material may be modified—for example, oxidation of an alcohol group to carboxyl forming a uronic acid. This explanation fits exactly the observations of Brauns and Lewis that their highly purified pulp had a uronide matrix. It is striking that two independent investigations have demonstrated particles, resolved from fibrils, of almost identical size. These have been termed "ellipsoid particles" (*10*) and "cylindricoids" (*3*), but irrespective of name they appear to be derived from the same structure. Since the measurements recorded in this paper were made on dry fibrils, all that is necessary to concur with Farr's diameter of 1.1 μ is to add the amount of swelling caused by water (10 to 15 per cent) which then gives 1.1 μ as the water-swollen diameter. The obvious explanation of the similarity in length of these particles is that sufficient ends of micelles occur at one point to cause a weak spot in the fibril.

That such a wide range of plants yields uniform fibrils is decidedly interesting. This would suggest that cellulose formation and condensation are conditioned only by chemical considerations and probably are merely expressions of identical equilibria in many, if not all, cellulose-producing plants; as such, they take precedence over the later function and location of the cell in the plant.

Several investigators (*1*, *4*, *13*) have reported what appears to be an anastomosing system of fibrils, the size of fibrils reportedly diminishing to invisibility. These observations have been made on more or less integral lamellae or fibers, usually after drastic swelling treatment. The "acid test" of anastomosing fibrils would appear to be actual isolation, which has never been accomplished. The complete absence, by any observer, of forked isolated fibrils, the uniformity of particle diameter observed; the general uniformity of unit fibril diameter throughout the entire length, the general absence of tapering ends of fibrils (which would be present if torn from an anastomosing structure), and the 230 μ length of some isolated fibrils (*15*) would appear to offer convincing evidence that fibrils are unbranched filaments. It seems probable that transverse sections of fiber walls containing extremely tenuous zones, obtained by drastic swelling techniques and susceptible to the complications of progressive peptization and coagulation, should be interpreted as effects of chemical action or combined chemical and mechanical treatment, rather than as structural features, if and until fibrils of this size are actually isolated, and by less objectionable technique. The fact that two independent investigations (*3*, *6*) have demonstrated a pulp fraction which is completely incapable of being gelatinized by comminution in water, in contrast to a swelling treatment which may peptize cellulose completely, is reasonably conclusive evidence that the action of the two processes is different in kind.

The concentric ring appearance of etched or swollen transverse sections and the apparent absence of radial markings on these rings have led some workers (*1*, *4*) to conclude that each lamella is continuous and integral. Therefore they formulated the hypothesis that fibrils formed by rupture of what seemed to be a homogeneous sleeve were of random size, in spite of the visibility of more or less uniform longitudinal markings in longitudinal sections. The error in concluding that each lamella is continuous would appear to arise from two considerations: (*a*) that the importance of these longitudinal markings was overlooked and due explanation for the absence of the corresponding markings in transverse sections was not insisted upon; and (*b*) that the gaps between fibrils in a single lamella, when viewed in transverse section, slanted sufficiently from the axis of vision so that the optical contrast was below that required for threshold visibility. Undoubtedly responsible for this continuous appearance of lamellar cross sections, then, are the rather large angle of fibril orientation from the vertical, the nearly perfect optical homogeneity of the specimen, the impossibility of obtaining any but a refraction and diffraction image, and the presence of peptizing agents, peptization or degradation products, and a partially peptized mother specimen; all contribute to fusion of refractive index and thus make optical differentiation and resolution impossible.

Undoubtedly much remains to be learned about fiber laminations. In cotton the number of laminations appears to be related to diurnal light and temperature changes (*2*) yet wood fibers and tracheids, fully protected from light and partially protected from temperature changes by several or more inches of bark, show almost identical laminar and fibrillar structure. It would appear tenable that the laminations might be primarily due to diurnal changes in the rate of metabolism and thus cause a corresponding change in the rate of carbohydrate condensation on the cell wall. There is no evidence to indicate that a given lamination in a wood fiber is deposited on a certain day or time of day. Undoubtedly hysteresis exists between formation and deposition. How much is unknown, but it seems probable that thickness of laminations and unit fibril diameters are controlled by chemical equilibria. In other words, light and temperature effects in the leaves would have about as much influence on fibril diameter as the melting of snow fields at the headwaters of a river would have on the change in water level or the size of waves at the river mouth.

In conclusion, it should be repeated that different chemical treatments might explain small size differences, and that hydrolysis and oxidation are conducive to smaller diameters by reducing the amount of gel coated on the surfaces of the fibrils. This is undoubtedly the explanation of the high value for pebble-milled aspen soda pulp which has no other treatment. If we neglect the overwhelming statistical proof of unit fibrils for the purposes of discussion, it would still appear far from reasonable that, from a possible size range of about 0.1 to 10 μ (i. e., 100 to 1) an unprejudiced observer should be able, merely by visual memory, to select several hundred fibrils not varying from one another by more than 1 per cent of this range. It is by no means implied that smaller fibrils do not exist, but it is believed that the unit fibril is a natural morphological unit, probably associated with all plant cellulose. It is possible that chemical treatment, alone or prior to physical treatment, might subdivide unit fibrils into the smaller particles reported by some investigators (*1*, *2*, *4*, *5*, *13–16*).

Finally, the most significant finding of this study is not the exact dimension of the unit fibril, but the evidence that such a unit exists, with the manifold contingent implications, such as the presence of a gel, the nature of the physical disintegration of fibers, fibrillar reactions, viscosity effects, changes in freeness and hydrolysis number, development of strength, and other associated phenomena.

Conclusions

1. Cellulose unit fibrils appear to have one more or less common and constant diameter, 0.9 to 1.0 μ, independent of origin, chemical treatment, or mechanical processing.
2. At least two physical materials occur in the fiber wall, one a cementing gel, the other a compact fibril incapable of being gelatinized in water by ordinary methods.
3. Fiber laminations have alternately strong and weak spots; the distance from center to center of either is of the order of one micron.
4. Zone markings on drastically swollen material are a doubtful basis from which to infer fibril dimensions.
5. Anastomosing of fibrils appears to be extremely improbable.
6. Following the beating operation by viscosity, freeness, or any other single property is empirical and fundamentally inaccurate.
7. A mechanism is provided for the explanation of fibrillar reactions, fiber disintegration, and the numerous physical and chemical changes which accompany this disintegration.
8. By inference, true wall laminations would appear to be at least one micron thick, and thicker if heavily coated with gel.

Acknowledgment

The authors desire to express their appreciation to Phillip T. Schneider for making the micrometric observations.

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Correction—Utilization of Industrial Wastes

In this paper which appeared on pages 1323–30 in November, 1939, we find an error on page 1324, second column. It is stated that *p*-cymene is used in the manufacture of paint remover to the extent of 750,000 gallons annually. We now learn through other sources that not over 20,000 gallons of *p*-cymene are recovered annually and that its chief outlet is in the manufacture of carvacrol, although at one time the proposal was made to use *p*-cymene for the purpose first stated. It was later found uneconomical to do so.

H. E. Howe
F. J. Van Antwerpen

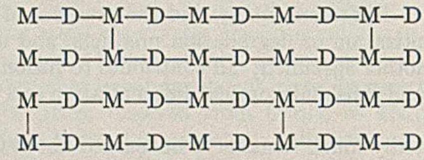
Copolymerization of Maleic Polyesters

JOHN B. RUST
Ellis-Foster Company, Montclair, N. J.

THE air-drying properties of glycol maleate esters were previously reported by Bradley, Kropa, and Johnston (*1*) and Vincent (*3*), and the correspondence between the conjugated system, $-C{=}C-C{=}C-$, found in certain natural drying oils and the carbon-oxygen conjugation, $-C{=}C-C{=}O$, occurring in maleic alkyd resins was postulated to account for the oxygen convertibility of these esters. A further qualitative property—namely, surface wrinkling of oxygen-converted films of glycol maleate—is likewise a property of drying oil films, and this correspondence was held to be significant. Under substantially oxygen-free conditions, the reaction of maleic anhydride with glycol is one of condensation in a manner analogous to the formation of saturated esters such as glycol succinate resins. The structure of the glycol maleate esters formed by condensation is essentially that of a linear polymer which may be represented by

M—D—M—D—M—D—M—D—M—D

where M is the maleic radical and D the glycol radical. In such an ester there is no possibility of cross linking by condensation, but the unsaturated portion of the maleic radical represents a potentially active point where addition polymerization may occur. Oxygen is an active catalyst for addition polymerization and activates the ethylene bond of the maleic radical so that cross linking may occur to form a system which may qualitatively be represented by:



In the presence of oxygen-yielding catalysts, glycol maleate esters undergo addition polymerization with the formation of gelled masses. Upon the application of heat these masses may be converted to tough hard resins having a variety of commercial applications. The esters are first formed under substantially oxygen-free conditions and result in linear condensation polymers in which addition polymerization has been inhibited. Further polymerization resulting in a thorough cure of the esters is effected solely through addition polymerization involving the system $-C{=}C-C{=}O$ which is activated by oxygen.

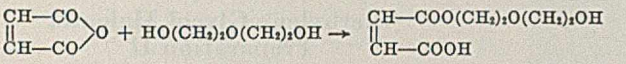
For the first time it has been shown that glycol maleate esters are capable of undergoing copolymerization with vinyl derivatives. The catalyst, temperature, and ratio of vinyl derivative to glycol maleate exert a determining influence on the final product from the standpoint of conversion rate, hardness, and elasticity. Definite limits of compatibility of the vinyl derivative in cured vinyl acetate–glycol maleate mixtures exist which are dependent to a great extent upon the type of vinyl compound employed. The explanation was advanced to account for the existence of these limits by showing that the properties of the resin were dependent upon the predominance of any one or more of three types of reaction which may occur at any instant during conversion of the mixture.

Glycol maleate esters are highly unsaturated in character and thus exhibit a relatively active tendency to polymerize or become converted to gels. It is obvious that the longer the linear chain of the glycol maleate, the greater will become the number of unsaturated linkages per molecule. It follows, therefore, that less activation will be required for an ester of high molecular weight than for one of low molecular weight to produce a corresponding increment in the average molecular weight of the polyester. In other words, the rate of conversion of a high-molecular-weight glycol maleate will be greater than that of one with a lower molecular weight. Dykstra (*2*) showed that additive polymerization of maleic esters containing one unsaturated linkage results in linear polymers. Bradley, Kropa, and Johnston (*1*) demonstrated that glycol maleate esters must contain more than one condensation unit to be capable of undergoing oxygen conversion to three-dimensional polymers. Styrene may be polymerized by heat to give soluble, fusible linear polymers. On the other hand, divinylbenzene which has two functional points capable of addition polymerization yields insoluble, infusible polymers. A qualitative analogy may be drawn, on the one hand, between styrene and monohydric alcohol derivatives of maleic acid and, on the other hand, between divinylbenzene and glycol maleate containing a multiplicity of unsaturated linkages.

The present communication is concerned with the further development of maleic polyesters. It has been found that the gelled esters may be further converted into hard tough resins. The unique category which these alkyds seem to occupy has led to their examination as molding, laminating, casting, lacquer, and adhesive resins. The study of the conversion of glycol maleate in relatively large masses has demonstrated their utility as extending the field of usefulness of alkyd resins. Because the structure $-C{=}C-$ in conjugation with a carbonyl group can actively undergo addition polymerization, its ability to copolymerize with vinyl derivatives was also recognized as a possibility. Such copolymerized resins, it was thought, would combine the inherent properties of both alkyd resins and vinyl polymers. It has actually been found that such copolymerized mixtures represent an entirely new type of synthetic resin.

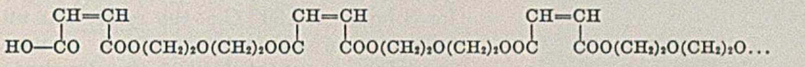
Cast Glycol Maleate Resins

The initial reaction of maleic anhydride with a glycol such as diethylene glycol first proceeds with the formation of the half ester. This reaction is accomplished with no elimination of water:



$$\begin{array}{l}\mathrm{CH{-}CO}\\ \|\\ \mathrm{CH{-}CO}\end{array}\!>\mathrm{O} + \mathrm{HO(CH_2)_2O(CH_2)_2OH} \rightarrow \begin{array}{l}\mathrm{CH{-}COO(CH_2)_2O(CH_2)_2OH}\\ \|\\ \mathrm{CH{-}COOH}\end{array}$$

On further heating, condensation occurs with the formation of a linear polyester:



$$\mathrm{HO{-}CO{-}CH{=}CH{-}COO(CH_2)_2O(CH_2)_2OOC{-}CH{=}CH{-}COO(CH_2)_2O(CH_2)_2OOC{-}CH{=}CH{-}COO(CH_2)_2O(CH_2)_2O\ldots}$$

When equal gram-molecular proportions of maleic anhydride and glycol are employed and reaction takes place under oxygen-free conditions, linear molecules are obtained which have a terminal hydroxyl and a terminal carboxyl group; or a mixture is obtained, part of whose molecules contains two terminal carboxyl and part two terminal hydroxyl groups. At any given instant, however, the average effect will be of one terminal carboxyl group and one terminal hydroxyl group per molecule. The terminal carboxyl may be titrated, and acid number would bear the following relation to molecular weight:

$$\text{Mol. weight} = 56{,}100/\text{acid No.}$$

This relation may be written in terms of the number of condensation units in an average molecule of glycol maleate:

$$\text{C. U.} = \frac{312.1}{\text{acid No.}} - 0.0968 \text{ (for diethylene glycol maleate)}$$

Acid number determinations give a good check upon the progress of the condensation of glycol with maleic anhydride, although refractive index and viscosity determinations offer a more rapid check in large-scale operation.

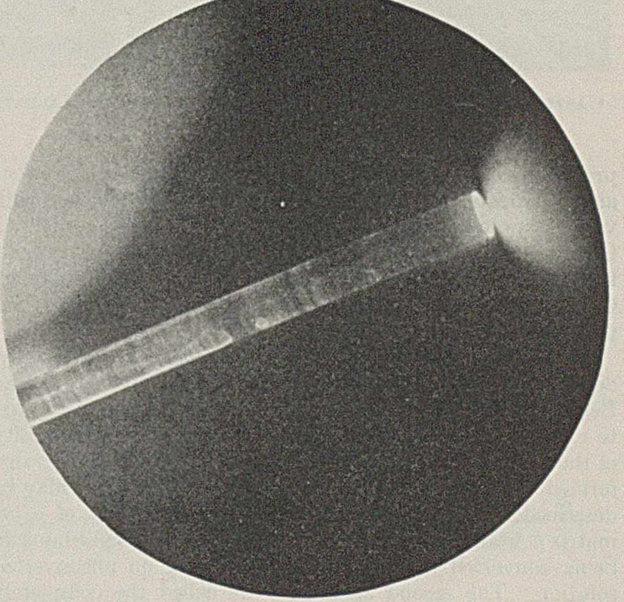
Diethylene Glycol Maleate, Preparation I

Six hundred grams (6.12 gram moles) of maleic anhydride were condensed with 670 grams (6.32 gram moles) of diethylene glycol in a three-necked Pyrex glass flask equipped with an inlet for carbon dioxide, an electric stirrer, and a short air condenser. The reaction temperature was maintained at 200° C. for 8 hours, in which time a viscous, clear ester having an acid number of 11.6 was obtained. At room temperature (26° C.) the ester was not solid but flowed very sluggishly. The acid number was determined by titration with 0.1 *N* potassium hydroxide, using bromocresol purple as the indicator to secure a sharp end-point reading.

To 28.2 grams of diethylene glycol maleate, 0.5 gram of benzoyl peroxide dissolved in 3 grams of benzene was added. The ester and solution were blended thoroughly and poured into a test tube. The solvent for the benzoyl peroxide was necessary since the latter is difficultly soluble in the viscous polyester. In 24 hours at room temperature the contents of the test tube had been converted to a hard rubbery gel which was totally insoluble in dioxane, in which unconverted diethylene glycol maleate is readily soluble. The test tube with its gelled contents was then placed in an electric oven thermostatically controlled for 50° C. for 48 hours. In this time the gel had been converted to a hard tough resin. It could be easily removed from the test tube in the form of a glass-clear rod. The rod could be easily machined by sawing, drilling, and shaping on a lathe with wood-turning tools. The machined parts could be polished to a high luster in the same manner as phenolic, vinyl, or methacrylate cast resinoids. The rod had a Rockwell hardness of L 55. This hardness could be duplicated if the benzoyl-peroxide-catalyzed diethylene glycol maleate were placed directly in an oven at 50° C. and baked for 50 hours.

Copolymerization of Glycol Maleate

To determine the extent to which a solution of vinyl acetate and diethylene glycol maleate could be polymerized, 80 grams of diethylene glycol maleate (preparation I) were mixed with 20 grams of monomeric vinyl acetate. A clear solution resulted to which was added 0.3 gram of benzoyl peroxide. The solution was transferred to a test tube and allowed to remain at room temperature. Within 24 hours the entire contents of the tube had hardened to a tough, glassy, transparent solid. When this experiment was repeated at 50° C., the polymerization reaction was so violent as to harden the solution within 6 hours. The reaction was exothermic and resulted in a badly cracked and discolored rod casting. The reaction is considered to be one of copolymerization, since no resinous product could be obtained when the ground, cured resin was extracted for a long time.



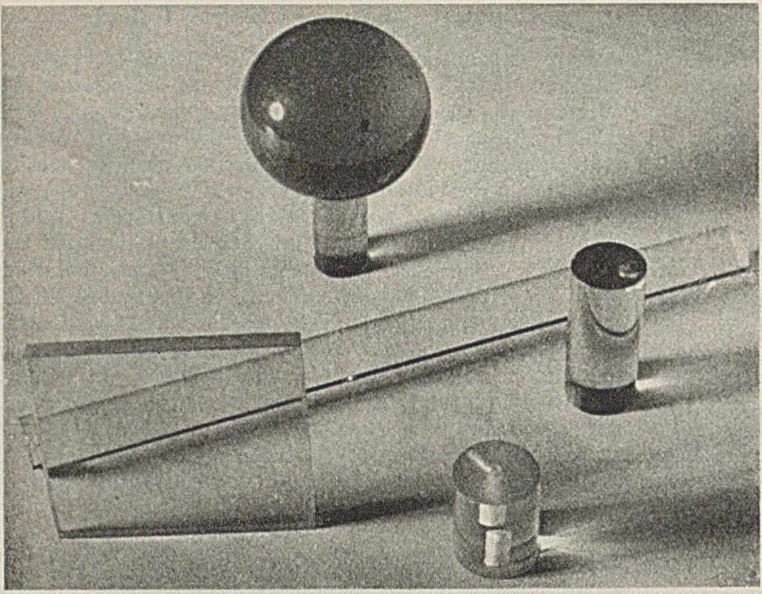
LIGHT TRANSMISSION OF VINYL ACETATE–DIETHYLENE GLYCOL MALEATE COPOLYMER

Several factors control the conversion rate of mixtures of vinyl derivative and glycol maleate. Some of the more important are molecular weight of glycol maleate, type and proportion of catalyst, ratio of vinyl derivative to glycol maleate, and type of vinyl derivative. Secondary factors influencing the cure and properties of the converted mixtures are type of glycol maleate and mass of casting and mold.

Obviously the molecular weight of the glycol maleate or the number of condensation units in the linear condensation polymer has the same qualitative effect on copolymerized glycol maleate as it has upon the rate of conversion of the glycol maleate itself, as Bradley, Kropa, and Johnston (*1*) demonstrated.

The type and proportion of catalyst plays an important role in the rate of conversion of vinyl derivative and glycol maleate mixtures and also determines to a large extent the properties of the final product. Of the oxygen-yielding catalysts benzoyl peroxide and acetyl benzoyl peroxide have proved to be among the most efficacious.

A diethylene glycol maleate, having an acid number of 55.5 and formed by the condensation of 6 gram moles of diethylene glycol with 6 gram moles of maleic anhydride at 180° C. for 10 hours, was mixed with vinyl acetate in the



Castings of Vinyl Acetate–Diethylene Glycol Maleate Copolymer

proportion 32 per cent vinyl acetate to 68 per cent diethylene glycol maleate. Rod castings in test tubes were made with varying amounts of benzoyl peroxide and heated at 50° C. Curing times of 160 hours for 0.005 per cent benzoyl peroxide to 90 hours for 0.05 per cent benzoyl peroxide were obtained. On the other hand, 0.1 per cent benzoyl peroxide gave a completely cured product within 24 hours.

The conversion of mixtures of glycol maleate and vinyl derivative may be recognized in several distinct stages. Before the first recognizable stage an induction period appears to exist during which no noticeable increase in the viscosity of the solution occurs. The solution then is uniformly transformed to a slimy gelatinous mass. This first stage may be described as a partial gel and consists essentially of a gel matrix containing unconverted solution which is continuously being converted into a soft gel containing no unconverted solution. The second stage may be called the completely gelled stage. As reaction continues, this soft gel becomes harder until it reaches a hard rubbery state which can be designated as the third stage. The hard rubbery gel is hardened further to produce a solid, no longer rubbery but lacking in strength; it may be classed as a relatively soft flexible resin. The final stage of cure is a hard, tough, glassy solid.

Table I. Influence of Catalyst Content on Rate of Conversion of Vinyl Acetate–Diethylene Glycol Maleate Solutions

Benzyl peroxide, %	0.005	0.01	0.02	0.03	0.05	0.1
Conversion rate, hours:						
Partial gel	...	...	...	...	..	..
Complete gel	20	...	...	...	..	..
Hard gel	45	20	20	20	..	..
Soft resin	100	80	80	60	20	..
Hard resin	160	140	140	130	90	24

Influence of Temperature. Heat will affect the conversion of vinyl derivative and glycol maleate mixtures alone and in the absence of oxygen. When oxygen is present, however, conversion is much more rapid and small changes in temperature produce relatively large changes in the rate of cure. Besides affecting the rate of copolymerization, the temperature has a great effect upon the properties and physical appearance of the final resin such as hardness, elasticity, transparency, and color.

Diethylene Glycol Maleate, Preparation II

A 690-gram sample of diethylene glycol (6.51 gram moles) was condensed with 637 grams of maleic anhydride (6.50 gram moles) for 8 hours at 180° C.; the result was an ester with an acid number of 98.1. A mixture of 68 per cent diethylene glycol maleate and 32 per cent vinyl acetate was divided into a number of equal parts, and 0.0033 per cent of benzoyl peroxide was added to each. The solutions were heated at 39°, 50°, and 64° C., respectively. At the higher temperature, cure was accomplished in the relatively short time of 80 hours. Since the amount of benzoyl peroxide was almost vanishingly small, the effect of temperature on the copolymerization reaction became the important factor influencing conversion.

Ratio of Vinyl Derivative to Glycol Maleate

In the polymerization of mixtures of vinyl acetate and vinyl chloride the ratio of the constituents may be varied to produce resins with a varied range of properties. Moreover, the polymerized mixture has characteristics widely different from either constituent polymerized alone or a physical mixture of the independently polymerized materials. The polymerized mixtures possess one common quality—they are all transparent. It has been found, however, that for mixtures of vinyl derivative and glycol maleate, well-defined limits of transparency exist; on one side clear resins are produced, and on the other side, cloudy opaque materials. For vinyl acetate and diethylene glycol maleate this limit is about 32 per cent vinyl acetate, a greater proportion of vinyl acetate yielding opaque, cured resins. The unconverted mixture of vinyl acetate and glycol maleate forms clear solutions, no matter what the ratio of vinyl acetate to glycol maleate; but in curing the mixture, opacity develops with all proportions greater than 32 per cent:

% Vinyl Acetate	% Diethylene Glycol Maleate	Appearance
5	95	Clear
25	75	Clear
32	68	Clear
35	65	Turbid
40	60	Cloudy
50	50	Opaque
75	25	Opaque, nonhomogeneous
90	10	Opaque, granular
95	5	Pptn. of glycol maleate

Three general addition polymerization reactions may be expected to occur at any instant during the conversion of mixtures of glycol maleate and vinyl derivative: (*a*) polymerization of vinyl derivative with itself, (*b*) polymerization of glycol maleate with itself, and (*c*) polymerization of vinyl derivative with the glycol maleate. The properties of the final resin are determined to a large degree by the predominance of any one or more of these reactions. The predominance of any one reaction would be determined in turn by its reaction coefficient and the concentration of the constituents entering into the reaction. Thus, since vinyl acetate has a greater polymerization activity than glycol maleate, in mixtures containing a high proportion of vinyl acetate, reaction *a* would predominate and reaction *c* would be secondary. Polymerized vinyl acetate is almost completely immiscible with glycol maleate and completely incompatible with converted glycol maleate. Therefore the turbidity and opacity

TABLE II. INFLUENCE OF TEMPERATURE ON RATE OF CONVERSION OF VINYL ACETATE–DIETHYLENE GLYCOL MALEATE SOLUTIONS

	Conversion Rate, Hours		
	39° C.	50° C.	64° C.
Partial gel	100	...	...
Complete gel	150	...	...
Hard gel	240	20	...
Soft resin	...	70	20
Hard resin	...	140	80

of converted vinyl acetate–glycol maleate mixtures containing more than 32 per cent of vinyl acetate are explainable in the light of the foregoing. When the concentration of vinyl acetate is low, as in mixtures containing less than 32 per cent vinyl acetate, reactions *b* and *c* would predominate; but in view of the greater activity of vinyl acetate, reaction *c* would probably occur most readily.

Vinyl derivatives other than vinyl acetate show different limits of compatibility in the cured resin. Styrene, for instance, has a limit about that of vinyl acetate, whereas a mixture of equal parts of vinyl acetate and styrene will yield clear, cured masses when present in amounts up to 40 per cent of the casting solution. Methyl methacrylate, on the other hand, is compatible in all proportions.

Miscellaneous Properties of Glycol Maleate Copolymers

By the purification of maleic anhydride and diethylene glycol on vacuum distillation and reaction under controlled oxygen-free condition, water-white diethylene glycol maleate may be prepared. Copolymerization of this material with purified water-white vinyl acetate, styrene, or methyl methacrylate yields water-white resins. From tests on a Fade-ometer these castings have been found to be almost completely light-fast.

The Rockwell hardness of copolymerized vinyl acetate–glycol maleate ranges from L 50 to L 110, which is comparable to commercially available cast phenolic resinoids as well as to the vinyl, acrylic, and methacrylic resins. The greatest commercial virtue of these copolymerized resins lies in their rapidity of cure and ability to be made in light colors or water-white, as desired. With relatively nonvolatile vinyl derivatives such as styrene, molding compositions have been made which exhibit curing rates comparable to those of urea resin compositions. Molding temperatures of 130–140° C. were employed with pressures of 2000 pounds per square inch to give set-up periods of 15 seconds and curing times of 2 minutes as compared to 30-second set-up and 2-minute cure for urea resin compositions under similar conditions.

Acknowledgment

The author wishes to thank the Ellis-Foster Company for their kind permission to publish these results.

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PRESENTED before the North Jersey Section of the American Chemical Society.

Explosibility of Aluminum Powder–Silica Dust Clouds

RALPH B. MASON AND CYRIL S. TAYLOR
Aluminum Research Laboratories, New Kensington, Penna.

THE discovery that aluminum powder is an effective agent in the prevention of silicosis (*1*) has raised a number of questions regarding its application in practice. For example, does the introduction of the necessary amount (1 per cent) of aluminum powder into the silica dust created in mine atmospheres by drilling and blasting create an explosion hazard? Fortunately, the answer is no. Although the explosion-preventing effect of the silica dust on concentrated suspensions of aluminum dust could easily be predicted from the well known effect of rock dust in coal mines (*3*), it was thought worth while to determine the facts experimentally.

Previous work from this laboratory (*2*) showed that the lower explosive limit of mixtures of aluminum powder and dry air was approximately 40 mg. of aluminum powder per liter of air (40 ounces per 1000 cubic feet). That work also showed that aluminum dust cloud explosions could not be initiated when the air was so diluted with either carbon dioxide or nitrogen that the oxygen content was below 10 per cent. A study has now been made of the effect of silica dust upon the explosibility of aluminum powder–silica dust clouds in air.

The apparatus for this investigation and the details of procedure were given in the previous paper (*2*). The method consists essentially in raising, with a measured puff of air, a uniformly distributed dust cloud in a closed glass tube. An igniter is then fired at the proper moment, and the pressure produced is recorded on a pressure recorder. The air used in the present experiments was not dried, as other experiments indicate that the presence of normal amounts of moisture has no effect on the explosive limits.

The aluminum powder used in these experiments was the extremely fine, light, fluffy powder designated in the previous paper as powder B, which had an average flake thickness of about 0.14 micron. The silica used was dust collected from the girders in the crushing plant of the McIntyre-Porcupine Mines, Ltd., and was furnished through the kindness of J. J. Denny. It passed easily through a 325-mesh screen.

In one series of experiments aluminum dust was used in such an amount that the concentration obtained in the explosion chamber was approximately 106 mg. per liter, or over twice the minimum amount required to produce an explosive mixture in air. This is more than enough to produce a sharp explosion in the absence of an inhibiting agent. The addition of an equal weight of silica dust (106 mg. per liter) practically prevented an explosion; with double that weight of silica dust no appreciable increase in pressure was obtained when ignition of the suspension was attempted. Apparently some aluminum dust, within the zone of high temperature produced by the ignition, burned and added its increment of heat, but the blanketing effect of the silica prevented propagation of the ignition and thus prevented any explosion.

In another series of experiments, the concentration of the aluminum dust in the explosion chamber was maintained at approximately 212 mg. per liter, or more than five times the amount required to produce an explosive mixture with clean air. This, of course, would produce a violent explosion if ignited in the absence of any inhibiting material. The addition of silica dust in the concentration of 106 mg. per liter (one half the concentration of the aluminum powder) did not prevent an explosion; but when the silica content was increased to approximately 160 mg. per liter, the reaction was less violent and only a moderate increase in pressure was recorded. Upon increasing the silica dust content to 424 mg. per liter (twice the concentration of the aluminum powder), no appreciable increase in pressure was recorded when an attempt was made to ignite the suspension.

It was practically impossible to produce a uniform dust cloud when attempts were made to suspend larger amounts of aluminum dust and silica dust in the explosion chamber. Therefore recourse was had to qualitative experiments.

As a qualitative experiment, a mixture of one part silica dust and one part aluminum powder was blown through the flame of a Fisher burner; it ignited with a vivid flash. When, however, two parts of silica dust and one part of aluminum dust were used, the mixture barely burned in the flame. In blowing the material through a flame, the actual concentrations of dust obtained are naturally many times those used in the explosion chamber experiments.

In actual practice, we understand that an ounce of aluminum powder has been found to be enough to insolubilize the silica in a dust cloud of 8000 cubic feet volume, produced by a blast at a mine face. In order to produce an explosive mixture, this ounce of aluminum dust would have to be concentrated in a volume of not more than 25 cubic feet of clean air. Silica dust present in the atmosphere effectively reduces the explosibility of aluminum powder at even higher concentrations. With large proportions of silica dust, such as would be present when the aluminum dust was used to prevent silicosis, it would be impossible to initiate an explosion, even if the concentration of the aluminum dust were accidentally increased until it passed the normal lower explosion limit. This effect is obviously similar to that of rock dust in preventing coal dust explosions, and presumably results from the absorption of radiated heat by the inert mineral powder.

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Flow Characteristics of Lime-Base Greases

J. F. T. BLOTT AND D. L. SAMUEL

Asiatic Petroleum Company, Ltd., London, England

THE physical nature of petroleum greases constitutes a problem to which no agreed solution has yet been found. Greases are described vaguely as colloidal dispersions of soaps in oils, or as water in oil emulsions stabilized by soap. Lawrence (*6*) classifies them as (*a*) true gels, in which class he places lime-base greases, and (*b*) pseudo gels or pastes of fully crystalline soaps suspended in oils, in which he includes soda- and aluminum-base greases.

However greases may be classified, there is no doubt that they belong to the category of plastic materials. These are bodies which may have a yield value and whose viscosities are dependent on the shearing stress applied to them.

Yield value, which may be defined as the minimum tangential force per unit area necessary to cause flow, is possessed to some degree by the majority of commercial greases. If a force greater than this critical value is applied, the lubricant will flow, but the rate of flow will not be directly proportional to the applied stress.

When grease is applied to a bearing, it is subjected to a shearing stress which will depend on the speed of rotation and the clearances involved. Under these conditions it will flow and its viscosity will become an important factor in the satisfactory running of the moving parts.

Some attempts to measure the viscous properties of greases have been made in recent years. Porter and Gruse (*8*) made use of a modified form of Bingham and Green plastometer to examine the flow under stress of a number of cup greases. They measured a yield value and mobility as defined by Bingham (*3*). A consistometer designed to measure the flow of plastic materials under stress was developed by Bulkley and Bitner (*4*) in 1930. This apparatus was restricted to measuring comparatively low rates of flow under pressures not exceeding one atmosphere.

Later, in 1932 Arveson (*1*) carried out a number of experiments with cup greases in his constant-shear viscometer in which the material was forced through a capillary at a constant speed and the pressure drop through the capillary was measured. In 1934 Arveson (*2*) published a paper in which the effect of temperature was taken into consideration. For the calculation of his results Arveson used the Poiseuille equation:

$$\eta_\alpha = \frac{P\pi R^4}{8QL} = \frac{PR/2L}{4Q/\pi R^3} = \frac{F}{S}$$

where η_α = apparent viscosity, poises
P = pressure in dynes/cm.^{2}
R = radius of capillary, cm.
L = length of capillary, cm.
Q = rate of efflux, cc./sec.
F = shearing stress at walls = $(PR/2L)$ dynes/cm.^{2}
S = rate of shear = $(4Q/\pi R^3)$ sec.$^{-1}$

The apparent viscosity calculated in this manner is not the true viscosity of the grease but that of a Newtonian liquid which would flow at the same rate as the grease under these conditions.

Moreover, the expression $4Q/\pi R^3$ is the rate of shear at the walls of a capillary only when the viscosity coefficient of the fluid is a constant—i. e., in the case of a true liquid. In general, this expression does not represent the rate of shear at the walls or at any other point in the capillary, and it is misleading to assume that it does so with non-Newtonian fluids.

The rate of shear (otherwise, the velocity gradient) involved when a fluid is flowing through a capillary is expressed in its most general form by dv/dr where v is the velocity in cm. per second at a distance r from the center of the tube.

Mooney (*7*) showed how the absolute viscosity of a non-Newtonian fluid can be calculated from experimental data obtained by a capillary tube viscometer without making the assumptions so generally used in this type of work. His method has resulted in the formulation of the following expression:

$$\frac{d(Q/\pi R^3)}{dF} = \frac{1}{\eta} - \frac{3}{F} \times \frac{Q}{\pi R^3}$$

where η = absolute viscosity

The capillary tube experiments give a direct measure of both Q and F, and thus it is possible to deduce the viscosity of the material under test.

Another method for deducing the viscosity of a plastic material from such experimental data was published by Saal and Koens (*9*). Their procedure, however, is not so convenient to use as that evolved by Mooney.

A search of the literature reveals that no measurements of the absolute viscosity of greases have been made. The work described here shows how this absolute viscosity may be measured with the help of Mooney's equation. The results obtained represent the first attempts in this direction.

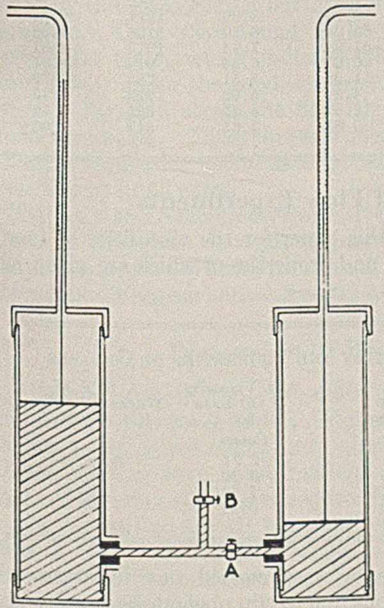

FIGURE 1. CONSISTOMETER FOR EXAMINING THE FLOW PROPERTIES OF LUBRICATING GREASES WITH A DEVICE FOR REMOVING OCCLUDED AIR

Apparatus and Procedure

The apparatus used for this work was of the capillary-tube type and consisted essentially of a U-tube, with a horizontal glass capillary connecting two vertical limbs. The grease with which it was filled could be made to flow back and forth through the capillary, and all the results could thus be obtained upon the same sample of material.

The two vertical limbs were constructed of mild steel tubes 2 inches i. d. and 8 inches long, and were fitted with screw caps at each end. They were also provided with short side tubes in which the capillary was set by means of corks.

The absolute viscosities at 25° C. of a number of lime-base greases have been determined in a capillary viscometer over a certain range of shearing stresses, and some approximate yield values have been measured in a concentric-cylinder torsion viscometer. Some empirical measurements have been made on the flow of the greases under comparatively high shearing stresses.

Mathematical expressions to the flow curves in the capillary viscometer have been found. These agree satisfactorily with the experimental results except in the neighborhood of the yield values.

The evidence of these experiments suggests that the viscosity of the oil base is the main factor determining the viscosity of the grease at shearing stresses well removed from the yield value and that the soap content probably controls the magnitude of the yield value.

A diagram of this consistometer is shown in Figure 1, but the capillary is here replaced by a device for removing air from the grease, to be described later.

The limbs of the apparatus carried light metal plungers, capable of moving freely in a vertical direction. These were necessary to prevent the compressed gas used as a source of pressure from making blowholes through the material and also to indicate the levels of the grease in each arm.

The upper screw caps carried long glass tubes which were graduated in centimeters and which served as guides for the plunger stems. These tubes were connected through suitable taps to the source of pressure and to the flowmeter used for measuring the rates of flow through the capillary. It was so arranged that each side of the consistometer could be connected either to the pressure source or to the flowmeter.

Pressure was applied to the grease in the apparatus by means of compressed nitrogen gas acting through an equalizing chamber of about 10 gallons capacity. A mercury manometer indicated the pressure applied.

The flowmeter adopted was of the differential pressure type and was provided with a number of calibrated capillary leaks so that the rates of flow over a wide range could be accurately measured. The consistometer and the essential portions of the flowmeter were maintained in a thermostat when runs were being made.

The measurements made with this apparatus were necessarily effected on a worked grease. It was impossible to carry out any tests on the unworked material since, even if the consistometer could be filled without undue working of the grease, constant passage through the capillary would eventually cause a certain amount of breakdown. In any case, a number of preliminary runs were made with each grease until reproducible results were obtained.

To carry out a test, one limb of the consistometer was completely filled, while the other was filled only to the level of the side tube. It was found impossible to avoid the inclusion of air in the grease during the filling operation and, since air would upset all flow rate measurements, it had to be removed before a run was made. This was effected by means of the device connecting the two limbs shown in Figure 1. It consisted of a T-piece in which both the horizontal and vertical tubes were provided with taps. It was filled with the grease under test and attached to the consistometer as shown. Pressure was then applied to the full arm of the apparatus; tap A was open and tap B shut so that grease could flow slowly from one side to the other. As soon as an air bubble entered the T-piece, however, tap A was closed and tap B opened, so that it was diverted from the main stream and removed.

By passing the grease through this device one or more times, visible air bubbles were eliminated together with any dirt or foreign matter. After this treatment the grease probably still contained some finely dispersed air, which did not interfere with the subsequent measurements, and also dissolved gas; however, the same is likewise true of the grease in practical operations.

To determine the viscosity of a grease in an apparatus of this type, it is necessary to measure the pressure required to force the material through the capillary. When pressure is applied to the grease, some of this is utilized in forcing the grease to the entrance to the capillary and is thus not available for flow within the capillary itself. This must be deducted from the total measured pressure before the results can be evaluated.

Blank experiments were therefore carried out in which the horizontal capillary tube was replaced by a disk pierced with a hole of the same diameter as that of the capillary to be used. The pressures necessary to force the grease through this orifice at various rates of flow were then determined, and a curve was drawn from these results. Thus when runs were made with the capillary in place, the total pressure recorded for any particular rate of flow could be corrected by reference to these blank experiment curves. All measurements of flow rates were made when the height of grease in each arm was the same, as indicated by the plunger stems.

After the blank tests had been concluded, the actual capillary experiments were made. It was necessary to remove air bubbles from the grease at fairly frequent intervals during these runs as the backward and forward flow of the material resulted in the incorporation of appreciable quantities of air.

The capillary was filled with air-free grease and attached to the two limbs, one of which contained the bulk of the sample under test.

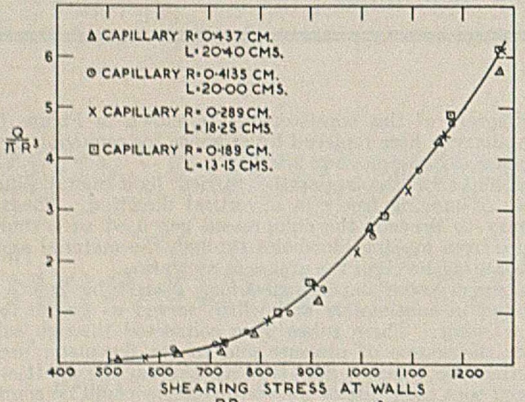

Figure 2. Results of Flow Experiments on Grease A

The apparatus was then placed in the thermostat and allowed to come to the required temperature of 25° C. in all the experiments. The pressure in the equalizing chamber was raised to the highest value to be attained in that run and was then applied to that side of the apparatus which contained the greater part of the grease. The other side of the apparatus was connected to the flowmeter. The grease flowed through the consistometer, displacing air at a rate recorded by the flowmeter. When the levels in both limbs were the same, as indicated by the plungers, readings of the rate of flow and the applied pressure were taken. The flow was allowed to proceed until the major part of the contents had been transferred to the other limb, when the pressure on the apparatus was released. The pressure in the equalizing chamber was then reduced by releasing a certain quantity of nitrogen, and readings were taken of the flow in the reverse direction under this new pressure. The process was repeated, the grease passing backward and forward through the capillary tube until the rates of flow over the desired pressure range had been recorded.

The apparatus as constructed was not suitable for pressures above one atmosphere, and thus the capillaries used were necessarily somewhat large in diameter.

To evaluate the results of these experiments, a flow curve was constructed by plotting $Q/\pi R^3$ against F. Tangents were drawn to this curve which allowed numerical values of $\left(d \frac{Q}{\pi R^3}\right)/dF$ to be obtained. With this information the absolute viscosity of the grease could be determined from Mooney's equation.

After the viscosity of the grease was obtained at various shearing stresses, the rates of shear involved were calculated from the equation:

$$F = \eta \, dv/dR$$

Results of a typical series of runs are given in Table I which shows how the experimental readings were dealt with.

Table I. Experimental Readings on Grease *A*

Capillary Dimensions	Total Pressure	Flow 60Q	Pressure Cor. for Blank	Shearing Stress at Walls F	$\frac{Q}{\pi R^3}$
	Cm. Hg	*Cc./min.*	*Cm. Hg*	*Dynes/cm.²*	
R = 0.4135 cm.; L = 20.00 cm.	10.86	62.76	8.57	1180	4.71
	10.30	50.20	8.08	1113	3.76
	9.55	33.09	7.43	1023	2.48
	8.74	19.29	6.72	926	1.45
	8.20	13.08	6.23	858	0.98
	7.55	8.18	5.65	778	0.61
	7.00	4.90	5.17	712	0.37
	6.37	3.21	4.58	631	0.24
R = 0.289 cm.; L = 18.25 cm.	14.44	27.96	12.12	1278	6.14
	13.25	20.11	11.01	1161	4.42
	12.53	15.37	10.36	1092	3.38
	11.51	10.07	9.41	993	2.21
	10.65	6.86	8.61	908	1.51
	9.66	3.72	7.73	815	0.82
	8.75	1.97	6.88	726	0.43
	7.21	0.55	5.44	574	0.12
R = 0.189 cm.; L = 13.15 cm.	15.67	7.81	13.30	1274	6.13
	14.63	6.13	12.30	1178	4.81
	13.03	3.65	10.88	1042	2.87
	11.53	1.97	9.47	907	1.55
	10.68	1.24	8.70	833	0.97
	9.54	0.53	7.60	728	0.42
R = 0.437 cm.; L = 20.40 cm.	11.24	90.14	8.90	1271	5.72
	10.34	69.03	8.10	1156	4.38
	9.21	41.08	7.13	1017	2.61
	8.41	20.60	6.44	919	1.31
	7.48	11.28	5.51	786	0.72
	6.76	4.64	5.06	722	0.29
	6.05	2.92	4.45	635	0.19
	5.13	0.88	3.65	518	0.06

Results of Flow Experiments

Results are given in this paper for the viscosities of four greases, the composition and properties of which are given in Table II.

Table II. Composition and Properties of Greases

Grease	Soap Content	Abs. Viscosity of Oil Base at 25° C.	A. S. T. M. Worked Penetration at 25° C.
	%	*Poises*	
A	7	2.74	Too soft
B	11.5	0.29	290
C	13.25	1.52	295
D	15.0	0.29	260

Preliminary experiments were carried out to ascertain whether any complications due to slip phenomena were to be expected under these conditions of flow. It has been shown by Mooney that, if slippage is absent and the viscosity of the material is simply a function of the shearing stress, the curves obtained by plotting $Q/\pi R^3$ against F will be coincident for all capillaries. On the other hand, if slippage is present, these curves will show some deviation.

Figure 2 shows the results obtained with grease A with four capillaries of different radii. Within experimental error, the points fall on one curve. It can therefore be assumed that flow due to slippage is absent in these experiments.

Another property of plastic materials which would tend to upset viscosity measurements is thixotropy. In a thixotropic substance, the viscosity varies with the time during which it is subjected to the shearing stress. With such a material the length of the capillary tube would be expected to

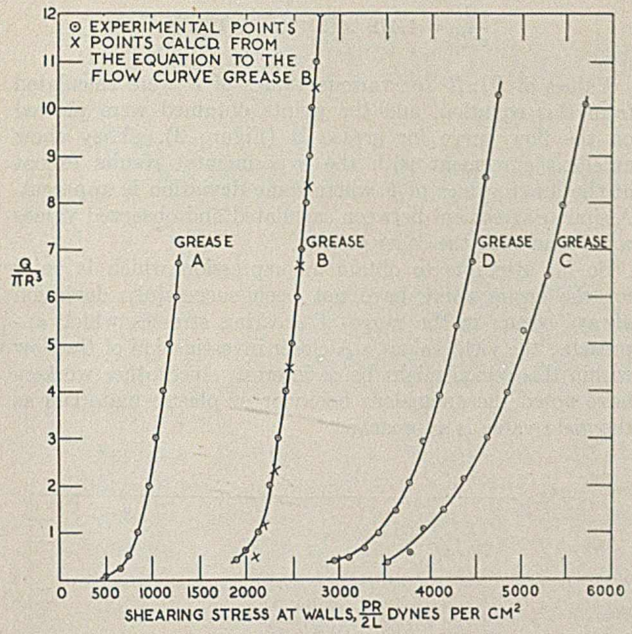

Figure 3. Flow Curves of Greases A, B, C, and D

influence the results, since for the same shearing stress the plastic would be sheared for a longer period in a long tube than in a short one. The flow curves of grease B with five capillaries of the same radius but of different lengths were determined. They were found to be coincident within experimental error, which indicates that thixotropic effects were absent under the conditions prevailing in these experiments. Figure 3 shows the flow curves of the four greases under discussion. These curves represent runs in at least two different capillaries and thus establish that slip phenomena were absent in all cases.

Figures 4 and 5 illustrate, respectively, the variation of the absolute viscosities determined from the flow curves with the shearing stresses and with rates of shear; Figure 6 shows the relation between shearing stress and rate of shear.

Discussion of Results

A comparison of the viscosities of the four greases is afforded by Figures 4 and 5. Figure 5 perhaps represents the more convenient relationship, since the rates of shear for all the samples were approximately the same, whereas the range of shearing stresses varied from grease to grease.

The viscosities are all comparatively high at the lower rates of shear. As the shear increases the viscosities at first decrease rapidly, but later the rate of decrease with shear falls off considerably.

A comparison of the viscosity curves with the A. S. T. M. penetration figures shows that these do not necessarily place the greases in the same order. Thus grease C appears to be more viscous than D although the A. S. T. M. penetration ranks it as the softer product.

An examination of the composition figures of Table II reveals that grease C has the more viscous oil base of the two. This has evidently resulted in a grease of somewhat higher viscosity even though the soap content of grease C is lower than that of D.

According to this reasoning, grease A should possess the highest viscosity of the group since it contains the most viscous oil base. However, it has a smaller yield value than the other three and flows easily at shearing stresses under which the stiffer products move slowly, if at all.

Unfortunately it was not possible to increase the range of this apparatus so that viscosities could be determined at shearing stresses of a higher order, far removed from the influence of yield values. Nevertheless, empirical measurements were obtained by determining the rates of flow through a small orifice at high shearing stresses, probably in the neighborhood of 10^6 dynes per cm.² Under these conditions grease A flowed at a considerably lower rate than the other members of the group; grease C flowed more slowly than B or D.

This behavior of greases was examined under practical conditions. A soft, almost fluid grease, made with a very viscous oil base, was compared with a considerably stiffer material containing four times the quantity of soap but made with a less viscous oil base. These lubricants were tested in a commerical high-pressure greasing equipment, operating at a pressure of 5000 pounds per square inch in which the material is pumped through a considerable length of hose at a shearing stress calculated at approximately 10^6 dynes per cm.² In these trials the stiff grease was pumped at many times the speed possible with the semifluid product.

The experiments in the laboratory, which were all made at pressures not exceeding about one atmosphere, suggest that the viscosity of the oil base is the main factor which determines the viscosity of the grease at high shearing stresses. The practical tests under high pressures were also in agreement with this generalization, but it should be mentioned that in those cases no allowance was made for the effect of the high pressure on the viscosities of the oils (*5*).

It is apparent from these results that the A. S. T. M. penetration figures are valueless when the flow properties of greases are under review. On the other hand, these penetration figures appear to bear some relation to the yield values involved.

So far it has not been possible to devise a method for determining yield values which is completely satisfactory. However, such experiments as have been made indicate that the yield values are much lower than might be expected from the flow curves in Figure 3. It seems that these curves

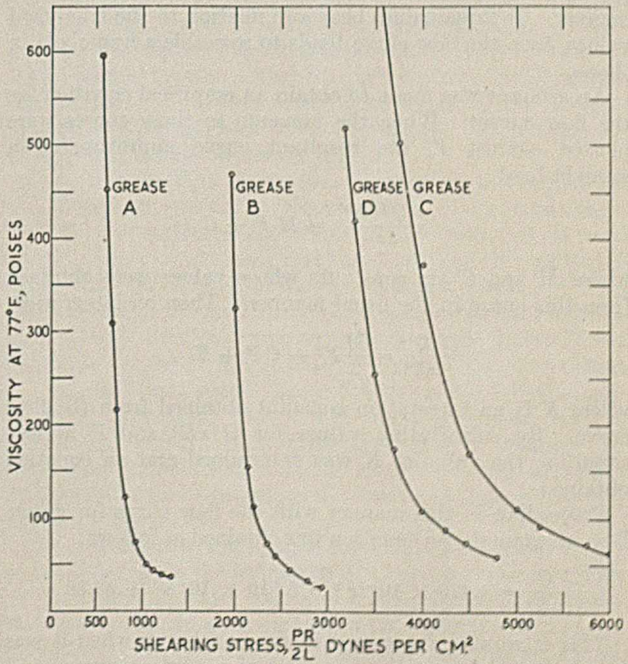

Figure 4. Variation of Viscosity with Shearing Stress

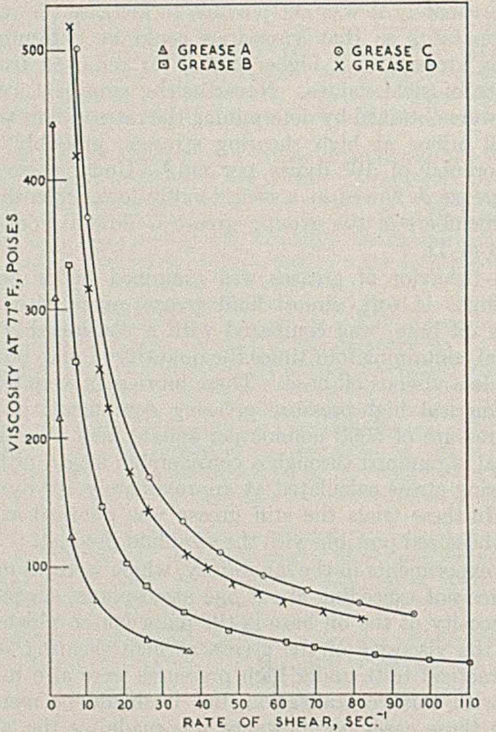

Figure 5. Variation of Viscosity with Rate of Shear

might meet the F axis at a point not far removed from the lowest values of F recorded experimentally.

Some experiments have been carried out in a concentric cylinder apparatus in which the gap between the cylinders was filled with grease. A torque was applied to the inner cylinder, and a value was found for that force which just failed to cause rotation.

Yield values calculated from these results gave a value of 260 dynes per cm.^{2} for greases B and C and 305 dynes for D; that of grease A was too low to be measured in this manner. If these values bear any relation to the true yield values, then the flow curve tends to resemble a hyperbola in shape.

An attempt was made to obtain an empirical equation for the flow curves. When the tangents to these curves were plotted against F, the resultant curve approximated a straight line:

$$\frac{d(Q/\pi R^3)}{dF} = MF + C$$

where M and C are constants whose values were obtained from this curve in the usual manner. Then on integrating,

$$\frac{Q}{\pi R^3} = \frac{M}{2}F^2 + CF + K$$

where K is an integration constant obtained from the flow curve. By substituting values for $Q/\pi R^3$ and F in this equation, the value of K was determined and an equation obtained.

Proceeding in this manner with the flow curve for grease B as an example, an equation was obtained as follows:

$$\frac{Q}{\pi R^3} = 1.479 \times 10^{-5}F^2 - 5.619 \times 10^{-2}F + 53.38$$

This quadratic was solved in the usual way when it was found that the equation was that of a perfect square and could be expressed as

$$\frac{Q}{\pi R^3} = 1.479 \times 10^{-5}(F - 1900)^2$$

Values of $Q/\pi R^3$ for various values of F were calculated from this equation, and the points obtained were plotted on the flow curve for grease B (Figure 3). They show excellent agreement with the experimental results except at the lower values of F where some deviation is apparent. A similar agreement between calculated and observed values was found with the other greases.

So far attempts to obtain an expression which is valid for the entire curve have not been successful; deviation always occurs in the range of shearing stresses which approaches the yield values. A closer investigation of the flow within this region might be of interest, since other workers have noted the anomalous behavior of plastic materials as the yield value is approached.

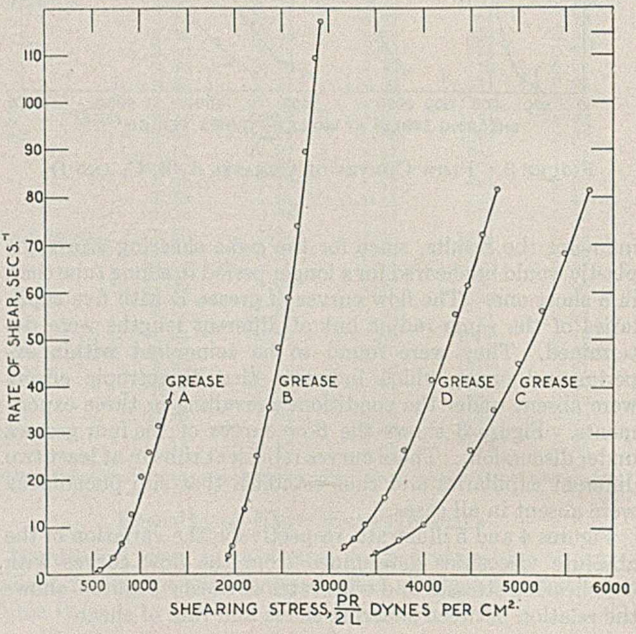

Figure 6. Relation between Shearing Stress and Rate of Shear for Greases A, B, C, and D

It is realized that the foregoing determinations of the viscosities of greases have so far covered an extremely limited range of shearing stresses. Nevertheless, the results are considered to be sufficiently interesting for publication, espeically since comparatively little work appears to have been done on this subject.

Acknowledgment

The authors wish to express their thanks to the Directors of the Asiatic Petroleum Company for permission to publish this investigation.

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Hydrogenation of Typical North American Splint Coals

ABNER EISNER, GEORGE C. SPRUNK,
LOYAL CLARKE, C. H. FISHER, AND H. H. STORCH
Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Penna.

Several typical and important North American splint coals were hydrogenated under conditions used previously to liquefy bright coals in excellent yields. The results show that American splint coals are similar to European splint coals in being less suitable for hydrogenation than bright coals. The liquefaction yields of twelve splint samples were found to be inversely proportional to both the carbon and opaque matter contents. The hydrogenation residues were opaque, which indicates that spores, resins, and other translucent constituents had been liquefied.

ONE conclusion drawn from the numerous investigations of the hydrogenation (*19*) of European coals is that bright coals are more suitable for conversion into motor fuel than dull or splint coals (*2, 4, 10, 11, 15*). South African bright coals (*16*) also were found preferable to splint coals for hydrogenation purposes. Although it was shown (*5, 9, 13*) that several American bright coals are amenable to hydrogenation, there have been few data on American splint coals that can be used for purposes of comparison. This paper gives the results obtained on hydrogenating several typical splint coals under conditions used previously (*5, 8*) to liquefy bright coals and anthraxylon, the characteristic constituent of bright coals.

Properties of Splint Coals

In America four classes of coals are differentiated through their appearance, structure, microscopic composition, and suitability for certain uses (*20*)—bright coals, splint coals, cannel coals, and boghead coals. The first named is the most common. However, splint coals (durains) are important in West Virginia and Kentucky, particularly in the beds of the Upper Pottsville formation. The splint coals from this region have long been known as excellent steam and domestic fuels. They commonly have a dull luster, grayish black color, and compact structure. They are hard and tough and break with an irregular, rough, sometimes splintery fracture into large lumps and slabs (Figure 1) that stand handling and transportation remarkably well.

The beds known as splint coals and sold as such to consumers are seldom more than 75 per cent splint and more often are considerably less. The splint is usually associated with one or more layers of bright or semisplint coal, the latter being intermediate in properties between bright and splint coals. Figure 2 is an example of one of the typical splinty coal beds. In this bed there are two layers of splint, two layers of bright coal, and two layers classed as mixtures; the bed contained 53 per cent splint, 14 per cent semisplint, and 33 per cent bright coal.

Because many of the beds are mixtures it is difficult to identify the type of coal from ultimate and proximate analyses of the face or bed sample. However, when a splint coal is compared with a bright coal from the same bed and mine, the splint coal generally has the higher ash and total carbon contents and the higher softening temperature of ash; usually the bright coals have the higher moisture, hydrogen, nitrogen, oxygen, and sulfur contents. Volatile matter may vary in either direction and depends upon the exact composition of the bright or splint coals—that is, whether they are spore-rich or resin-rich. In some instances the relation between the volatile matter and the hydrogen-carbon ratio can be used to distinguish between bright and splint coals (*4, 17*).

The splint coals are easily identified by thin sections under the microscope. They are characterized by a semiopaque to opaque groundmass or attritus, as in Figure 5, whereas the bright coal sections have a groundmass or attritus that is predominantly translucent (Figure 3). The opaque attritus is not homogeneous; it is opaque in medium thin sections, but in extremely thin sections a portion of it becomes semitranslucent or brown. Other fragments can be found in various degrees of translucence and some, even in the thinnest sections, appear to rival fusain in opacity. Some finely divided fusain is also invariably present.

It is believed that the opaque material is the result of a high degree of rotting or decomposition in the peat stage. Possibly the moisture conditions in the peat bog favored growth of microorganisms, and the decomposition continued for a longer period than in the case of bright coals.

The transformation of tissues into opaque matter might be illustrated by a series of photographs, but only the early and late stages are shown in this paper. Figure 3 is a cross section of a typical bright coal. Figure 4 shows a wood strand (anthraxylon or vitrain) with a well-preserved center and the outer edges partly transformed into opaque matter. In Figure 5, a typical splint coal, the greater decomposition has resulted in irregular fragmented tissues and high concentration of opaque matter.

It is possible that the opaque constituents represent an intermediate stage in the formation of fusain, for in some splints one can detect a greater degree of opacity in the groundmass than in others. In such instances the opaque constituents more closely resemble fusain, and the sections must be ground exceptionally thin before any of the particles become translucent.

Table I. Analyses of Splint Layers

Sample No.	State	County	Bed	Mine	Proximate			Ultimate[a]					Calorific Value	C/H Ratio
					As Received									
					Moisture	Ash	Volatile matter[a]	H	C	N	O	S		
					%	%	%	%	%	%	%	%	*Gram-cal.*	
1	Ky.	Johnson	Miller's Creek	Consolidation 155	3.1	5.5	44.4	5.5	81.8	1.6	7.7	3.4	8206	14.9
2	W. Va.	Boone	Coalburg	Silush	2.7	2.2	43.1	5.6	84.2	1.6	7.9	0.7	8378	15.0
3	Ky.	Harlan	High Splint	Clover Splint	1.5	9.2	31.9	4.7	85.4	1.4	8.1	0.4	8172	18.2
4	Ky.	Letcher	Elkhorn	No. 204	1.6	3.7	38.1	5.4	85.9	1.5	6.6	0.6	8483	15.9
5	W. Va.	Mingo	Upper Cedar Grove	Junior	1.4	5.2	39.6	5.4	86.2	1.4	6.1	0.9	8483	16.0
6	W. Va.	Kanawha	Dorothy	No. 10	1.2	9.3	33.1	5.1	86.8	1.5	6.0	0.6	8439	17.0
7	W. Va.	Mingo	Lower Cedar Grove	Junior	1.5	4.9	35.6	5.2	87.0	1.5	5.8	0.5	8467	16.7
8	W. Va.	Wyoming	Sewell	Wyoming	0.6	15.6	20.2	4.6	89.7	1.1	4.3	0.3	8556	19.5

[a] Dry ash-free basis.

Hydrogenation Procedure

Details of the experimental procedure have been given in previous papers (*5, 6*):

> Unless otherwise stated, 100 grams of splint sample (pulverized to pass 200 mesh), 100 grams of tetrahydronaphthalene, and 1 gram of stannous sulfide were placed in the 1.2-liter converter; the air was removed by flushing with nitrogen and hydrogen, and hydrogen was introduced until the pressure at 20° C. was 1000 pounds per square inch (70.3 kg. per sq. cm.). About 1.5 hours were consumed in bringing the temperature to 430° C., where it was maintained for 3 hours. Experiments made with other coals (*5, 8*) indicated that these conditions are enough to liquefy bright coals of low and intermediate rank in high yields.
>
> The products of hydrogenation were transferred to 250-cc. bottles and centrifuged to separate mineral matter and insoluble carbonaceous material. Specific gravities of centrifuged oils were determined with a hydrometer; these data are of questionable accuracy because of the presence of traces of water. The centrifuge residues were washed six times with acetone at room temperature and then extracted with benzene in Soxhlet apparatus for at least 24 hours and until the extract was colorless. Distillation of the centrifuged oil and first three acetone washings through a 6-inch (15.2-cm.) Vigreux-type column gave the pitches and distillates described in Tables VII and X.

To procure samples rich in opaque attritus, the characteristic constituent of splint coals, layers of coal containing high concentrations of opaque matter were selected from several important and typical North American splint coals (Tables I and II). Sample 8 was taken from a splint layer that constituted only 4 per cent of the entire Sewell bed (Wyoming mine), which is chiefly bright coal. Ultimate and proximate analyses are given in Table I, where the coals are arranged in order of increasing carbon content. Petrographic analyses are given in Table II. The proportion of matter in the opaque attritus that is inert to hydrogenation is also given in Table II. These data are subject to inaccuracies, because the content of inert matter was calculated on the assumption, only approximately correct, that fusain is completely inert but that anthraxylon (*9*), translucent matter (*8*), spores (*3, 8*), and resins (*3, 8*) are completely liquefied by hydrogenation.

Figure 1. Lump of Typical Splint Coal from Dorothy Bed, Kanawha County, W. Va.

Table II. Petrographic Composition of Splint Layers (Per Cent)

Sample No.	Anthraxylon	Attritus		Fusain	Inert Matter in Opaque Attritus[a]
		Translucent	Opaque		
1	24	37	34	5	21
2	13	52	33	2	46
3	3	35	60	2	57
4	17	50	31	2	56
5	9	38	51	2	27
6	8	41	50	1	44
7	8	45	46	1	44
8	13	32	50	5	61

[a] Calculated from hydrogenation data obtained at 430° C. by assuming fusain completely resistant and all constituents other than fusain and opaque attritus completely liquefied.

Liquefaction Yields

The splint coals gave comparatively low liquefaction yields in all instances, which confirmed the prevailing opinion (*4, 10, 11*) that splint coals are not so suitable for hydrogenation as bright coals. Table III shows that the conversion of dry, ash-free splint coals into gases, liquids, and soluble material ranged from 58 to 87 per cent. These yields are considerably lower than those obtained previously under the same conditions with bright coals (*5, 9*), spores (*8*), resins (*8*), translucent attritus (*8*), and anthraxylons (*9*).

The present data and those obtained previously with several samples of opaque attritus (*7, 8, 14*) indicate conclusively that

Table III. Liquefaction Data

Sample No.	Hydrogenation Temp.	Products		Loss	Centrifuged Oil[a]	Conversion of Pure Coal[b]
		Liquids, solids	Gases			
	° *C.*	*Grams*	*Grams*	*Grams*	%	%
1	430	182.9	5.9	15.6	71	86.7
2	430	187.1	6.5	11.4	66	81.8
3[c]	430	187.3	7.6	7.6	49	59.8
3A[d]	440	183.6	7.6	15.9	70	78.2
4	430	187.2	6.8	9.9	62	79.7
5	430	188.8	7.4	8.2	65	82.9
6	430	189.8	6.7	7.6	55	74.4
6A[d]	440	184.0	8.3	14.2	69	84.6
7	430	185.6	6.5	12.7	64	77.2
8	430	189.5	5.8	7.7	46	57.5
8A[e]	440	183	7.3	14.8	58	72.4

[a] Per cent by weight of material centrifuged.
[b] Dry ash-free basis.
[c] From previous work (*8*).
[d] Cold, initial hydrogen pressure was 1800 lb. per sq. in.
[e] Cold, initial hydrogen pressure was 1500 lb. per sq. in.

the opaque matter is the principal constituent, other than fusain, responsible for the low liquefaction yields obtained with some coals of low and intermediate rank. This has been suggested before (*10*, *21*), but previously there have been few supporting data. Calculations from data obtained with the eight splint samples of Table I and with four splint samples from a previous paper (*8*) show that the average liquefaction yield of opaque attritus (at 430° C. for 3 hours in the presence of stannous sulfide and with initial hydrogen pressure of 1000 pounds per square inch) is about 60 per cent. For reasons discussed later, however, the liquefaction yields for the individual samples of opaque attritus range from about 39 to 79 per cent (Table II). It is possible that other samples of opaque attritus, depending upon the nature and degree of opacity, will give liquefaction yields outside this range.

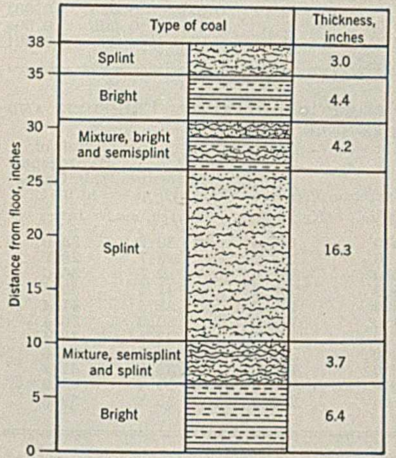

FIGURE 2. TYPES OF COAL IN HIGH SPLINT BED, HARLAN COUNTY, KY.

Several attempts were made by earlier workers (*12*, *16*, *18*) to predict hydrogenation yields from the proximate and ultimate analyses of the coal. The results were disappointing, although a rough correlation between carbon content of the coal and liquefaction yield was found. Probably this is partly because the carbon content of splint coals can be used as a rough measure of the content of opaque attritus and partly because both the rank (*17*) and difficulty of hydrogenation (*12*) of bright coals increase with increase in carbon content.

In view of the relation between carbon content and hydrogenation yield observed by previous workers, it is considered interesting to compare the yields of the present work with carbon contents of the splint samples hydrogenated. The results (Figure 6) show that the carbon content cannot be used satisfactorily to predict the liquefaction yields of splint coals. Probably this can be attributed in part to the presence of low-carbon constituents, such as spores and resins, which may obscure the presence of considerable amounts of high-carbon opaque attritus. In Figure 7 residue yields of splint samples of this and a previous paper (*8*) are plotted against total opaque matter (fusain plus opaque attritus). Figure 7 seems to show that, although the correlation is far from satisfactory, the residue yield of splint samples can be predicted as well from the content of opaque matter as from carbon content. If all types of coals and constituents are included, the residue yield can be predicted more satisfactorily from the petrographic composition than from the carbon content. For example, fusain (*6*), opaque attritus (*8*), and anthraxylon (*9*), each containing 89 per cent carbon, would give vastly different liquefaction yields, although this result would not be predicted from the carbon content.

The prediction of hydrogenation yields from petrography can undoubtedly be improved when an estimate of the nature as well as amount of the different constituents is available. For example, opaque attritus has been found microscopically to be heterogeneous, containing substances which vary greatly in opacity. Although detailed data are lacking, it is

FIGURE 3. THIN CROSS SECTION OF BRIGHT COAL, INCLUDING A WELL PRESERVED WOODY (ANTHRAXYLON) BAND AT THE BOTTOM (× 200)

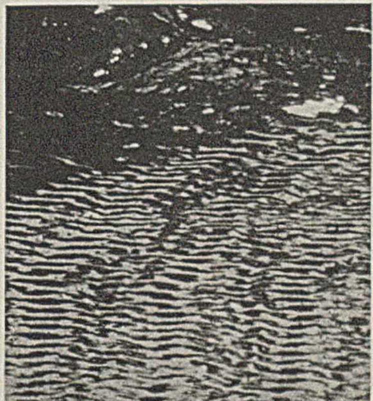

FIGURE 4. THIN CROSS SECTION OF BRIGHT COAL, SHOWING DISINTEGRATION OF WOODY TISSUES IN EARLY STAGE OF SPLINT COAL FORMATION (× 200)

FIGURE 5. THIN CROSS SECTION OF TYPICAL SPLINT, SHOWING A HIGH CONCENTRATION OF OPAQUE MATERIAL AND FRAGMENTED REMAINS OF WOODY TISSUES (× 200)

reasonable to assume that the carbon content, carbon-hydrogen ratio, and difficulty of hydrogenation increase roughly with the degree of opacity. This assumption can be used to explain some of the discrepancies in Figure 7. The splint sample from the Chilton bed (No. 3 in Figure 7 and in a previous paper, *8*) gave an astonishingly high liquefaction yield on the basis of its high content (80 per cent) of opaque matter. However, microscopic examination showed that an unusually high proportion of the opaque matter was brown or semiopaque. Therefore, this sample could be expected to hydrogenate more readily than attritus which is much more opaque. Probably it is only a coincidence that unusually poor conversions were obtained with the splint samples (Table I) of high ash content.

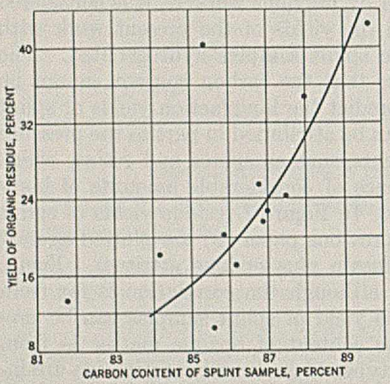

Figure 6. Relation between Carbon Content of Splint Samples and Yield of Insoluble Carbonaceous Residue (Dry Ash-Free Basis)

It is interesting that more drastic conditions of hydrogenation give much higher liquefaction yields (Table III) than standard conditions (430° C. for 3 hours, initial hydrogen pressure of 1000 pounds). It is likely that semiopaque matter is the additional material liquefied by the more drastic treatment.

Table IV gives the composition and yields of the gaseous products. As in previous work (*5*, *8*) only traces of carbon monoxide and unsaturated hydrocarbons were found. The chief components of the hydrogenation gases are methane and higher saturated hydrocarbons, the latter occurring in preponderant amounts. The amount of carbon dioxide formed appears to decrease with increase in carbon content of the parent coal. Increasing the pressure and temperature of hydrogenation (from 430° to 440° C.) decreased the yield of carbon dioxide but increased the yield of saturated hydrocarbons. The coal (sample 1) of highest sulfur content gave the highest yield of hydrogen sulfide. Table V gives the maximum pressures, pressure drop, and hydrogen consumed.

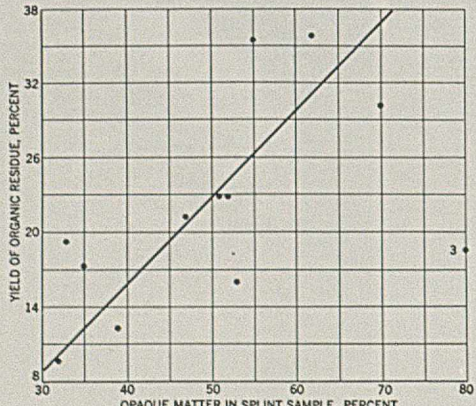

Figure 7. Relation between Opaque Matter Content of Splint Samples and Yield of Insoluble Carbonaceous Residue

Table IV. Composition of Hydrogenation Gases (in Grams)

Sample No.	H	CO	C_2H_4	CH_4	C_2H_6	CO_2	H_2S	NH_3
1	2.51	0.1	0.1	1.6	3.3	0.355	0.461	0.001
2	1.99	0.2	0.1	2.2	3.5	0.427	0.112	...
3	4.49	0.3	0	2.7	3.6	0.828	0.152	0.004
3A	4.65	0.3	0.1	3.4	3.2	0.483	0.111	...
4	3.00	0.2	0.1	2.3	3.6	0.416	0.230	...
5	2.50	0.2	0.1	2.3	4.3	0.281	0.202	0.021
6	2.88	0	0.1	2.2	4.1	0.254	0.061	0.021
6A	5.17	0.2	0.2	2.4	5.3	0.044	0.157	0.001
7	2.16	0.1	0.1	1.9	4.1	0.317	0.025	0.001
8	3.91	0.4	0.3	1.5	3.5	0.139	0.005	0.004
8A	4.73	0.1	0.2	2.4	4.6	0.011	0.006	0.001

Table V. Hydrogen Absorption, Maximum Pressure, and Pressure Drop

Sample No.	Hydrogen Consumed	Maximum Pressure		Pressure Drop	Vol. of Hydrogenation Gases at 0° C.
	Grams	*Lb./sq. in.*	*Kg./sq. cm.*	*Kg./sq. cm.*	*Liters*
1	3.43	2510	176.4	30.2	33.0
2	3.95	2180	153.2	38.7	28.2
3	1.86	2670	187.9	12.7	56.6
3A	6.05	4400	309.2	41.5	59.3
4	2.94	2600	182.7	22.5	41.4
5	3.44	2480	174.3	30.2	36.4
6	3.06	2540	178.5	27.4	38.4
6A	5.53	4300	302.1	45.7	66.6
7	3.78	2280	160.3	33.7	61.2
8	2.03	2610	183.4	20.4	48.9
8A	4.07	3600	253.0	35.8	59.8

Nature of Products

Table VI gives the specific gravities of the centrifuged oils, which are colloidal solutions of the primary liquefaction products in tetrahydronaphthalene. Since the specific gravity of the vehicle is about 0.967 at 25° C., the solute or liquefaction products must be quite dense to give solutions of the specific gravity shown in Table VI. The considerable variations in specific gravity probably are due to differences in nature and concentration of the solute. For example, the presence of considerable amounts of products from spores and resins (*7*, *8*) would lower the specific gravity.

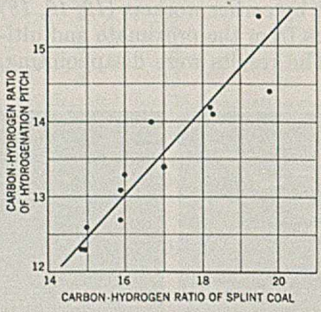

Figure 8. Relation between Carbon-Hydrogen Ratios of Splint Samples and Hydrogenation Pitches

Although some of the pitches (Table VII) have rather high carbon-hydrogen ratios, the ratios were always lower than those of the antecedent coals. Figure 8, which contains data from this and a previous paper (*8*), shows that the carbon-hydrogen ratios of the hydrogenation pitches are roughly proportional to those of the parent splint coals.

Table VI. Specific Gravities of Centrifuged Oils

No.	Sp. Gr.	Temp. ° *C.*	No.	Sp. Gr.	Temp. ° *C.*
1	1.006	25.5	6	1.023	24
2	1.022	25	6A	0.999	24
3A	1.002	24	7	1.027	25.5
4	1.024	25	8	1.024	25
5	1.013	24			

Table VIII gives the composition and amounts of the dry benzene-insoluble residues. The carbon-hydrogen ratios and composition (calculated from data in Table VIII) of the organic portion of the residues are shown in Table IX. Because

HAND-PICKED FUSAIN, SHARON BED

HYDROGENATION RESIDUE FROM FUSAIN, SHARON BED

HYDROGENATION RESIDUE FROM SPLINT COAL, DOROTHY BED

FIGURE 9 (× 150)

of errors involved in analyzing such residues (*1*) and in correcting to the dry mineral-matter-free basis, the data in Table IX are not absolutely accurate. The ratios of carbon to hydrogen are higher than those of the original coals and lower than those of residues obtained in high yield by hydrogenating fusain (*6*).

All the hydrogenation residues from the splint coals have a similar appearance under the microscope. The individual particles are usually less than 5 microns in diameter, although they may be grouped into larger masses. Figure 9 shows that they are smaller and more rounded than the sharply angular particles from fusain residues (*8*). However, both types of residues have little (probably less than one per cent) translucent material other than mineral matter; this indicates that constituents in the splints, such as spores, anthraxylon, and residues, were almost completely converted into liquid or soluble products.

Analyses of the products obtained by distilling the centrifuged oils to about 215° C. are shown in Table X. It is evident from these data that the largest component of the distillates is the vehicle, tetrahydronaphthalene. The distillates (samples 3A, 6A, and 8A) from the experiments made at 440° C. have lower specific gravities and phenol contents but higher saturated-hydrocarbon contents than the corresponding distillates (samples 3, 6, and 8) obtained under standard conditions. The phenol contents are roughly proportional to the liquefaction yields (Table III). The neutral oils, consisting largely of aromatic hydrocarbons, contained traces of olefins (soluble in 85 per cent sulfuric acid). The neutral oils also contained small amounts of saturates. Since coal resins, spores, and oil algae have been observed (*8*) to give comparatively high yields of saturated hydrocarbons boiling below about 215° C., it is believed that the presence of different amounts of these materials in the parent coals may cause some of the variations in saturated hydrocarbon content of the neutral oil.

TABLE VII. PITCHES

Sample No.	H	C	N	O	S	Calorific Value	C/H Ratio
						Gram-cal.	
1	7.3	89.8	1.4	1.3	0.2	9398	12.3
2	7.1	89.5	1.4	1.7	0.3	9369	12.6
3	6.4	90.9	1.1	1.5	0.1	9330	14.2
3A	6.6	91.3	1.2	0.8	0.1	9369	13.8
4	6.9	90.1	1.4	1.4	0.2	9367	13.1
5	6.8	90.7	1.2	1.0	0.3	9386	13.3
6	6.8	90.8	1.2	1.0	0.2	9366	13.4
6A	7.2	91.1	1.0	0.5	0.2	9522	12.7
7	6.5	90.9	1.4	1.0	0.2	9296	14.0
8	6.0	92.2	0.9	0.7	0.2	9243	15.4
8A	6.4	92.3	0.8	0.3	0.2	9395	14.4

TABLE VIII. BENZENE-INSOLUBLE RESIDUES (DRY)

Sample No.	Found	Calcd. from Ash Content	H	C	N	O	S	Ash
	Grams	*Grams*	%	%	%	%	%	%
1	18.6	19.0	2.3	54.7	0.9	...	9.0	34.2
2	20.4	21.1	3.0	75.5	1.3	3.5	1.5	15.2
3	45.8	47.2	3.1	70.9	1.1	2.6	0.7	21.6
3A	28.5	32.3	2.7	60.9	0.9	3.0	0.9	31.6
4	23.7	24.9	3.1	72.6	1.1	2.6	1.7	18.9
5	21.6	23.9	2.7	64.2	0.9	5.0	1.3	25.9
6	32.6	34.6	2.7	61.4	0.9	4.2	1.0	29.8
6A	23.5	25.0	2.3	50.6	0.7	4.0	1.2	41.2
7	26.9	28.4	2.9	69.6	1.0	4.6	1.1	20.8
8	51.0	55.0	2.8	60.6	0.7	5.1	0.6	30.2
8A	38.1	42.2	2.5	52.7	0.5	4.2	0.8	39.3

TABLE IX. BENZENE-INSOLUBLE RESIDUES[a]

Sample No.	% by Weight				C/H Ratio
	H	C	N	O	
1	3.8	95.5	1.5	...	25.1
2	3.6	90.1	1.5	4.1	25.0
3	3.9	90.5	1.4	3.5	23.2
3A	4.0	89.5	1.3	4.5	22.4
4	3.9	90.7	1.4	3.3	23.2
5	3.7	87.6	1.2	6.8	23.7
6	3.9	88.0	1.3	6.1	22.6
6A	3.9	87.0	1.2	7.2	22.3
7	3.7	88.5	1.3	5.8	23.9
8	4.0	87.0	1.0	7.3	21.8
8A	4.1	87.3	0.8	7.1	21.3

[a] On a dry ash-free basis; excluding 0.7 per cent, sulfur was assumed to be inorganic (*1*).

TABLE X. COMPOSITION OF DISTILLATES

Sample No.	Distn. End Point	Distillate				Neutral Oil	
		Amount	Sp. gr., 15.6° C.	Tar bases	Phenols	Sp. gr., 15.6° C.	Saturates
	° *C.*	*Cc.*		*% by volume*			*% by vol.*
1	220	106	0.969	0.5	3.3	0.967	0.6
2	220	101	0.971	0.8	3.4	0.971	2.2
3	215[a]	98	0.976	0.2	2.5	...	0.5
3A	217[a]	104	0.962	0.7	2.2	0.959	1.3
4	220	102	0.969	0.2	2.8	0.967	2.2
5	220	104	0.968	0.2	3.0	0.965	0.8
6	220	96	0.967	0.1	2.8	0.966	0.5
6A	220	108	0.957	0.5	2.2	0.956	1.9
7	220	102	0.969	0.3	2.4	0.965	0.5
8	220	94	0.966	...	1.6	0.966	0
8A	212[a]	99	0.959	0.1	1.3	0.958	0.2

[a] Distillation difficult beyond this temperature.

Acknowledgment

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Evaluation of Nitrocellulose Lacquer Solvents

A Study of Hydrocarbon Diluents by the Constant-Viscosity Procedure

V. W. WARE AND W. M. BRUNER

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

THE first paper of this series (*9*) described in detail the constant viscosity procedure for the evaluation of the solvent strength of nitrocellulose lacquer solvents. By this method a single value may be assigned to the combined viscosity characteristics and hydrocarbon acceptance of a solvent in such a way that a separate study of the two is eliminated, and it may be used, in turn, to relate this combined solvency value to the cost of application. This method of evaluation has been applied to a number of commercially available esters (ethyl acetate, ethyl propionate, isobutyl acetate, *n*-butyl acetate, isobutyl propionate, and Pentacetate) in their reaction to toluene dilution (*10*). It gives a complete picture of the reaction of nitrocellulose lacquer solvents to hydrocarbon addition throughout the entire range of dilution and affords a means of obtaining an accurate comparison of their solvent action at the viscosity most applicable to the problem at hand.

The "dilution ratio" of a nitrocellulose solvent has been defined (*1*) as expressing the limit of tolerance of a solvent for a nonsolvent; but as Gardner (*6*) points out, the end points are rather indefinite, and considerable experience is necessary to be able to check the results. Doolittle (*3*) made worthwhile advances in defining the limits and the conditions under which dilution ratios should be determined, but they still remain an unsatisfactory and uninformative type of analytical procedure. Moreover, Stewart (*8*) reported that the inclusion of resin in the experimental formulation tends to make the end point still more difficult to check than in the case of solutions of nitrocellulose alone. Dilution ratio is used in evaluation of the activity of diluents as well as solvents, and from the above considerations it is obvious why this method is still more unsatisfactory in diluent evaluation than in the evaluation of solvents. This also indicates why the constant viscosity procedure, which eliminates the dilution ratio completely and measures the action of the diluent by means of changes in the viscosity or in the solids which will dissolve at a given viscosity, offers advantages for this purpose.

The viscosity and hydrocarbon tolerance of a solvent are but two of the several important factors which contribute to the value of the material, and it is not the intention of this series of papers to overemphasize that importance. The intent is, rather, to make available to the industry certain pertinent data that give a clearer view of the subject and to point out the more obvious and logical deductions from these data.

Stated briefly, the constant viscosity procedure for measuring the power of solvent and solvent-diluent mixtures to dissolve nitrocellulose involves viscosity determinations of nitrocellulose solutions in three or more concentrations in the range of spray viscosity. From these data curves are drawn by plotting viscosity against weight of nitrocellulose per 100 cc. of base lacquer. The exact solids concentration at any viscosity within the chosen range may be obtained from the curve, and curves may be set up from experimental data in this way for any number of solvent-diluent mixtures. These values for nitrocellulose concentration at any chosen standard viscosity are in themselves an accurate means of comparing the solvent strengths of two or more solvent mixtures since they combine in one set of values all of the information which previously has required both dilution ratio and viscosity determinations. However, the usefulness of the data may be extended much further; by plotting the solvent-diluent composition against nitrocellulose or solids concentration, as obtained from the first set of curves, a second curve may be obtained (*9*, *10*) from which the ratio of solvent to diluent which will dissolve a given amount of nitrocellulose at that viscosity may be read. Then, knowing the apparent value of the diluent and of the solvent in use as standards, the comparative value of the solvent or diluent under test may be established.

Data obtained by the constant viscosity procedure for nitrocellulose solvent evaluation are presented for three types of hydrocarbon diluent: pure coal tar (toluene), pure aliphatic (gasoline), and mixed aromatic-aliphatic or so-called high-solvency naphtha. These diluents have been studied in conjunction with four commercially available esters: isobutyl acetate (90 per cent), *n*-butyl acetate (90 per cent), isobutyl propionate (80 per cent), and Pentacetate (87 per cent). The comparisons were made in the presence of nitrocellulose alone and also with a 2 to 1 mixture of nitrocellulose and resin.

The value as a diluent decreases in the order, toluene, high-solvency naphtha, gasoline; this decrease is considerably greater with nitrocellulose-resin mixtures than it is when the nitrocellulose composes the entire make-up of the solids ingredients, but in no case is it enough to be of any great practical value until a dilution beyond 20 per cent is used.

The complete similarity and equivalency of isobutyl acetate and *n*-butyl acetate, as concerns their solvency characteristics and diluent acceptance with the three types of hydrocarbons throughout the entire dilution range at spray viscosity, is demonstrated. This equivalency is not noticeably affected by the presence of resin in the formulation.

The superior solvent strength of isobutyl propionate as the high-boiling ingredient of nitrocellulose lacquers is shown.

While previous communications have dealt primarily with the constant viscosity procedure as a means of assigning a value to the solvent strength of the active solvent constituents of a lacquer, it is the object of this paper to show how the method may be applied advantageously to the evaluation of diluents as well. For this purpose one each of the three general types of hydrocarbon diluent now used in commercial lacquers was chosen—pure aromatic, pure aliphatic or gasoline type naphtha, and the mixed aromatic-aliphatic or so-called high solvency naphtha. Commercial 2° C. toluene is used in the first case. A commercial naphtha with a distillation range of 90–130° C. is used in exemplifying the pure aliphatic type; it will be referred to hereafter simply as gasoline. The mixed aromatic-aliphatic naphtha used is a commercial material with a distillation range of 95–132° C., containing approximately 30 per cent aromatics; it will be referred to as H. S. naphtha. Each of these naphthas evaporates at approximately the same rate as toluene.

The high-solvency naphtha type of diluent has been described (*7*) as being far superior to mineral spirits and approaching in solvent power and compatibility the coal tar solvents. Since these diluents are being used rather extensively in lacquer formulations, it seemed appropriate that they be examined in the light of the constant viscosity procedure. It has been shown (*4*) that both the solvent balance and solvent action are influenced by the type and concentration of the nonvolatile portion. Therefore it seemed likely that, whereas the pure aliphatic naphtha and the mixed naphtha may show similar dilution effects on nitrocellulose alone, the differences may be much more pronounced in the presence of certain resins because of the selective action of the aromatic portion in the one case. For this reason and in order to avoid any possibility of misinterpretation, it seemed advisable to compare the action of these diluents, not only on nitrocellulose alone, but on mixtures of nitrocellulose and resin as well. Hence a series of tests is included which is based upon a mixture of nitrocellulose and resin in proportions of 2 to 1; this approaches the composition often used in commercial lacquers. The resin was an alkyd modified with a nondrying oil. Obviously, the reaction of other resinous materials in the presence of nitrocellulose will not be the same as this particular one; this information is furnished in order to emphasize the importance of studying the effect of the resin, as well as the nitrocellulose, on solvent behavior.

Experimental Procedure

The experimental details are identical with those described in a previous paper (*9*). Browne (*2*) states, in connection with paints, that "most of the useful properties of paint are determined at least to a first approximation by the proportions of ingredients by volume: volume, not weight, governs the area coverable with a film of suitable thickness, governs the concentration of opaque pigments in the film necessary to give the desired hiding power, and the concentration and proportions of total solids required for good consistency in application and for optimum durability." In the belief that this applied just as well to nitrocellulose lacquers and enamels and that the conventional formula in percentages by weight has a tendency to obscure certain relations because of the great variation in the specific gravity of the various ingredients, the work has been continued on a volume rather than a weight basis. Hence all solids concentrations are expressed as grams per 100 cc. of solution, and all solvent-diluent ratios refer to percentage by volume.

Dry, $^1/_2$-second nitrocellulose from the same lot as that in the experiments previously described (*9, 10*) was used throughout, and the same accuracy in weighing and volume measurements was maintained. All viscosity measurements were made on the Parlin No. 7 cup (*5*) at 25° C. ± 0.1°. Viscosity values were obtained for three or more solids concentrations with each mixture, and the quantity of solids was chosen so that these values cover the entire range of spray viscosity. All samples were tumbled at an identical rate for 24 hours to ensure complete solution. The recorded viscosity in seconds for the three or more solids concentrations with each solvent-diluent mixture is plotted against grams of nitrocellulose, and the curves so obtained are shown. In the previous articles (*9, 10*) tables were included to show the amount of nitrocellulose which dissolved at certain standard viscosity readings, but for purposes of brevity they are not given here. The curves shown indicate graphically the behavior of a solvent mixture; the derived values are most useful in those cases where it seems necessary to calculate the ultimate comparative cost values of solvents or diluents.

The diluents used in this work were commercial 2° toluene, the high-solvency naphtha offered by the Union Oil Company of California under the name of "Solvent #8", and "Bayway Naphtha #55" from the Standard Oil Company of New Jersey. The *n*-butyl and isobutyl acetates possessed a saponification value of approximately 90 per cent, the isobutyl propionate 80 per cent, and the Pentacetate 87 per cent. The remainder in each case was composed of the alcohol from which the ester was derived. Isobutyl propionate with an alcohol content of 20 per cent possesses optimum properties as far as the viscosity and hydrocarbon acceptance of this ester are concerned, hence the choice of this strength for the work. The other three esters are offered commercially at approximately the alcohol content used in these experiments, but these may or may not represent the mixture of optimum solvent properties.

Viscosity Data

The experimental viscosity values for solutions of nitrocellulose in 90 per cent isobutyl acetate at various dilutions with toluene, high-solvency naphtha, and gasoline are shown in Table I*A*. No values are given for 40:60 dilution with gasoline because at this point nitrocellulose is incompletely soluble in the mixture.

Table I*B* contains the experimental values for 90 per cent *n*-butyl acetate with the three hydrocarbons. Here again it was not possible to obtain readings at a gasoline dilution of 60 per cent because of the insolubility of nitrocellulose in the composition.

In Table I*C* the experimental values for 80 per cent isobutyl propionate diluted with the three hydrocarbon diluents are shown. A comparison of the values for toluene dilution here with those given for the 87 and 99 per cent ester in a previous communication (*10*) will indicate the striking increase in solvent strength obtained with small increases in the alcohol content of this ester. Dilution of 80 per cent isobutyl propionate to 40:60 with either of the hydrocarbons results in incomplete solubility of the nitrocellulose, although clear solutions are obtained in each case at 50:50 dilution.

Table I*D* gives the corresponding information for 87 per cent Pentacetate, which accepts dilution to about the same extent as the propionate, although the viscosities with the latter are considerably lower.

Table I. Viscosity–Nitrocellulose Content of Solutions at Various Hydrocarbon Dilutions

Diluent	Solvent: Diluent Ratio	Nitrocellulose/100 Cc. Base Lacquer[a]				
		6 grams	7 grams	8 grams	9 grams	10 grams
		Sec.	*Sec.*	*Sec.*	*Sec.*	*Sec.*
		A. Isobutyl Acetate Solutions				
None	100:0	...	...	42.0	54.0	71.0
Toluene	80:20	...	...	41.5	55.6	78.5
H. S. naphtha	80:20	...	37.2	45.0	57.7	78.7
Gasoline	80:20	...	37.5	44.3	56.5	77.3
Toluene	60:40	...	38.8	48.4	62.7	89.7
H. S. naphtha	60:40	...	40.0	53.0	72.7	103.3
Gasoline	60:40	35.0	42.6	57.0	79.3	...
Toluene	50:50	...	39.0	52.3	71.9	...
H. S. naphtha	50:50	35.4	45.0	64.2	94.2	...
Gasoline	50:50	40.4	54.1	81.0	...	...
Toluene	40:60	38.0	46.3	67.3	101.0	...
H. S. naphtha	40:60	39.5	62.0	122.0	...	...
		B. *n*-Butyl Acetate Solutions				
None	100:0	...	...	41.7	52.5	67.2
Toluene	80:20	...	...	42.0	54.9	71.4
H. S. naphtha	80:20	...	36.7	45.3	57.7	76.5
Gasoline	80:20	...	36.8	45.1	56.7	76.4
Toluene	60:40	...	38.0	47.3	62.1	86.0
H. S. naphtha	60:40	...	40.1	52.2	73.2	...
Gasoline	60:40	34.0	41.4	52.9	75.1	...
Toluene	50:50	...	40.0	51.6	70.5	...
H. S. naphtha	50:50	35.0	46.0	64.1	95.7	...
Gasoline	50:50	37.0	48.9	70.0	...	...
Toluene	40:60	36.0	46.0	63.3	96.7	...
H. S. naphtha	40:60	41.4	56.2	113.3	...	...
		C. Isobutyl Propionate Solutions				
None	100:0	...	38.5	46.2	61.2	82.5
Toluene	80:20	...	39.8	49.7	65.6	85.7
H. S. naphtha	80:20	...	39.0	50.5	66.2	96.9
Gasoline	80:20	34.6	41.3	50.8	73.7	...
Toluene	60:40	...	40.1	50.0	68.2	...
H. S. naphtha	60:40	36.0	44.7	60.2	91.5	...
Gasoline	60:40	38.0	51.8	68.2	...	...
Toluene	50:50	35.2	42.1	58.4	84.4	...
H. S. naphtha	50:50	41.6	61.3	93.8	...	...
Gasoline	50:50	47.3[b]	75.3	...	...	...
		D. Pentacetate Solutions				
None	100:0	...	40.3	53.0	72.3	
Toluene	80:20	...	40.5	55.5	75.1	
H. S. naphtha	80:20	35.3	43.0	57.3	80.0	
Gasoline	80:20	35.4	42.4	56.0	...	
Toluene	60:40	34.8	45.1	60.5	87.8	
H. S. naphtha	60:40	36.2	46.8	71.7	...	
Gasoline	60:40	39.4	52.4	79.2	...	
Toluene	50:50	38.0	48.6	67.5	...	
H. S. naphtha	50:50	42.9	64.8	97.0	...	
Gasoline	50:50	50.0[c]	78.9	...	...	

[a] Viscosity in No. 7 cup at 25° C.
[b] Viscosity at 5 grams, 37.2 seconds.
[c] Viscosity at 5 grams, 38.1 seconds.

Table II*A* includes the experimental viscosity values for isobutyl acetate with the three types of hydrocarbon; the solids, instead of being composed of nitrocellulose alone, were made up on a weight basis of 2 parts of nitrocellulose to 1 part of resin. For comparative purposes the practice of expressing the results on the basis of grams of nitrocellulose per 100 cc. of base lacquer has been continued, and it becomes necessary to multiply the weights of nitrocellulose used by the factor 1.5 in order to study the viscosity variation on the basis of total solids. When the contents of Table II*A* are compared with those of Table I*A* for nitrocellulose alone, the increase in viscosity when the solids are increased 50 per cent by means of resin is seen to be relatively small. Some of this increase is due to the fact that a certain amount of the solvent mixture has been replaced by an equal volume of resin.

Table II. Viscosity–Nitrocellulose Content of Isobutyl Acetate at Various Hydrocarbon Dilutions with a Nitrocellulose: Resin Ratio of 2:1

Diluent	Solvent: Diluent Ratio	Nitrocellulose/100 Cc. Base Lacquer[a]				
		5 grams	6 grams	7 grams	8 grams	9 grams[b]
		Sec.	*Sec.*	*Sec.*	*Sec.*	*Sec.*
		A. Isobutyl Acetate				
None	100:0	...	...	42.4	53.0	72.3
Toluene	80:20	...	35.5	43.3	54.3	76.7
H. S. naphtha	80:20	...	38.1	44.6	60.2	87.8
Gasoline	80:20	...	39.2	46.5	66.0	94.6
Toluene	60:40	...	36.9	46.8	69.5	...
H. S. naphtha	60:40	...	40.8	54.6	85.0	...
Gasoline	60:40	36.0	48.7	72.8	...	...
Toluene	50:50	...	39.3	51.4	75.8	...
H. S. naphtha	50:50	37.3	51.2	72.1	...	...
Gasoline	50:50	Not soluble				
Toluene	40:60	34.8	44.0	68.3	...	...
H. S. naphtha	40:60	Not soluble				
		B. *n*-Butyl Acetate				
None	100:0	...	...	41.5	51.9	70.3
Toluene	80:20	...	...	41.4	54.2	73.2
H. S. naphtha	80:20	...	...	42.2	56.4	78.9
Gasoline	80:20	...	35.8	43.0	57.2	81.7
Toluene	60:40	...	36.5	46.7	65.6	94.3
H. S. naphtha	60:40	...	39.5	53.6	78.5	...
Gasoline	60:40	33.8	45.3	65.0	...	...
Toluene	50:50	...	39.0	50.3	73.2	...
H. S. naphtha	50:50	35.7	48.7	71.6	...	...
Gasoline	50:50	Not soluble				
Toluene	40:60	35.0	43.8	66.5	...	...
H. S. naphtha	40:60	Not soluble				

[a] Viscosity in No. 7 cup at 25° C.
[b] To obtain corresponding total solids, multiply by 1.5.

Table II*B* gives similar information for *n*-butyl acetate with the three diluents and the nitrocellulose-resin mixture. In the case of both of these esters the nitrocellulose-resin mixture will not dissolve at 50 per cent gasoline dilution or at 60 per cent high-solvency naphtha dilution. Toluene, however, maintains its excellent diluent properties at 60 per cent dilution although there is a noticeable viscosity increase with the addition of the resin over that observed with the nitrocellulose alone.

Curves Derived from Data

The experimental viscosity values in the tables are plotted against nitrocellulose concentration. Figure 1 shows the curves for the four esters with nitrocellulose alone and the two

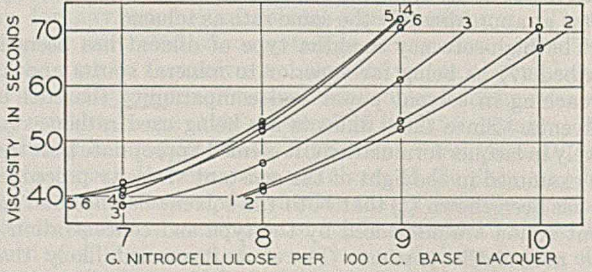

Figure 1. Viscosity–Nitrocellulose Content Curves for 100 Parts Solvent

1. Isobutyl acetate (90 per cent)
2. *n*-Butyl acetate (90 per cent)
3. Isobutyl propionate (80 per cent)
4. Pentacetate (87 per cent)
5. Isobutyl acetate (nitrocellulose:resin = 2:1)
6. *n*-Butyl acetate (nitrocellulose:resin = 2:1)

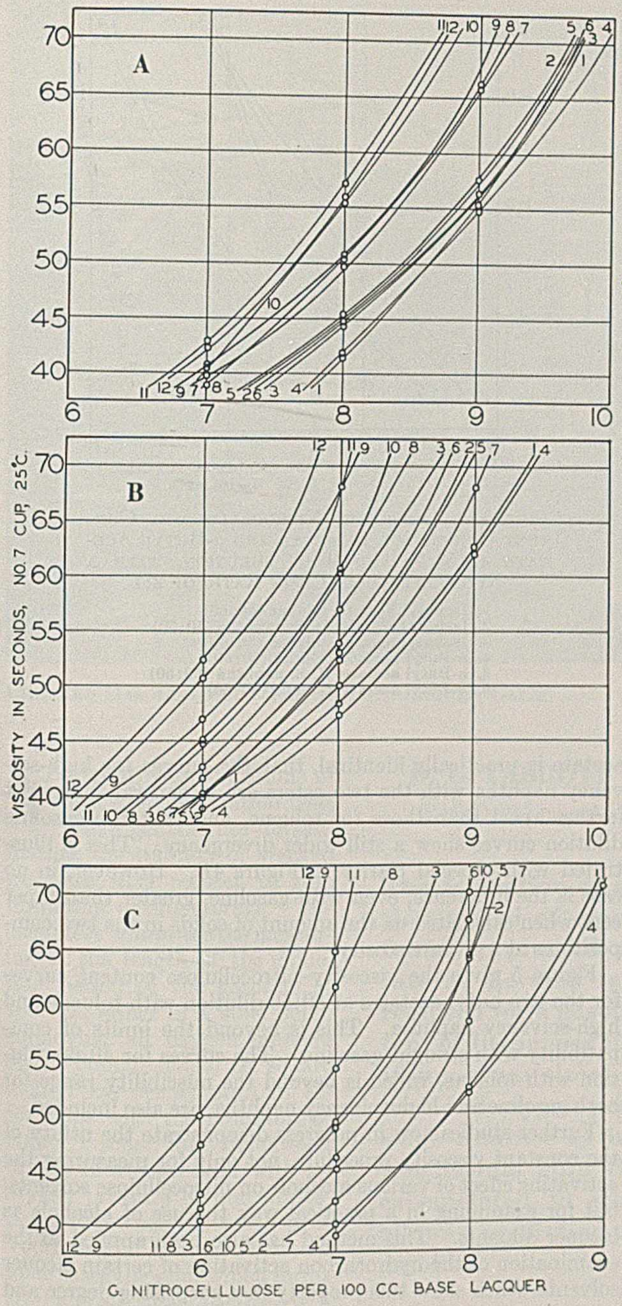

FIGURE 2. VISCOSITY–NITROCELLULOSE CONTENT CURVES

A, 80:20 dilution; *B*, 60:40; *C*, 50:50.

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H. S. naphtha
3. Isobutyl acetate–gasoline
4. *n*-Butyl acetate–toluene
5. *n*-Butyl acetate–H. S. naphtha
6. *n*-Butyl acetate–gasoline
7. Isobutyl propionate–toluene
8. Isobutyl propionate–H. S. naphtha
9. Isobutyl propionate–gasoline
10. Pentacetate-toluene
11. Pentacetate–H. S. naphtha
12. Pentacetate-gasoline

butyl acetates with the nitrocellulose–resin composition, all in the absence of any diluent. Although viscosity values for the undiluted solvent are of little practical value from the standpoint of lacquer solvent evaluation, they are still widely used in the industry for evaluative purposes, and considerable emphasis is often placed upon the viscosity of the nitrocellulose solution in the solvent alone when comparisons are being made. The curves show the small differences which exist between the butyl acetates and indicate that these differences are practically the same whether or not resin is present in the formulation.

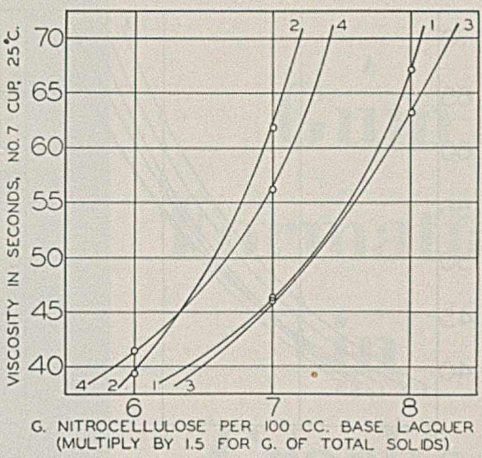

FIGURE 3. VISCOSITY–NITROCELLULOSE CONTENT CURVES FOR ISOBUTYL AND *n*-BUTYL ACETATE AT 40:60 DILUTION

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H. S. naphtha
3. *n*-Butyl acetate–toluene
4. *n*-Butyl acetate–H. S. naphtha

Figure 2*A* shows the reaction of these four esters to the three types of diluent at 20 per cent dilution. The curves indicate that, in the absence of resin or other material which might complicate the relation, there is little to be gained by the use of the aromatic over the pure aliphatic type hydrocarbon. The first six curves for the two butyl acetates show the almost complete coincidence of the two esters with gasoline and high-solvency naphtha, with toluene offering a slight advantage in each case. Isobutyl propionate lies about midway between Pentacetate and the butyl acetates in solvent action at this dilution.

Figure 2*B* gives the viscosity–nitrocellulose content curves for 40 per cent dilution. The differences between the three diluents are becoming more noticeable, with those between the esters (particularly between *n*-butyl and isobutyl acetate) remaining but slightly changed over those at lesser dilutions. Curves 1 and 4 for toluene dilution, 2 and 5 for high-solvency naphtha dilution, and 3 and 6 for gasoline dilution bear out the conclusion that for all practical purposes the butyl acetates possess the same solvency characteristics with any given hydrocarbon diluent. The most striking observation in this case is that concerning isobutyl propionate which has shown a remarkable increase in solvent strength relative to the other esters. This is especially true with toluene dilution (curve 7) which is but slightly inferior to the solvency of the butyl acetates. The reaction of isobutyl propionate to high solvency naphtha dilution is also extremely good; it is slightly lower than that of isobutyl acetate and almost identical with that of Pentacetate and toluene. With gasoline, however, the isobutyl propionate has shown a relative decrease in activity and is only slightly superior to Pentacetate.

At 50:50 dilution (Figure 2*C*) isobutyl and *n*-butyl acetate remain almost identical in their reaction to toluene and high-solvency naphtha addition. Although the difference is somewhat greater with gasoline, it is never more than 5 per cent based on solids in solution. Isobutyl propionate with toluene continues to show up extremely well, but the curves for both the high-solvency naphtha and gasoline with this ester are somewhat closer to those of Pentacetate with the same diluents.

Dilution with 60 per cent hydrocarbon is beyond the limits of compatibility for both isobutyl propionate and Pentacetate and also those of the butyl acetates with gasoline. Figure 3, therefore, shows only the curves for isobutyl and *n*-

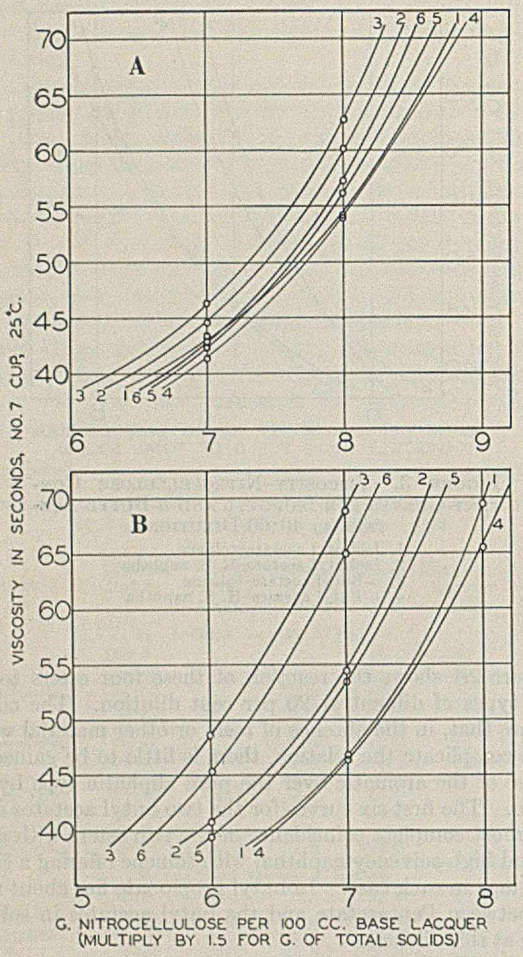

Figure 4. Viscosity–Nitrocellulose Content Curves for Isobutyl and *n*-Butyl Acetate at 80:20 (*A*) and 60:40 (*B*) Dilutions with a Nitrocellulose:Resin Ratio of 2:1

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H. S. naphtha
3. Isobutyl acetate–gasoline
4. *n*-Butyl acetate–toluene
5. *n*-Butyl acetate–H. S. naphtha
6. *n*-Butyl acetate–gasoline

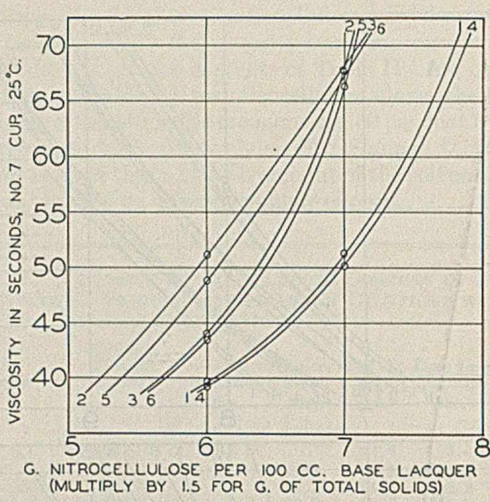

Figure 5. Viscosity–Nitrocellulose Content Curves for Isobutyl and *n*-Butyl Acetate at 50:50 and 40:60 Dilution, with a Nitrocellulose: Resin Ratio of 2:1

1. Isobutyl acetate–toluene (50:50)
2. Isobutyl acetate–H. S. naphtha (50:50)
3. Isobutyl acetate–toluene (40:60)
4. *n*-Butyl acetate–toluene (50:50)
5. *n*-Butyl acetate–H. S. naphtha (50:50)
6. *n*-Butyl acetate–toluene (40:60)

butyl acetate with toluene and high-solvency naphtha at this dilution.

Figure 4*A* is concerned with the reaction of isobutyl acetate and *n*-butyl acetate to 20 per cent hydrocarbon dilution in the presence of a 2 to 1 mixture of nitrocellulose and resin. At this low dilution there is only a small viscosity increase over that observed with the nitrocellulose alone, as the toluene is replaced by high-solvency naphtha and then by gasoline. The two esters possess essentially the same solvency with each diluent. The weight values given in Figures 4 and 5 refer only to the amount of nitrocellulose present in the mixtures, and these values should be multiplied by the factor 1.5 to obtain total solids. Also, in comparing these values with those for nitrocellulose alone, it should be kept in mind that a volume of the solvent-diluent mixture equal to the volume of the resin has been replaced by resin in each case.

At the dilution of 40 per cent (Figure 4 *B*) the effect of the presence of resin in the formulation becomes marked. This is particularly true at the higher solids contents and results in curves with a much steeper slope than occurs at the same dilution (Figure 2*A*) in the absence of any resin. It is interesting to note that in practically all of these cases the effect of toluene upon the solvent action of isobutyl acetate and *n*-butyl acetate is practically identical, that the curves for high-solvency naphtha with the two esters are in general somewhat farther apart than those for toluene, and that the gasoline dilution curves show a still wider divergency. This is illustrated with especial clarity in Figure 4*B*. However, in no case is the difference, even with gasoline, greater than 5 per cent when calculated on the amount of solids in the two compositions at a given viscosity.

Figure 5 gives the viscosity–nitrocellulose content curves for the two butyl acetates at 50:50 dilution with toluene and high-solvency naphtha. This is beyond the limits of compatibility with straight gasoline. The curves for 40:60 dilution with toluene, which is beyond the miscibility range for both gasoline and high-solvency naphtha, are also included.

Further studies now in progress demonstrate the utility of the constant viscosity procedure, not only for measuring the activating effect of various alcohols on nitrocellulose solvents, but for examining in a practical way the use of alcohols as lacquer diluents. This method has also been applied to the examination of the hydrocarbon activation of certain lacquer solvents which show this property in a surprising degree and to a much greater extent than occurs in the activation of esters by means of alcohols.

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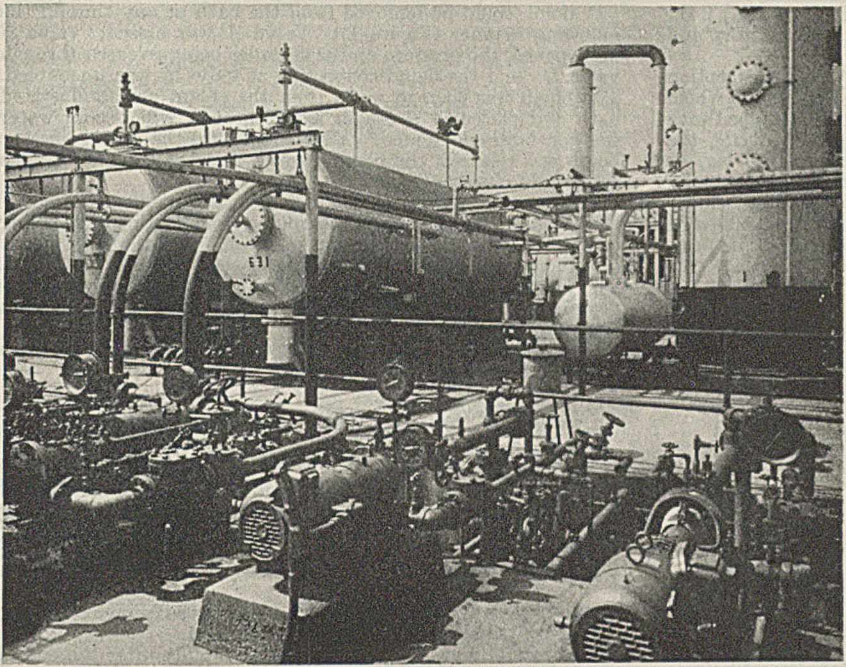
Presented before the Division of Paint and Varnish Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.

Gum Formation in Cracked Gasolines



Cracked Gasoline Soda Treater, Dominguez, Calif.

D. L. YABROFF and E. L. WALTERS
Shell Development Company, Emeryville, Calif.

The formation of gum during the induction period of cracked gasolines has been found to proceed at a simple exponential rate at elevated temperatures. The time required for a gasoline to reach a gum content of 10 mg. per 100 ml. (designated as the 10-mg. gum time) is affected by temperature and oxygen pressure in essentially the same manner as is the induction period. The 10-mg. gum time can accordingly be extrapolated to storage conditions, which allows a prediction of the storage life of the gasoline.

VARIOUS modifications of accelerated oxidation tests are in general use for estimating the stability of cracked gasolines with respect to gum formation during storage. The usual test comprises the measuring of the length of the induction period of the gasoline at 100° C., either in a steel bomb employing an oxygen pressure of 100 pounds (gage) per square inch (7 kg. per sq. cm.) in accordance with the procedure of Hunn, Fischer, and Blackwood (*5*), or in a glass flask with an oxygen pressure of one atmosphere following the method of Voorhees and Eisinger (*10*). In some cases the gum which forms after a given time (usually 4 or 5 hours) of accelerated oxidation under fixed conditions is taken as a measure of stability.

Extensive storage tests have been carried out in different laboratories (*3, 9, 11*) to correlate the storage life of a gasoline with its induction period. Although a general sort of correlation was found, the induction period did not appear to rate properly the stability of gasolines of different types, especially with regard to origin, refining treatment, and inhibitors.

The effects of temperature and oxygen pressure on the induction period have been investigated (*1, 2, 6*) and found to obey simple laws, allowing an extrapolation to storage conditions. This appears to be a definite improvement since the effect of temperature is very large but, more important, is a variable quantity which is dependent on the particular gasoline. Accordingly, the temperature susceptibility of the gasoline should be taken into account in any test which employs temperature as one of the accelerants.

The validity of the induction period as a measure of stability, even when extrapolated to storage conditions, has been questioned by Bridgeman (*2*) because the amount of gum formed when the end of the induction period has been reached in accelerated tests may be greatly in excess of 10 mg. per 100 ml., a value that is usually considered the maximum permissible gum content. He suggested that "a more rational procedure would be to measure the gum contents at various periods of time when the gasolines are heated at a number of elevated temperatures and by extrapolation to obtain information on the predicted times at storage temperatures at which the gum content would reach various values". After considerable experience with various stability tests, we too have been led to this conclusion, and the present paper presents the results of preliminary work along these lines. Throughout this paper the time required for a gasoline to reach a given gum content, under the particular conditions involved, will be designated as the gum time, preceded by the number of milligrams of gum per 100 ml. in question (e. g., 5-mg. gum time, 10-mg. gum time, etc.).

Experimental Methods

Equipment. The oxygen bombs and assembly used in the present investigation were identical to the Universal Oil Products type previously described (*4*) with the following modifications:

Less difficulty from leaks was encountered by using gaskets rather than relying on the natural metal-to-metal seal. The bomb cover lip making the seal with the body of the bomb was squared rather than rounded. Gaskets of a hot oil asbestos material [obtained from the Garlock Packing Company, No.

7022, $2^{15}/_{16}$ inches (7.46 cm.) o. d., $2^{7}/_{16}$ inches (6.19 cm.) i. d., and $^{1}/_{32}$ inch (0.8 mm.) thick] were found to be satisfactory and were suitable for two to three runs.

The bombs were enclosed in oil thermostats with the exception of one set which was operated only at 100° C. and for which a steam bath was used. The thermostats were all equipped with closed coils through which steam could be passed during the heating period to minimize the effect of temperature lag, or cooling water if it was desired to cool the entire bath rapidly. For one of the oil thermostats, which was appreciably larger than the others, it was found necessary to add a 2500-watt heater to assist in the initial heating of the bath. The temperature control was on the order of ±0.1° C.

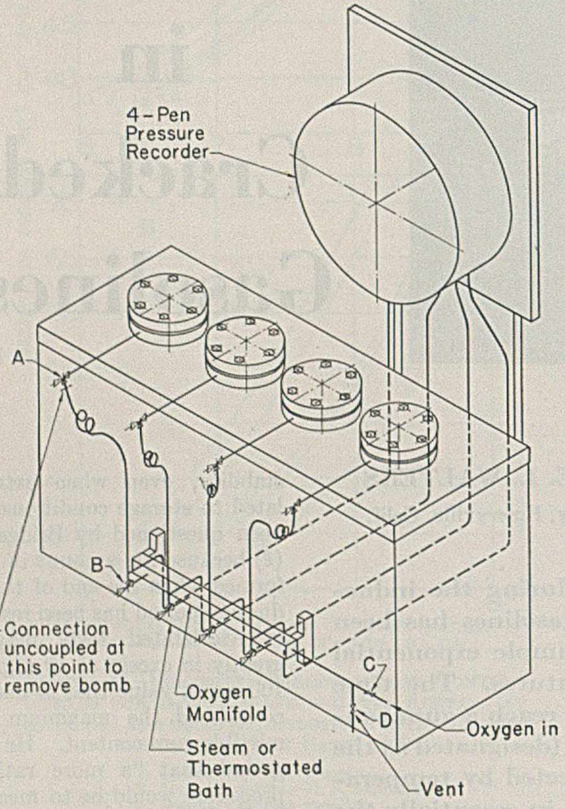


FIGURE 1. OXYGEN BOMB ASSEMBLY

The valve arrangement is indicated in Figure 1. Valve *A* was a $^{1}/_{4}$-inch (6.4-mm.) angle shut-off valve (obtained from the American Brass and Copper Company, Sylpak valve No. 192-C). Valves *B*, *C*, and *D* were ordinary $^{1}/_{4}$-inch needle valves. By proper manipulation of the valves, it was possible to remove a single bomb from the bath at any given time without disturbing the other bombs.

PROCEDURE. Eight-ounce oil sample bottles containing 100 ml. of the gasoline under test were placed in the bombs immersed in the thermostat or bath at an initial temperature of 21° ± 3° C. The bombs were flushed only once with oxygen under a pressure of 100 pounds per square inch in order to avoid undue loss of light ends, and oxygen at 100 pounds pressure was again admitted; the nitrogen content of the bomb gases was then about 1 per cent. The bombs were allowed to stand for some 15 minutes to make sure there were no leaks (valves *A* and *D* were open during this period, and valves *B* and *C* were closed). The occasional leaks encountered were most likely to occur at the removable flared connection at valve *A* and were fixed before proceeding further. The bomb pressure was then adjusted to exactly 100 pounds or any other value desired.

The heating-up procedure for the thermostats was standardized and adhered to rigorously. Essentially this consisted in passing steam through the auxiliary coils until the bath temperature was 5° C. above the desired temperature. The higher temperature (±1° C.) was then maintained for 10 minutes by adjusting the steam rate, after which the steam was shut off and the bath allowed to drop to the desired temperature, at which point it was maintained by conventional thermostatic controls. This procedure greatly reduced the temperature lag of the gasoline in the bomb.

A bomb could be removed from the bath at any time in the following manner (Figure 1): Valve *A* was closed; valve *B* was opened, the pressure on the recorder being released through valve *D*; and the flared connection at valve *A* was uncoupled. The bomb was then removed from the steam or thermostated bath and placed in a cooling bath through which cold water was constantly circulated. After 15 minutes the pressure in the bomb was released, the bomb opened, and the oxidized sample subjected to further tests.

The time corrections to be applied for the temperature lag of the gasoline in the bomb were computed from heating and cooling curves obtained under the exact operating conditions by means of a thermocouple passing through a special bomb top (*1*, *2*, *7*). The heating-up corrections ranged from 25 to 35 minutes, depending on the particular bath; the cooling-down corrections were 3 to 5 minutes.

Gum determinations were carried out in accordance with A. S. T. M. method D-381-36.

Effect of Temperature on Gum Formation

Preliminary experiments on the rate of gum formation were carried out at 100° C. and under an oxygen pressure of 100 pounds, with several cracked and reformed gasolines. These experiments indicated, in general, agreement with the findings of previous investigators:

About 25 to 100 mg. of gum per 100 ml. were formed when the end of the induction period had been reached.

The rate of gum formation increased rapidly after the end of the induction period.

The 10-mg. gum time (time required to reach a gum content of 10 mg. per 100 ml. of gasoline) was 30 to 75 per cent of the induction period for the various gasolines.

A more detailed study was made at several elevated temperatures and disclosed the fact that the rate of gum formation during approximately the first 90 per cent of the induction period was exponential; a plot of the logarithm of the gum content of the gasoline against the time of oxidation yielded straight lines for each of the several temperatures investigated. This relation is illustrated by Figure 2 for an uninhibited mid-continent cracked gasoline. By expressing the time of oxidation of the gasoline at the various temperatures as a percentage of its induction period at the temperature involved, the data of Figure 2 fall closely about one line as shown in Figure 3. This indicates that the rate of gum formation is affected by temperature in essentially the same manner as is the induction period. Accordingly, after a

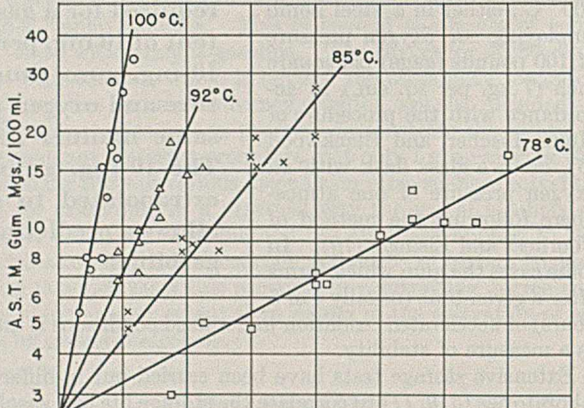


FIGURE 2. FORMATION OF GUM DURING THE INDUCTION PERIOD OF A MID-CONTINENT CRACKED GASOLINE UNDER AN OXYGEN PRESSURE OF 100 POUNDS GAGE

gasoline has reached a given percentage of its induction period through accelerated oxidation, the amount of gum thus formed should be nearly independent of the temperature of the oxidation.

It is then to be expected that the effect of temperature on the 10-mg. gum time may be expressed by an equation of the same form as for the induction period (*1*, *2*):

$$\log tg = A + B/T \qquad (1)$$

where tg = 10-mg. gum time, hours
T = absolute temperature, ° K.
A, B = constants which depend on the gasoline (this equation may be used for computing times to reach gum contents other than 10 mg. per 100 ml., in which case intercept A will have a different numerical value but B will be unchanged)

This is shown in Figure 4 where the logarithm of the induction period and of the 10-mg. gum time of the mid-continent cracked gasoline are plotted against the reciprocal of the absolute temperature.

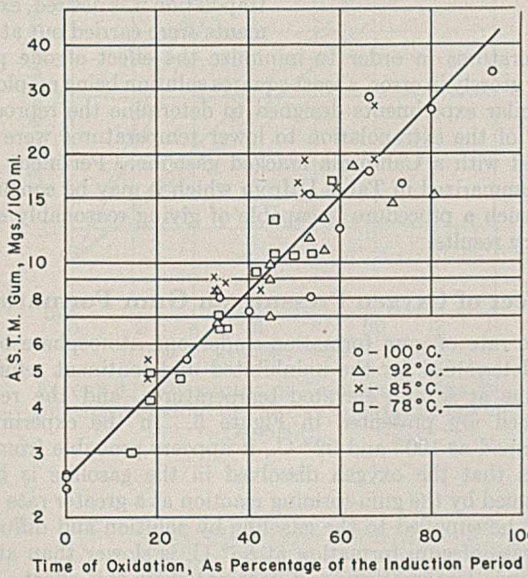


FIGURE 3. FORMATION OF GUM DURING THE INDUCTION PERIOD OF A MID-CONTINENT CRACKED GASOLINE UNDER AN OXYGEN PRESSURE OF 100 POUNDS GAGE

At constant temperature the rate of gum formation of a given gasoline may be expressed by the equation:

$$\log \text{gum} = kt + \log I \qquad (2)$$

where k = specific rate constant for formation of gum
t = time of aging or oxidation
I = initial gum content of gasoline, mg./100 ml.

The variation of k with temperature is a function of the energy of activation of the gum-forming reaction:

$$\frac{d \ln k}{d\, 1/T} = -\frac{\epsilon}{R} \qquad (3)$$

where ϵ = activation energy
R = gas constant

If a gum content of 10 mg. per 100 ml. is to be reached by a given gasoline at a fixed temperature, Equation 2 becomes

$$kt = \log 10 - \log I \qquad (4)$$

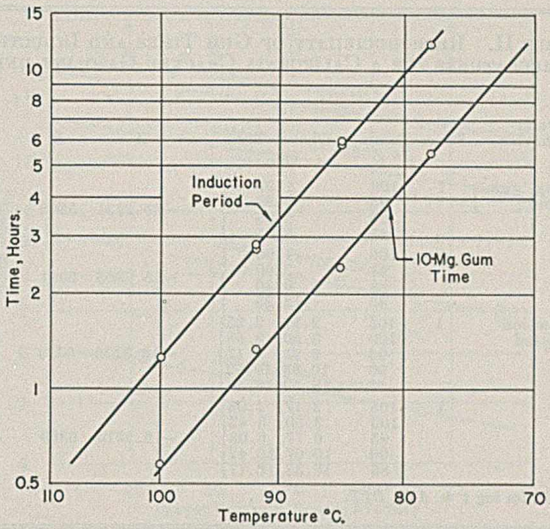


FIGURE 4. EFFECT OF TEMPERATURE ON INDUCTION PERIOD AND THE 10-MG. GUM TIME OF A MID-CONTINENT CRACKED GASOLINE UNDER AN OXYGEN PRESSURE OF 100 POUNDS GAGE

and the product kt is hence a constant quantity. Accordingly, the variation of the logarithm of t with the reciprocal of the absolute temperature will be identical to that of the logarithm of k (Equation 3), with the exception of the sign. The value of ϵ/R in Equation 3 is therefore equal to 2.3026 times the constant B of Equation 1 for the 10-mg. gum time (or any other gum time), or

$$\epsilon = 4.579B \qquad (5)$$

Any given gum time may be computed from the initial gum content of the gasoline and the 10-mg. gum time, for a given set of conditions, as long as the rate of gum formation obeys the simple logarithmic function noted above. The equation is

$$X\text{-mg. gum time} = 10\text{-mg. gum time}\,\frac{\log X - \log I}{\log 10 - \log I}$$

A summary of the data obtained for two gasolines, the mid-continent cracked and a mid-continent reformed, with

TABLE I. INDUCTION PERIODS AND GUM TIMES FOR A MID-CONTINENT CRACKED AND A MID-CONTINENT REFORMED GASOLINE AT ELEVATED TEMPERATURES UNDER 100 POUNDS OXYGEN PRESSURE

Gasoline	Added Inhibitor	Initial Gum Content	Temp.	Observed Times: Induction period	Observed Times: 10-mg. gum time	Obsvd. Ratio, 10-Mg. Gum Time/Induction Period	Calcd. Ratio, 5-Mg./10-Mg. Gum Time
		Mg./100 ml.	*° C.*	*Hr.*	*Hr.*		
Mid-continent reformed	None	0.8	100	1.75	1.20	0.69	0.726
			92	4.42	2.87	0.65	
			85	9.50	5.97	0.63	
	A	1.0	108	2.17, 2.25	1.33	0.60	0.699
			100	4.58, 4.58	2.82	0.62	
			92	11.17, 11.25	6.75	0.60	
	B	1.0	108	1.75, 1.75	0.97	0.55	0.699
			100	4.00, 4.08	2.08	0.52	
			92	9.67, 9.42	4.67	0.49	
Mid-continent cracked	None	2.6	100	1.25, 1.25	0.58	0.46	0.485
			92	2.75, 2.83	1.34	0.48	
			85	5.83, 6.00	2.41	0.41	
			78	12.00, 12.08	5.50	0.46	
	A	2.8	108	2.08, 2.00	0.97	0.48	0.455
			100	4.33, 4.42	1.92	0.44	
			92	10.83, 11.08	4.37	0.40	
	B	3.8	108	1.58, 1.50	0.47	0.31	0.284
			100	3.58, 3.58	1.11	0.31	
			92	9.08, 9.17	2.62	0.29	

Table II. Reproducibility of Gum Times and Induction Periods Extrapolated to Low Temperatures for a California Cracked Gasoline under 100 Pounds Oxygen Pressure

Determination	Series	Temp.	Obsvd. Time	A	B	Calcd. Time[a]	Extrapolated Time 100° F.	Extrapolated Time 80° F.	ε, Activation Energy of Gum-Forming Reaction
		° C.	Hr.			Hr.	Mo	Mo.	
10-mg. gum time	1	100	1.97	−15.2751	5808	1.95	3.55	17.5	26,600
		95	3.22			3.18			
		90	5.08			5.25			
		85	8.95			8.78			
	2	100	1.90	−15.6368	5941	1.93	4.14	21.1	27,200
		94	3.60			3.52			
		88	6.60			6.55			
		82	12.25			12.42			
Induction period	1	105	2.17, 2.25	−16.3776	6320	2.18	12.4	70.4	....
		100	3.50, 3.58			3.65			
		95	6.25, 6.17			6.18			
		90	10.83, 10.92			10.67			
		85	18.50, 18.50			18.67			
	2	105	2.17, 2.08	−16.5213	6369	2.10	12.9	73.8	....
		100	3.50, 3.42			3.55			
		95	6.17, 6.08			6.03			
		90	10.67, 10.42			10.47			
		85	18.33, 18.17			18.38			

[a] From $\log t = A + B/T$.

and without added inhibitors, is given in Table I. The values for the ratio of the 10-mg. gum time to the induction period (column 7) are roughly independent of the temperature for a given gasoline sample. In several cases there appears to be a considerable variation, but we are inclined to believe that this is not real but is due essentially to the personal factor involved in selecting the end of the induction period, particularly for the longer induction periods at the lower temperatures where the pressure breaks may be rather gradual.

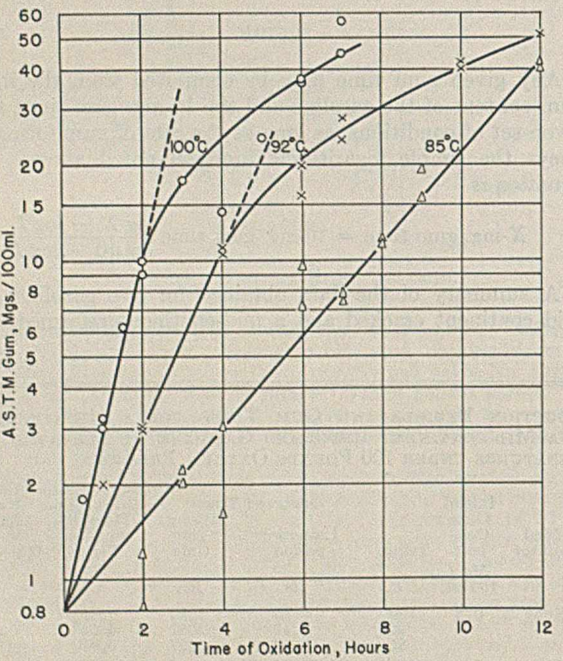


Figure 5. Formation of Gum during the Induction Period of a Mid-continent Reformed Gasoline under One Atmosphere of Air

The ratio of 10-mg. gum time to induction period is not a constant quantity for a given gasoline but depends on the initial gum content and on the length of the induction period. As these change through the aging of the gasoline (i. e., the initial gum content increases and the induction period decreases), the ratio of 10-mg. gum time to induction period will decrease. For this reason the samples listed in Table I are not directly comparable with one another. Nevertheless, in spite of its shortcomings, the ratio of 10-mg. gum time to induction period is of interest since the induction period has served in many cases as the only criterion for gum stability, even without regard for the initial gum content of the gasoline.

The data of Table I are not sufficiently accurate to extrapolate to lower temperatures, essentially because some of the gum times involved are so short that errors of the order of 5 to 10 minutes will be greatly magnified in the extrapolated value. In all later work where an extrapolation was desired, experiments were carried out at four temperatures in order to minimize the effect of one point being grossly in error, a least squares solution being employed.

Similar experiments designed to determine the reproducibility of the extrapolation to lower temperatures were performed with a California cracked gasoline. Pertinent data are summarized in Table II from which it may be concluded that such a procedure is capable of giving reasonably satisfactory results.

Effect of Oxygen Pressure on Gum Formation

The rate of gum formation under one atmosphere of air was determined for the uninhibited mid-continent reformed gasoline at several elevated temperatures, and the results obtained are presented in Figure 5. In the experiments performed at 100° and 92° C., it appears probable from the curves that the oxygen dissolved in the gasoline is being consumed by the gum-forming reaction at a greater rate than it can be supplied to the gasoline by solution and diffusion. The rate of gum formation at 85° C. is slower than at the other two temperatures and does not show this effect. The ratios of the 10-mg. gum times under 1 atmosphere of air to those under an oxygen pressure of 100 pounds (the latter values from Table I) are 1.65, 1.34, and 1.28 for 100°, 92°, and 85° C., respectively. The trend in the ratios with de-

Table III. Effect of Oxygen Pressure on 10-Mg. Gum Time and on Induction Period of California Cracked Gasoline[a]

Temp.	Oxygen Pressure	Induction Period[b]	10-Mg. Gum Time	Pressure Ratio, 1 Atm. Air/100 Lb. O_2 (Gage) Induction period	Pressure Ratio, 1 Atm. Air/100 Lb. O_2 (Gage) 10-mg. gum time
° C.	Lb. gage	Hours	Hours		
100	125	7.00, 6.83	....	1.26	1.26
	100	7.25, 7.33	4.85		
	75	7.75, 7.67	....		
	50	7.92, 8.00	....		
	25	....	5.67		
	−12[c]	9.17	6.12		
85	125	13.25	....	1.20	1.24
	100	13.92, 13.75	11.27		
	75	14.25, 14.33	....		
	50	14.83, 15.08	....		
	25	15.75, 15.58	13.00		
	−12[c]	16.55	13.95		

[a] The gasolines run at the two temperatures are not identical.

[b] The end of the induction period ("the break") was taken as the time at which the oxygen pressure showed a drop of approximately 2 pounds from the maximum pressure.

[c] Extrapolated to −12 (1 atm. air).

creasing temperature is in agreement with the explanation offered.

The effect of the oxygen pressure on the induction period and on the 10-mg. gum time was determined further for a different sample of a California cracked gasoline at 100° and at 85° C.; several oxygen pressures were used, the lowest of which was 25 pounds (gage) per square inch (1.75 kg. per sq. cm.). The gasoline sample run at 85° C. was first given two 20 per cent volume washes with 10 per cent aqueous sodium hydroxide to extract natural inhibitors and thereby reduce the induction period so that the sample could be more conveniently handled; and so the gasolines run at the two temperatures are not identical. The results are presented in Table III and in Figures 6 and 7. The effect of the oxygen pressure is quite small in this case and is the same for the induction period and for the 10-mg. gum time at the two temperatures within the limit of experimental error. A plot of the logarithm of the induction period against the oxygen pressure fits the data reasonably well (Figure 7).

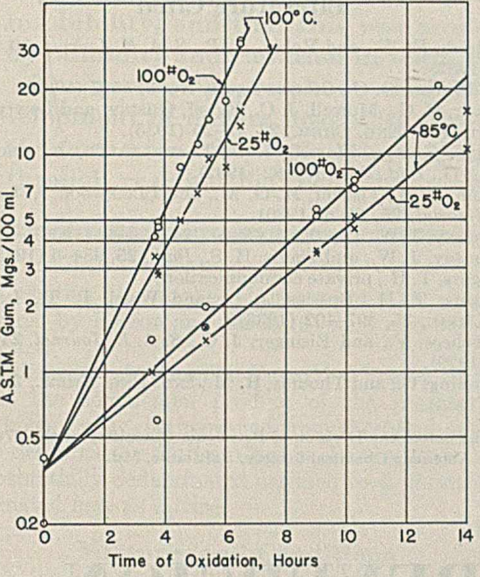


FIGURE 6. FORMATION OF GUM DURING THE INDUCTION PERIOD OF A CALIFORNIA CRACKED GASOLINE

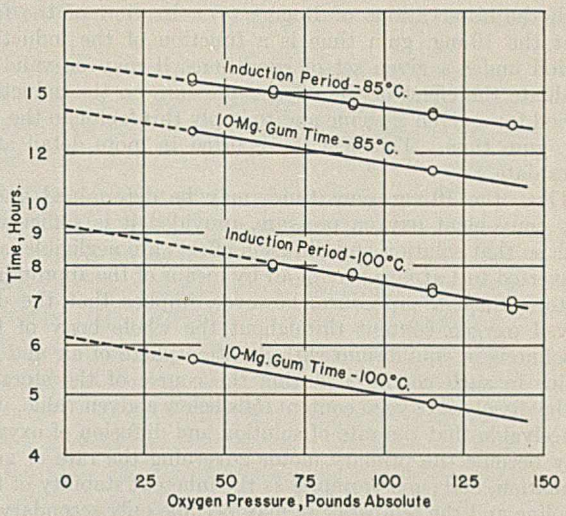
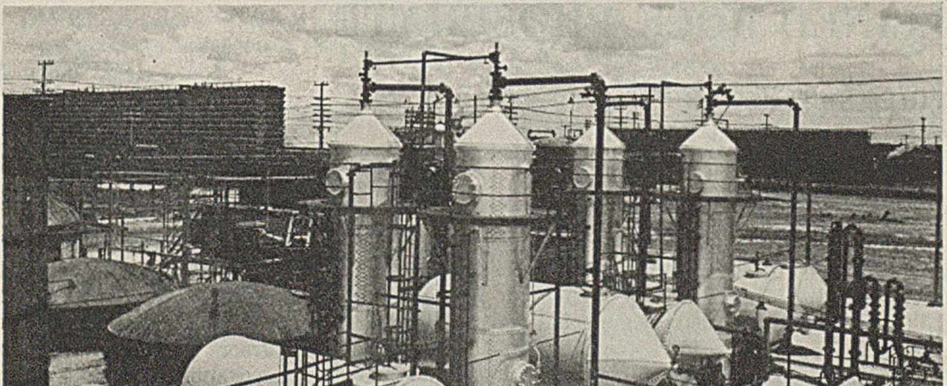


FIGURE 7. EFFECT OF OXYGEN PRESSURE ON THE INDUCTION PERIOD AND THE 10-MG. GUM TIME FOR A CALIFORNIA CRACKED GASOLINE

Preliminary results from further work have indicated that the oxygen pressure effect is not a constant for all gasolines but may vary greatly in certain cases. This is in agreement



DOCTOR AND ACID TREATERS, HOUSTON, TEXAS with the observations of Rogers (*8*). In view of the fact that the 10-mg. gum time is a function of the induction period under a given set of conditions, it may be valid to evaluate the effect of the oxygen pressure on the induction period for a given gasoline and to apply this factor to the 10-mg. gum time. This will be reported in more detail at a later date.

Thus, the 10-mg. gum times may be determined under any convenient oxygen pressure, provided it is sufficiently high so that solution and diffusion effects are negligible, and converted to 1 atmosphere of air by means of the appropriate factor. Such a procedure, however, implies that the dissolved oxygen content throughout the whole body of the gasoline is in equilibrium with an atmosphere of air and remains in such condition during the course of the storage. If the dissolved oxygen content falls below a given value, it is conceivable that the rate of solution and diffusion of oxygen may become the primary factor governing the rate of gum formation, and such variables as the inherent stability of the gasoline and the temperature may become only secondary in importance.

Conclusions

Experiments are now under way to correlate extrapolated gum times for various gasolines with controlled storage at reduced temperatures. In the meantime it is believed that extrapolated gum times may well serve as a gasoline stability specification, but the time consumed by the test may be so great as to preclude its use except in special cases where large quantities of gasoline may be involved. The methods presented here may also be utilized effectively as research tools in determining the relative efficacy of various refining treatments, in comparing gasolines of different stocks, etc.

It is obvious that such a lengthy test is unsuited for the daily control of refinery products, but it is likely that a single induction period or the gum formed after a given time of accelerated oxidation may prove satisfactory for this purpose, provided that such correlating information is available for the particular gasoline as the ratio of the 10-mg. gum time to the induction period for different degrees of refining, the temperature coefficient of the 10-mg. gum time, etc.

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FLUORIDE-INDUCED REVERSION

IN MIXTURES OF SUPERPHOSPHATES AND CALCINED ROCK PHOSPHATE

W. H. MacINTIRE and L. J. HARDIN
The University of Tennessee Agricultural
Experiment Station,[1] Knoxville, Tenn.

ADMIXING of raw rock phosphate to condition phosphatic fertilizers is common practice in certain localities. It has been contended that available P_2O_5 content is thereby increased (*14*), although the acidic components of cured superphosphates are practically inert toward phosphorite. Superphosphates react readily, however, with calcined-defluorinated rock phosphate, the high availability of which has been shown by both chemical and vegetative tests (*3, 5, 12, 13*). Beeson and Jacob (*2*) studied mixtures of calcined rock with superphosphate and ammonium sulfate, and found that substantial proportions of the alkaline calcine caused losses of ammonia. They also found that "there was an immediate increase in citrate-insoluble phosphorus and a further increase during storage" and observed that this result "was considerably enhanced by increasing the relative humidity from 79.2 per cent to 90.5 per cent" (*2*). Beeson and Jacob did not investigate "the nature of the citrate-insoluble compound or compounds formed in these mixtures" (*2*), but they noted that reversions induced by admixed calcic materials had been attributed to engendered fluorphosphate (*9, 10*). (The term "reversion" is used here to connote enhancement in citrate-insoluble P_2O_5.)

The present authors found that component fluorides induced marked development of basic phosphates of meager solubility in aged mixtures of triple superphosphate and calcium silicate slag (*9*). The citrate insolubility induced by the slag greatly exceeded that induced by similar admixtures of limestone (*10*). The fluoride content of the slag-superphosphate mixture was, however, considerably greater than that of the limestone superphosphate mixtures, since the slag contained 6.5 per cent of calcium fluoride in contrast to the trace in the limestone. Moreover, citrate insolubility developed rapidly in a moist mixture of 1 part of precipitated calcium fluoride and 12 parts of precipitated tricalcium phosphate, and the admixed fluoride crystals disappeared upon moderate elevation in temperature (*10*). Those findings were attributed to the formation of fluorphosphate. The experiments of the present paper were planned to de-

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[1] In cooperation with the Department of Chemical Engineering, Tennessee Valley Authority.

When superphosphates and calcined rock phosphate are mixed, the water-soluble phosphates and tricalcium phosphate react quickly to form dicalcium phosphate. It would seem, therefore, that calcined rock phosphate would be preferable to raw rock phosphate as a fertilizer conditioner. Beeson and Jacob found, however, that there was a concomitant development of citrate insolubility, and that this was accelerated by humidity and elevation in temperature.

The present paper shows that this development of citrate insolubility is due to the formation of fluorphosphate, primarily through reaction between the fluorides of the superphosphate and the tricalcium phosphate of the calcine. Substantial reversion of the calcine to a phosphate-fluoride compound, similar to the native phosphorite of raw rock phosphate, militates against the use of the calcine, which otherwise could be used advantageously to condition and to supplement the available P_2O_5 content of fertilizers. The defluorinated calcine can be mixed with fluoride-free superphosphates in any proportion without loss of P_2O_5 availability. This utility and the demand for by-product fluorine should stimulate efforts to produce fluoride-free superphosphates commercially.

termine whether the marked decreases in P_2O_5 availability encountered by Beeson and Jacob (*2*) were also due to that formation.

The calcined rock phosphate used by Beeson and Jacob and also the commercial product of the present studies should, however, be distinguished from the fused and glassy product described by Curtis, Copson, Brown, and Pole (*4*). The substantially defluorinated calcined rock phosphate will be designated here as calcine.

Mixtures and Conditions

The experiments of Beeson and Jacob (*2*) were repeated and amplified by control mixtures of calcine with a special triple superphosphate of negligible fluoride content and made by the acidulation of Appalachian marble with phosphoric acid (*8*). The nine formulations of Table II were used in the comparisons of Tables III, IV, and V, and were representative of mixtures of one ton of calcine with variable proportions of the other components and with total P_2O_5 contents in range between 20.4 and 22.8 per cent.

TABLE I. PERCENTAGE ANALYSES OF MATERIALS USED IN MIXTURES OF SUPERPHOSPHATES WITH CALCINED ROCK PHOSPHATE

Material	Mesh	Moisture	Fluorine	P_2O_5 Total	P_2O_5 Water-sol.	P_2O_5 Citrate-insol.
Calcined rock phosphate[a]	80	None	0.15	36.80	...	5.00[c]
Standard superphosphate	40	7.70	2.05	19.50	17.50	0.15
Triple superphosphate	40	7.00	1.60	43.40	32.00	3.50
Special "fluoride-free triple superphosphate"[b]	40	5.30	0.02	52.80	52.00	None

[a] A commercial product obtained from Darling & Company, Chicago. It contained 0.17% "free" CaO, 52.96% total CaO, and 9.38% CaO over that accounted for by a $Ca_3(PO_4)_2$ content of 80.4%.

[b] Obtained by reaction of H_3PO_4 upon Appalachian marble (*8*).

[c] Charge of 0.5 gram gave 4.6%.

The analyses of the several phosphatic materials used are given in Table I. Ratios of standard superphosphate to calcine in the first three formulations of Table II and in mixtures *A* to *C'* of Tables III, IV, and V were 1 to 5, 1 to 2, and 1 to 1, respectively. Comparable formulations in mixtures *D* to *F'* of the same tables were provided by Wilson Dam triple superphosphate diluted 1 to 1 with ground quartz; and in mixtures *G* to *I'*, by the more concentrated special "fluoride-free triple superphosphate", diluted by quartz in the ratio 3 to 2. The moisture content of each superphosphate, unless otherwise stipulated, was brought to approximately 7 per cent. The bone-dry calcine was devoid of water-soluble P_2O_5, and its leachate was distinctly alkaline.

Twelve identical mixtures of each of the nine formulations detailed in Table II were used to obtain the data of Table III. Analytical charges, each charge carrying 1 gram of calcine, were placed in separate glass vials and immediately compacted. Reference to 1- and 0.5-gram charges in the text will connote the uniform inclusion of these respective amounts of calcine in the variable analytical charges of the several

TABLE II. COMPONENTS OF MIXTURES OF A CONSTANT CHARGE OF CALCINED ROCK PHOSPHATE WITH SUPERPHOSPHATES AND AMMONIUM SULFATE[a]

Mixtures: Material[b]	Mixtures: Parts	Relative Humidities Maintained during Aging, %
Standard superphosphate	400	*A* 79.2, *A'* 90.5
Calcined phosphate	2000	
Ammonium sulfate	1500	
Standard superphosphate	1000	*B* 79.2, *B'* 90.5
Calcined phosphate	2000	
Ammonium sulfate	1500	
Standard superphosphate	2000	*C* 79.2, *C'* 90.5
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	200	*D* 79.2, *D'* 90.5
Triple superphosphate	200	
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	500	*E* 79.2, *E'* 90.5
Triple superphosphate	500	
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	1000	*F* 79.2, *F'* 90.5
Triple superphosphate	1000	
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	240	*G* 79.2, *G'* 90.5
Special "fluoride-free triple superphosphate"	160	
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	600	*H* 79.2, *H'* 90.5
Special "fluoride-free triple superphosphate"	400	
Calcined phosphate	2000	
Ammonium sulfate	1500	
Ground quartz	1200	*I* 79.2, *I'* 90.5
Special "fluoride-free triple superphosphate"	800	
Calcined phosphate	2000	
Ammonium sulfate	1500	

[a] Ground quartz was added to mixtures *D–I* and *D'–I'* to bring the P_2O_5 content of those mixtures to approximately the same as that of the standard superphosphate mixtures.

[b] The four phosphatic materials are those of Table I.

Table III. P_2O_5 Transitions in the Mixtures of a One-Gram Constant of Calcined Rock Phosphate with Variable Proportions of Three Types of Superphosphate and Ammonium Sulfate during Curing at Two Humidities[a]

		P_2O_5 Values, %								
		Water-sol. after days[b]:			Available after days[b]:			Citrate-insol. after days[b]:		
Mixture	Total	0	28	84	0	28	84	0	28	84
With Standard Superphosphate										
A	21.00	1.89	0.69	0.52	18.29	16.82	16.28	2.71	4.18	4.72
A'	21.00	1.89	0.66	1.10	18.29	16.95	15.32	2.71	4.05	5.68
B	20.80	3.66	1.33	0.75	17.98	16.23	14.27	2.82	4.57	6.53
B'	20.80	3.66	0.76	0.67	17.98	14.85	11.96	2.82	5.95	8.84
C	20.40	5.52	2.69	1.56	18.11	15.31	13.53	2.29	5.09	6.87
C'	20.40	5.52	1.75	1.02	18.11	14.00	10.66	2.29	6.40	9.74
With Triple Superphosphate										
D	20.50	2.05	1.07	0.92	17.58	17.32	16.86	2.92	3.18	3.64
D'	20.50	2.05	0.71	1.38	17.58	17.12	16.81	2.92	3.38	3.69
E	21.40	3.66	2.00	1.29	18.38	18.12	17.09	3.02	3.28	4.31
E'	21.40	3.66	1.04	1.37	18.38	17.18	16.87	3.02	4.22	4.53
F	21.35	5.70	3.00	2.18	18.77	17.83	17.35	2.58	3.52	4.00
F'	21.35	5.70	2.72	2.87	18.77	16.35	15.97	2.58	5.00	5.38
With Special "Fluoride-Free Triple Superphosphate"										
G	20.80	2.10	1.18	1.18	18.14	18.24	18.24	2.66	2.56	2.56
G'	20.80	2.10	0.87	1.38	18.14	18.06	18.14	2.66	2.74	2.66
H	21.60	4.33	3.37	1.95	19.16	19.47	19.07	2.44	2.13	2.53
H'	21.60	4.33	2.66	2.25	19.16	19.47	19.47	2.44	2.13	2.13
I	22.80	6.85	5.48	3.56	20.90	21.02	20.98	1.90	1.78	1.82
I'	22.80	6.85	3.67	3.05	20.90	20.91	20.88	1.90	1.89	1.92

[a] Relative humidities of 79.2 and 90.5 % for *A–I* and *A'–I'*, respectively; constant of 30° C. Each replication of each mixture was an analytical charge containing 1 gram of calcined rock phosphate.

[b] Corresponding values were also determined after 7-, 14-, and 56-day periods, and the resultant data were used to construct the curves of Figures 1 and 2.

mixtures. One charge of each formulation was analyzed immediately. Five mixtures of each formulation were then cured at relative humidities of 79.2 and 90.5 per cent at a constant of 30° C. Water-soluble and citrate-insoluble P_2O_5 determinations were made after 7, 14, 28, 56, and 84 days. Tabulated analytical values are expressed as per cent of the actual mixtures. Only the initial results and those for the 28- and 84-day periods are given in Table III, but the analytical data for the other periods were utilized in the construction of the curves of Figures 1 and 2. In these figures, however, increases in citrate-insoluble and decreases in water-soluble P_2O_5 are shown in relation to the respective initial quantities of available P_2O_5.

The advantages of multiple units for periodic analyses, instead of a large single mixture to be disrupted by being subsampled at intervals, were pointed out by Beeson and Jacob (*2*). Certain disadvantages are also encountered, since grinding of the charges is inadmissible. All of the mixtures became quite hard, particularly those exposed to the higher humidity, and in most cases tedious effort was required to effect their disintegration. Minor inconsistencies in water-soluble results were probably due to persistence of gritty particles.

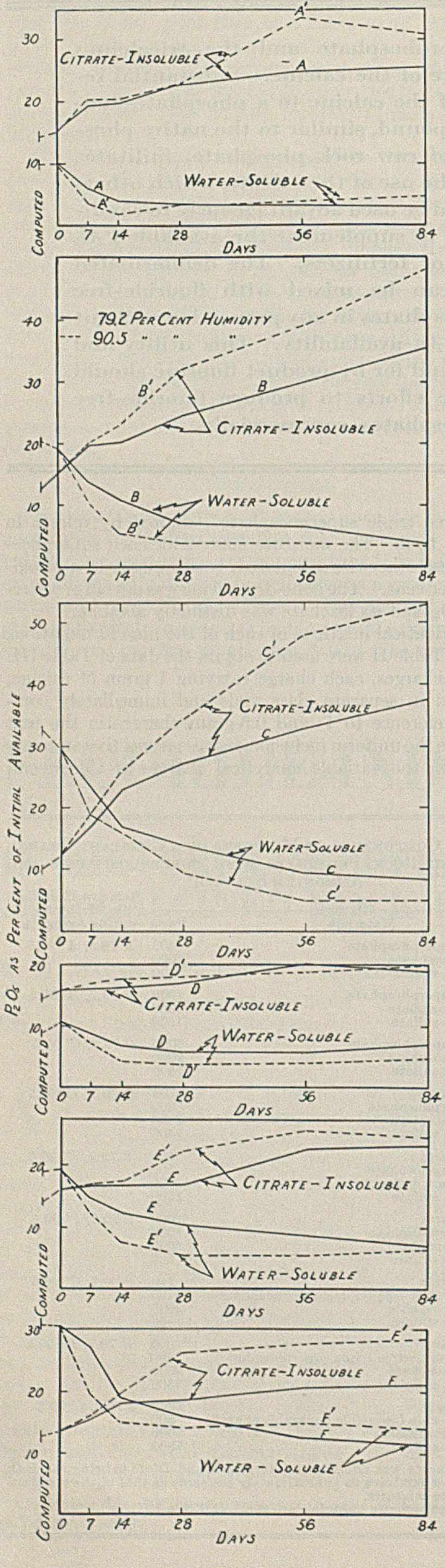

Figure 1. Progressive Fluoride-Induced Reversion and Diminution of Water-Soluble P_2O_5 in Mixtures of Constant Content of Calcined Rock Phosphate and Variable Proportions of Commercial Superphosphates, According to Formulations *A* to *F'* of Table II, during an 84-Day Curing Period at 30° C.

Fluoride-Induced Citrate Insolubility

Immediate reaction between calcine and superphosphates was indicated by quick rise in temperature. The mean of the immediately determined water-soluble values was, however, only 13 per cent less than the mean of the computed initial values. Such reactivity may be attributed in part to the calcic components of the calcine other than tricalcium phosphate, one fifth of the total CaO content being in those forms.

Diminutions in water-soluble P_2O_5 were progressive and more marked in those mixtures that carried the two larger proportions of superphosphate. No consistent relation was found for decreases in the

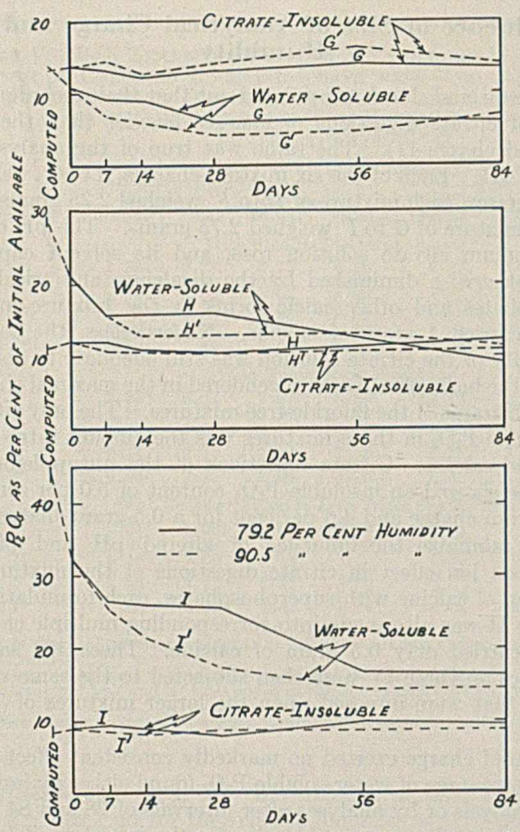

FIGURE 2. ABSENCE OF REVERSION AND DIMINUTION IN WATER-SOLUBLE P_2O_5 IN MIXTURES OF CONSTANT CONTENT OF CALCINED ROCK PHOSPHATE AND VARIABLE PROPORTIONS OF FLUORIDE-FREE SUPERPHOSPHATE, ACCORDING TO FORMULATIONS *G* TO *I'* OF TABLE II, DURING AN 84-DAY CURING PERIOD AT 30 °C.

water-soluble P_2O_5 content of the mixtures that contained the different superphosphates. Some water-soluble P_2O_5 was still present in every mixture after 84 days.

Substantial increases in citrate-insoluble P_2O_5 developed in the standard superphosphate mixtures, *A* to *C'*, and also in the corresponding triple superphosphate mixtures *D* to *F'*, all of which contained fluorides. These increases correlated with progression in the amounts of fluorides supplied by the three proportions of superphosphate in mixtures *A*, *B*, and *C*, in their respective parallels *A'*, *B'*, and *C'*, in the triple superphosphate mixtures *D*, *E*, and *F*, and in their respective parallels, *D'*, *E'*, and *F'*.

Reversion in mixtures *A'* to *F'* was consistently greater than in the corresponding mixtures *A* to *F* which were exposed to the lower humidity. This is in harmony with the findings of Beeson and Jacob (*2*), who used only fluoride-bearing commercial superphosphates. In marked contrast, only meager variations in citrate insolubility were found in the fluoride-free mixtures, *G* to *I'*, and most of these variations were well within experimental error. The essential variable between the first twelve and the last six mixtures of Table III was the introduction of fluorides by the two types of commercial superphosphates in mixtures *A* to *F'* and the practical absence of fluorides from mixtures *G* to *I'*. Synthesis of fluorphosphate could take place in each of the first twelve mixtures, and increases in citrate insolubility indicate that it did. Synthesis could not take place, however, in the last six mixtures in which no increase in citrate-insoluble forms occurred.

Figure 1 shows reversion in relation to initial available P_2O_5 content and demonstrates that ultimate reversion in the six standard superphosphate mixtures was about 1.66 times as much as in the six corresponding mixtures of triple superphosphate. The citrate-insolubility curves of Figure 2 for the fluoride-free mixtures are, however, practically horizontal lines.

Substantial proportions of water-soluble forms of P_2O_5 were quickly converted into dicalcic phosphates in all of the mixtures. Each calcine addition supplied more than enough tricalcium phosphate to effect that transition. The three proportions of calcine supplied, respectively, 9, 3.6, and 1.8 times the amount of tricalcium phosphate requisite for complete transitions to dicalcium phosphate. Even if the other calcic components of the calcine were not reactive toward acidic phosphates, each mixture would still contain a substantial residue of tricalcium phosphate. Since tricalcium phosphate was the dominant component of the commercial calcine, the most extensive reaction was undoubtedly that expressed by the equation:

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 \longrightarrow 4CaHPO_4$$

The mixtures were, therefore, soon composed chiefly of residues of the tricalcium phosphate content of the calcine and engendered dicalcium phosphate.

Occurrence of engendered tricalcium phosphate was necessarily delimited to localized reactions between the extraneous calcic components of the calcine and engendered dicalcium phosphate, as indicated by the equation:

$$2CaHPO_4 + CaSiO_3 \longrightarrow Ca_3(PO_4)_2 + SiO_2 + H_2O$$

The final step of fluorphosphate synthesis apparently had ensued even during the first 7-day period in those systems that contained commercial superphosphates, as indicated by enhanced citrate insolubility and as expressed by the equation:

$$3Ca_3(PO_4)_2 + CaF_2 \longrightarrow 3[Ca_3(PO_4)_2]CaF_2 \text{ [or } Ca_{10}F_2(PO_4)_6]$$

After periods of 28 and 84 days, reversion had become quite pronounced in the first twelve mixtures which contained those components requisite for synthesis of fluorphosphate. Extent of reversion in the mixtures was directly related to the proportions of the two included commercial superphosphates and therefore also to the quantities of incorporated fluorides. Indications of the formation of fluorphosphate were accordingly more extensive in those mixtures whose larger proportions of fluorides afforded greater surface contact between requisite reactants. As much as 54 per cent of the initial available P_2O_5 content underwent reversion. As noted, however, no such increase was found for the last six fluoride-free mixtures, in which the P_2O_5 transitions could not go beyond the formation of tricalcium phosphate. The meager fluoride content of the calcine can be considered as persisting in the form of phosphorite and therefore inert in the several mixtures. Since no enhancement in citrate-insoluble P_2O_5 occurred in the six fluoride-free mixtures *G* to *I'*, reversion in the twelve mixtures *A* to *F'* is attributed solely to the activity of the fluorides introduced by the commercial superphosphates.

Because of the calcium sulfate present in standard superphosphate mixtures *A* to *C'* of Table III, the ultimate reversion in each of these six mixtures was materially in excess of that found for the corresponding triple superphosphate mixtures in series *D* to *F'*. This is readily apparent by respective comparisons between curves *A*–*A'* and *D*–*D'*, *B*–*B'* and *E*–*E'*, and *C*–*C'* and *F*–*F'* of Figure 1. Reaction between the calcine and admixed ammonium sulfate liberated ammonia which accelerated the formation of tricalcium phosphate and the subsequent synthesis of fluorphosphate.

The reversion encountered in the commercial ammoniation of superphosphates is also more extensive in those that contain large proportions of calcium sulfate (*6*, *7*). In contradistinction, complete ammoniation of fluoride-free monocalcium phosphate can be effected without development of citrate insolubility.

It was noted that the respective amounts of admixed tricalcium phosphate in the formulations of Table II, and in the mixtures of Tables III, IV, and V were 9, 3.6, and 1.8 times those requisite for complete transitions of water-soluble P_2O_5 to dicalcium phosphate. Ultimately the other calcic components of the calcine might react with some of the engendered dicalcium phosphate to form tricalcium phosphate; but the initial dryness of the mixtures was such as to minimize that step during the first 7-day period. Nevertheless, considerable reaction between the tricalcium phosphate of the calcine and the fluoride content of the superphosphate is indicated by the reversions found after the first 7 days (Figure 1, curves *A–A′*, *B–B′*, and *C–C′*).

Reaction between ordinary tricalcium phosphate and precipitated calcium fluoride in mixtures of low moisture content is relatively slow at ordinary temperatures, as will be demonstrated later. The activation of the dry mixtures by moisture acquired from imposed humidity was soon registered, however, by further reversion in those mixtures that contained fluorides and also by diminution in water-soluble P_2O_5 of all mixtures. Localized reactions may aggregate considerable reversion in mixtures such as those of Table III without complete disappearance of acidic phosphates. Localized development of dicalcic, tricalcic, and fluorphosphates, in that progression, is induced in superphosphates by admixtures of high-calcic limestone and similar solids, even when the additions are considerably less than those requisite for complete transitions of the acidic components of the superphosphate to basic forms. Since the progressive reactions in the experimental mixtures were accelerated by the imposed humidities, localized reversions may have been induced by the dispersed particles of calcine in the mixtures of Table III, where quantities of water-soluble P_2O_5 persisted for 84 days.

Table IV. P_2O_5 Transitions in the Mixtures of a 0.5-Gram Constant of Calcined Rock Phosphate with Variable Proportions of Three Types of Superphosphate and Ammonium Sulfate during Curing at Two Humidities[a]

Mixture	Total	P_2O_5 Values, %								
		Water-sol. after days[b]:			Available after days[b]:			Citrate-insol. after days[b]:		
		0	28	84	0	28	84	0	28	84
With Standard Superphosphate										
A	21.00	1.78	0.82	0.62	18.34	17.93	17.12	2.66	3.07	3.88
A′	21.00	1.78	0.69	1.42	18.34	18.29	17.63	2.66	2.71	3.37
B	20.80	3.86	1.33	0.80	18.24	17.52	16.98	2.56	3.28	3.82
B′	20.80	3.86	0.96	1.40	18.24	17.52	17.07	2.56	3.28	3.73
C	20.40	6.02	2.69	2.46	18.58	16.40	15.02	1.82	4.00	5.38
C′	20.40	6.02	2.10	1.09	18.58	14.96	12.91	1.82	5.44	7.49
With Triple Superphosphate										
D	20.50	2.05	1.28	1.02	17.53	17.94	17.43	2.97	2.56	3.07
D′	20.50	2.05	1.32	1.23	17.53	16.82	16.80	2.97	3.68	3.70
E	21.40	3.86	2.40	2.00	18.56	19.28	18.82	2.84	2.12	2.58
E′	21.40	3.86	2.92	1.69	18.56	18.38	17.85	2.84	3.02	3.55
F	21.35	6.18	4.00	2.99	19.03	19.03	18.45	2.32	2.32	2.90
F′	21.35	6.18	4.07	3.20	19.03	18.44	17.86	2.32	2.91	3.49
With Special "Fluoride-Free Triple Superphosphate"										
G	20.80	2.05	1.38	1.23	18.12	18.50	18.14	2.66	2.30	2.66
G′	20.80	2.05	1.32	1.53	18.12	18.66	18.34	2.66	2.14	2.46
H	21.60	4.57	3.10	2.22	19.25	19.47	19.29	2.35	2.13	2.31
H′	21.60	4.57	2.48	2.22	19.25	19.16	19.20	2.35	2.44	2.40
I	22.80	6.54	4.72	2.54	21.13	20.91	21.06	1.67	1.89	1.74
I′	22.80	6.54	3.78	4.06	21.13	20.91	20.70	1.67	1.89	2.10

[a] Relative humidities of 79.2 and 90.5% for *A–I* and *A′–I′*, respectively; constant of 30° C. Each replication of each mixture was an analytical charge containing 0.5 gram of calcined rock phosphate.

[b] Corresponding values were also determined after 7-, 14-, and 56-day periods, and the resultant data were used to construct the curves of Figures 1 and 2.

Influence of Size of Analytical Charge and of Humidity

Beeson and Jacob (*2*) pointed out that their technique involved citrate digestions of charges heavier than the prescribed charge (*1*). The same was true of the analyses of Table III. Each of the six mixture-charges, *A* to *C′*, weighed 1.95 grams, each mixture of *D* to *F′* weighed 2.25 grams, and each mixture of *G* to *I′* weighed 2.75 grams. The pH of the ammonium citrate solution rose, and its solvent capacity was otherwise diminished by the dicalcium and tricalcium phosphates and other calcic forms in the mixture-charges that carried 1 gram of calcine. Nevertheless, the solvent capacity of the citrate solution was still adequate to dissolve all of the basic phosphates engendered in the maximal charges of 2.75 grams of the fluoride-free mixtures. The only citrate-insoluble P_2O_5 in those mixtures was the amount introduced by the calcine. Citrate digestions of the unsupplemented calcine showed an insoluble P_2O_5 content of 5.0 per cent for a 1-gram charge and 4.6 per cent for a 0.5-gram charge.

To minimize the influence of altered pH and of the common ion effect in citrate digestions of the mixtures of 1 gram of calcine with superphosphates, each formulation of Table II was also made into corresponding multiple charges that carried only 0.5 gram of calcine. These 108 smaller charges of Table IV were then subjected to the same conditions that were imposed upon the larger mixtures of Table III.

Size of charge exerted no markedly consistent effect upon the percentage of water-soluble P_2O_5 found either by immediate analysis or by analyses after intervals of 28 and 84 days. Near concordance prevailed also for the initial availabilities of the eighteen 1-gram units of Table III and the corresponding 0.5-gram units of Table IV. After periods of 28 and 84 days, however, this relation held only for the comparisons of the mixtures that contained the special "fluoride-free triple superphosphate". The reversions then registered by the smaller charge of the twelve fluoride-containing mixtures of Table IV were, in general, considerably less than those registered by the larger charge of Table III. After 28 days the mean increase in citrate-insoluble P_2O_5 content of the twelve fluoride-containing units *A* to *F′* of Table III were 1.68 per cent, in contrast to a variation of −0.12 per cent for the six fluoride-free units *G* to *I′*. For the 84-day period the mean of ultimate increases in citrate insolubility for the same twelve fluoride-containing mixtures was 2.94 per cent against a variation of only −0.06 per cent for the six fluoride-free mixtures.

The accelerative effect of the calcium sulfate content of the standard superphosphate was again evidenced by greater reversion in mixtures *A* to *C′* than in the corresponding triple superphosphate mixtures *D* to *F′*. The near concordance in the citrate-insoluble values obtained for the six fluoride-free superphosphate mixtures *G* to *I′* of Table III and the corresponding mixtures *G* to *I′* of Table IV, demonstrates that similar concordance would have obtained also for the commercial superphosphate mixtures, if the transitions in mixtures *A* to *F′* of Tables III and IV were due solely to the formation of dicalcium and tricalcium phosphates.

Reversions in both 0.5- and 1-gram calcine charges of the fluoride-bearing superphosphate mixtures were accelerated by humidity. After 28 days the six mixtures of the 1-gram calcine constant showed a mean increase of 1.25 per cent

TABLE V. P_2O_5 TRANSITIONS IN THE MIXTURES OF 1- AND 0.5-GRAM CONSTANTS OF CALCINED ROCK PHOSPHATE WITH VARIABLE PROPORTIONS OF THREE TYPES OF DRY SUPERPHOSPHATE[a] AND AMMONIUM SULFATE AFTER 84 DAYS CURING AT TWO HUMIDITIES AND CONSTANT TEMPERATURE OF 30° C.

	P_2O_5 Values, %							
	1-Gram Charge[c]				0.5-Gram Charge[c]			
	Water-sol.		Citrate-insol.		Water-sol.		Citrate-insol.	
Mixture[b]	Initial	Final	Initial	Final	Initial	Final	Initial	Final
With Standard Superphosphate								
A	2.38	0.77	2.72	4.56	2.25	1.12	2.46	3.38
A'	2.38	0.92	2.72	5.38	2.25	1.42	2.46	2.84
B	4.58	0.76	2.26	6.00	4.74	0.88	1.87	4.70
B'	4.58	0.80	2.26	8.22	4.74	0.88	1.87	5.60
C	7.09	0.76	2.07	6.87	7.34	0.73	1.67	5.38
C'	7.09	1.49	2.07	8.87	7.34	1.96	1.67	6.98
With Triple Superphosphate								
D	2.25	0.87	2.97	3.84	2.14	1.12	2.30	2.77
D'	2.25	0.87	2.97	3.84	2.14	1.74	2.30	2.84
E	4.35	1.42	2.71	4.08	4.26	1.76	2.66	3.28
E'	4.35	1.82	2.71	4.53	4.26	2.12	2.66	3.36
F	6.83	2.47	2.63	4.47	6.40	2.83	2.36	3.41
F'	6.83	2.80	2.63	5.16	6.40	3.20	2.36	3.64
With Special "Fluoride-Free Triple Superphosphate"								
G	2.61	1.03	2.56	3.02	2.51	1.42	2.56	2.46
G'	2.61	1.33	2.56	3.00	2.51	2.14	2.56	2.46
H	5.15	2.00	2.18	..	5.50	2.22	1.96	2.04
H'	5.15	2.00	2.18	2.22	5.50	3.10	1.96	2.22
I	7.63	2.83	1.81	2.00	8.14	3.27	1.64	1.82
I'	7.63	3.38	1.81	2.54	8.14	3.49	1.64	1.82

[a] Less than 1% moisture content; respective materials and proportions same as in Tables I, III, and IV.

[b] Connotes amount of calcined rock phosphate per mixture-charge.

[c] Mixtures *A* to *I* and *A'* to *I'* cured in respective relative humidities of 79.2 and 90.5 %.

citrate-insoluble P_2O_5 for the relative humidity of 79.2 and 2.11 per cent for the relative humidity of 90.5 per cent. For the same humidities the respective means of the ultimate increases were 2.29 and 3.59 per cent. For the 28-day period the mean increase for the 0.5-gram mixtures *A* to *F'* of Table IV was 0.67 per cent, against a mean increase of only 0.10 per cent for the six fluoride-free units *G* to *I'*. After 84 days the mean of increases in citrate insolubility for 0.5-gram mixtures *A* to *F'* of Table IV was 1.38 per cent, in contrast to a mean increase of only 0.05 per cent for fluoride-free mixtures *G* to *I'* of the same table.

The mean of the final citrate-insoluble results for the six fluoride-free 1-gram mixtures of Table III was 2.27 per cent, against 2.28 per cent for the six corresponding 0.5-gram mixtures of Table IV. It is evident that, without fluorides to induce the formation of fluorphosphate in the mixtures, the percentage of citrate-soluble P_2O_5 in the 1-gram calcine charge was practically the same as that in the 0.5-gram charge. Humidity therefore exerted no effect upon development of citrate insolubility in either 0.5- or 1-gram charges of those mixtures in which synthesis of fluorphosphate was precluded.

Influence of size of analytical charge was studied also by the use of the bone-dry mixtures of Table V which were otherwise identical with those of Tables III and IV. Comparisons of Tables III and V indicate that the retardative effect of the low initial moisture content of the incorporated superphosphates was not sustained fully in the large mixtures. The grand average of ultimate reversions for the twelve commercial superphosphate mixtures of Table III was 2.94 per cent, against a mean of 1.80 per cent for the reversions in the corresponding 1-gram charges of the initially bone-dry mixtures of Table V. But the same comparison for the 0.5-gram moist charges of Table IV with the initially dry mixtures of Table V gave respective means of 1.63 and 1.88 per cent for ultimate reversions.

The effect of component fluorides upon P_2O_5 retrogradation was likewise very marked in this series. The mean of reversions in 1-gram charges of the twelve fluoride-containing mixtures of Table V was 2.93 per cent against a mean reversion of only 0.38 per cent for the six fluoride-free mixtures. Mean reversions of 1.80 and 0.09 per cent were found for 0.5-gram charges of the corresponding fluoride-containing and fluoride-free mixtures.

Both analytical charge and humidity therefore exerted a marked influence upon the development of citrate insolubility in those mixtures that contained commercial superphosphates. In contrast, neither variation of charge nor humidity affected the citrate-insoluble values found for the mixtures that contained the special "fluoride-free triple superphosphate". This supports the conclusion that the reversions were due to reaction between component fluorides and tricalcium phosphate.

It is problematical to what extent tricalcium phosphate may have been engendered in these mixtures and to what extent the engendered form was responsible for the subsequent fluorphosphate reaction. Reversion was not delimited by the formation of the tertiary phosphate, however, since the tricalcium phosphate content of the calcine and fluorides react readily, as the mixtures of Table VI show. It is probable, therefore, that the large proportions of tricalcium phosphate introduced by the calcine were chiefly responsible for the fluorphosphate reaction and for the resultant increase in citrate insolubility in the aged mixtures.

Influence of Temperature

The substantial synthesis of fluorphosphate induced by humidity during extended aging at ordinary temperature is greatly accelerated when mixtures of tricalcium phosphate and precipitated calcium fluoride are subjected to moderate elevation in temperature (*10*). When superphosphates are processed by additions of high-calcic liming materials or by injections of ammonia and aged in bulk, resultant rise in temperature induces considerable reversion. Reversions encountered in commercial ammoniation (*6*, *7*) likewise can be attributed to the affinity of the reactive component fluorides for engendered tricalcium phosphate. Reversions such as those shown for the mixtures of Tables III, IV, and V probably would have been substantially more extensive at the higher temperatures that develop in commercial operations.

TABLE VI. OVERNIGHT DEVELOPMENT OF CITRATE INSOLUBILITY IN CALCINED ROCK PHOSPHATE CARRYING ADDITIONS OF CALCIUM FLUORIDE[a]

Conditions Imposed on Mixtures			
Moisture	Temp., ° *C.*	Fluorine addition[b] %	Citrate-Insol. P_2O_5 %
None	Room	None	5.00 (0.20)[c]
None	Room	2.0	5.15 (0.26)
None	Room	4.0	5.00 (0.29)
None	52	2.0	5.00 (0.30)
None	52	4.0	5.10 (0.28)
Moist	Room	2.0	5.00 (0.27)
Moist	Room	4.0	5.10 (0.30)
Moist	52	2.0	10.40 (0.28)
Moist	52	4.0	10.80 (0.31)

[a] "Precipitated" form.

[b] Equivalent to additions of 4.11 and 8.22% of CaF_2.

[c] Values in parentheses were obtained from parallels with dicalcium phosphate.

The comparisons of Table VI were made to demonstrate the mutual importance of moisture and temperature upon development of citrate insolubility during relatively short periods and to ascertain whether the results of Tables III, IV, and V can be attributed primarily to a return of the phosphatic content of the calcine to a form analogous to its original state. The comparisons were also intended to show whether calcium fluoride introduces the common ion effect during citrate digestion. Precipitated calcium fluoride in amounts to provide 2 and 4 per cent of fluorine were mixed with 1-gram charges of unsupplemented calcine. These mixtures were compacted and aged overnight under four conditions: dry at room temperature, dry at 52° C., moist at room temperature, and moist at 52° C.

The analyses of Table VI show that no development of citrate-insoluble P_2O_5 occurred overnight in the dry mixtures, either at room temperature or at 52° C., and also that none occurred in the moist mixtures at room temperature. In contrast, substantial reaction between calcine and calcium fluoride was indicated by the 100 per cent increases in citrate insolubility in the two moist mixtures subjected to a temperature of 52° C. overnight. The comparable increases induced by those two fluoride admixtures of Table VI also demonstrate that the comparatively high solubility of the calcine in the citrate solution so repressed the solubility of the relatively insoluble fluoride as to inhibit development of fluorphosphate during the citrate digestion. The uniformity of the citrate-insoluble P_2O_5 determinations for the calcine, with and without the two fluoride additions of the first three pairs of Table VI, also demonstrates that the relatively insoluble fluoride exerted no common-ion effect upon the solubility of the calcine. The results further indicate that the reversion of the tricalcium phosphate of the calcine to fluorphosphate is responsible for the marked decrease in citrate solubility that developed in the mixtures of Tables III, IV, and V. Since the analytical data of the present and related studies show that the mixtures of these three tables had become substantially mixtures of engendered dicalcium phosphate and incorporated tricalcium phosphate, with minor quantities of residual monocalcium phosphate, it seems logical to conclude that the fluoride-induced reversions in the aged mixtures were due chiefly to a return of the calcine to its original state. Nevertheless, in association with ammonium salts, the calcium sulfate in the standard superphosphate mixtures exerted an accelerative effect upon reversions shown by Tables III, IV, and V. Therefore, it cannot be said that the engendered tricalcium phosphate of similar mixtures would not enter into the formation of fluorphosphate.

In the discussion of Tables III, IV, and V it was pointed out that fluoride-induced reversion does not develop when P_2O_5 transitions extend only to the formation of dicalcium phosphate. To substantiate this, as applied to solids, the tricalcium phosphate mixtures of Table VI were compared with corresponding mixtures that contained a laboratory-prepared dicalcium phosphate of meager fluorine content. The parenthetical analytical values of Table VI demonstrate that citrate insolubility, indicative of formation of fluorphosphate, will not develop in phosphatic mixtures in which added basic materials do not cause transitions beyond the dicalcic stage.

Observations and Conclusions

The present experiment was planned to determine the cause for development of citrate-insoluble P_2O_5 when superphosphate is mixed with an industrial calcine of rock phosphate. The immediate result is a mixture composed substantially of engendered dicalcium phosphate and unchanged calcine.

Invariably the determined citrate-insoluble P_2O_5 contents of the mixtures of calcine and commercial superphosphate were substantially greater than insolubility values computed from separate analyses of the two materials. This disparity increased upon aging and was accelerated by humidity and by elevation in temperature. In contradistinction, citrate insolubility did not develop in corresponding mixtures of calcine and the special "fluoride-free superphosphate". The invariable and substantial increases in the citrate-insoluble P_2O_5 content of the commercial superphosphate–calcine mixtures are attributed primarily to the formation of fluorphosphate through reaction between the fluorides of the superphosphate and the tricalcium phosphate of the calcine. The extent of the fluorphosphate development was governed by the proportion of component fluorides. A secondary development of fluorphosphate apparently ensued when the water-soluble P_2O_5 content of the commercial superphosphates underwent successive transitions to di- and tricalcium phosphates and fluorphosphate through localized reactions induced by the nonphosphatic calcic components of the calcine. The loss in P_2O_5 availability is essentially an index of the return of the calcine to its original composition.

No formation of fluorphosphate can ensue in superphosphates until after incorporation of basic materials conducive to that formation. The fluorphosphate may develop, however, through localized reactions that develop spots of tricalcium phosphate in mixtures whose superphosphates are only partially neutralized. No reaction ensues between dicalcium phosphate and calcium fluoride in their mixtures at ordinary temperatures.

The citrate solubility of freshly formed and finely divided fluorphosphate is much greater than that of pulverized raw rock phosphate (*11*), and development of fluorphosphate in the mixtures was therefore probably not registered to full extent by the conventional citrate digestions. The engendered fluorphosphate is less available than tricalcium phosphate to growing plants, but it is decidedly more available than the phosphorite of pulverized rock phosphate. The diminution of P_2O_5 availability registered by the analyses materially decreases the commercial value of the calcine-superphosphate mixtures. Such diminution may not be registered, however, in equal extent by crop response under field conditions.

The present and related findings should dispel the uncertainty that has prevailed as to the exact cause of reversion that ensues when acidic fertilizers are processed by the incorporation of basic materials.

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Solubility of Carbon Dioxide in Benzene at Elevated Pressure

SHEN-WU WAN AND BARNETT F. DODGE
Yale University, New Haven, Conn.

THE increasing use of elevated pressures in chemical industry has made it desirable to have more data on the effect of pressure on the liquid-vapor-phase equilibria in various systems. Such data are fundamental to all operations in which these two phases are brought into contact—for example, in distillation, condensation, absorption, and drying. The data are needed not only for direct application in the development of industrial processes, but also to aid in the formulation and testing of generalizations to replace the simple laws of ideal solutions and ideal gases which are no longer applicable even under moderate pressures. At present the data in this field are confined to a relatively few systems under rather limited conditions of pressure, temperature, and concentration.

The general plan for our investigation in this field covered various combinations of gases and liquids over the temperature range 0° to 300° C. and at pressures up to 1000 atmospheres. The present paper reports some results on the composition of the coexisting liquid and vapor phases of the system carbon dioxide–benzene at 30°, 40°, 50°, and 60° C. and a maximum pressure of 95 atmospheres with a few scattered tests at 10°, 15°, and 20° C. The main reason for the choice of this particular system was that carbon dioxide is a gas of great industrial importance, and it is of interest to compare its solubility in various organic liquids with that in water. Benzene was chosen as a typical, nonpolar organic liquid.

The only previously published investigation of this system was that of Sander (*3*) in 1912, who determined the liquid-phase composition only, at 20°, 35°, 60°, and 100° C. up to a maximum pressure of 116 atmospheres. J. L. Marsh started an investigation on this system at this laboratory in 1930. He developed an apparatus based on a static method and made some measurements at 25° and 50° C. which have not been published. Difficulties with the operation of his apparatus led to its abandonment and the design, by the present authors, of a new one based on a dynamic method. Although a static method appears to be simpler and fundamentally sounder, the dynamic method seemed to offer practical advantages which made it more suitable for our purpose.

Apparatus and Procedure

GENERAL OUTLINE OF METHOD. In choosing a method and developing an apparatus, the main desideratum was a relatively simple apparatus that would not involve special complication in construction and operation, and yet would yield results of a fair order of accuracy—about 1 per cent or better.

Carbon dioxide from a storage cylinder is passed continuously at substantially constant pressure through a series of vessels containing benzene maintained at constant temperature. The first vessel, or presaturator, is maintained at a temperature above or below the point at which equilibrium is to be established in order to permit an approach to equilibrium from both sides. The equilibrium vessel is preceded by a second presaturator maintained at the equilibrium temperature. After a sufficient time, the pressure and temperature are noted, and both phases in the equilibrium vessel are sampled for analysis.

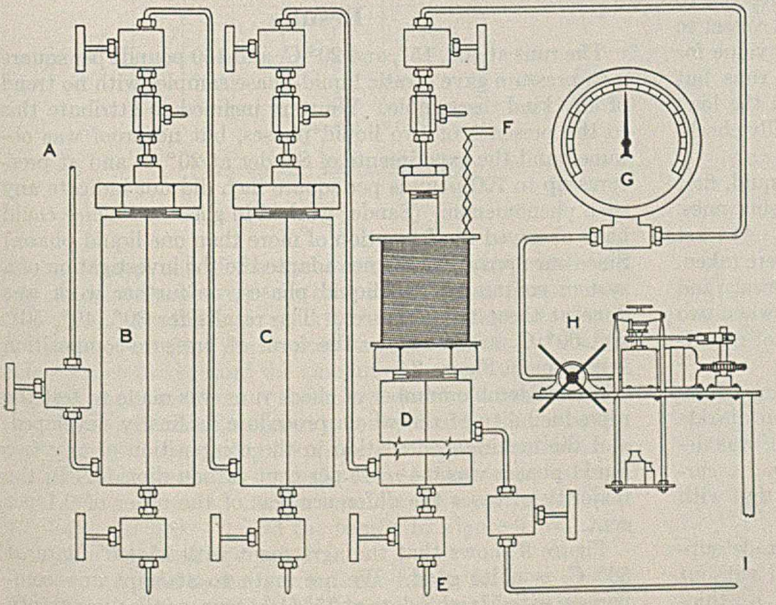

FIGURE 1. FLOW SHEET

APPARATUS. A flow sheet of the apparatus is shown in Figure 1. Carbon dioxide enters at *A*, flows through presaturators *B* and *C* into equilibrium vessel *D*, and is finally expanded into sampling line *I*. Liquid samples are withdrawn through line *E*. Bourdon gage *G* is for pressure control only, all final pressure measurements being made with the dead-weight piston gage, *H*. Contents of the equilibrium vessel are agitated by a magnetic stirrer operated by a solenoid, the connections to which are indicated at *F*. Details of the saturators and equilibrium vessel are shown in Figure 2. Being of substantially orthodox design, they require no special comment. The first presaturator is placed in one oil bath controlled to about 0.1° C., and the second presaturator and the equilibrium vessel are in a second oil bath, controlled to 0.01° C. Heating is obtained by an electric immersion heater. For operation below room temperature, the first bath is cooled by a standard household refrigerating unit.

The liquid-phase sampler is a small steel cylinder, approximately 3 cc. in volume, with valves at each end. The gas phase is expanded directly into the analysis train, consisting of two U-tubes and two glass absorption vessels. The U-tubes, packed with copper wool and immersed in solid carbon dioxide, serve to condense the benzene from the vapor. The absorbers contain sodium hydroxide solution for the removal of the carbon dioxide.

In a general way, the method and apparatus are somewhat similar to that employed by Saddington

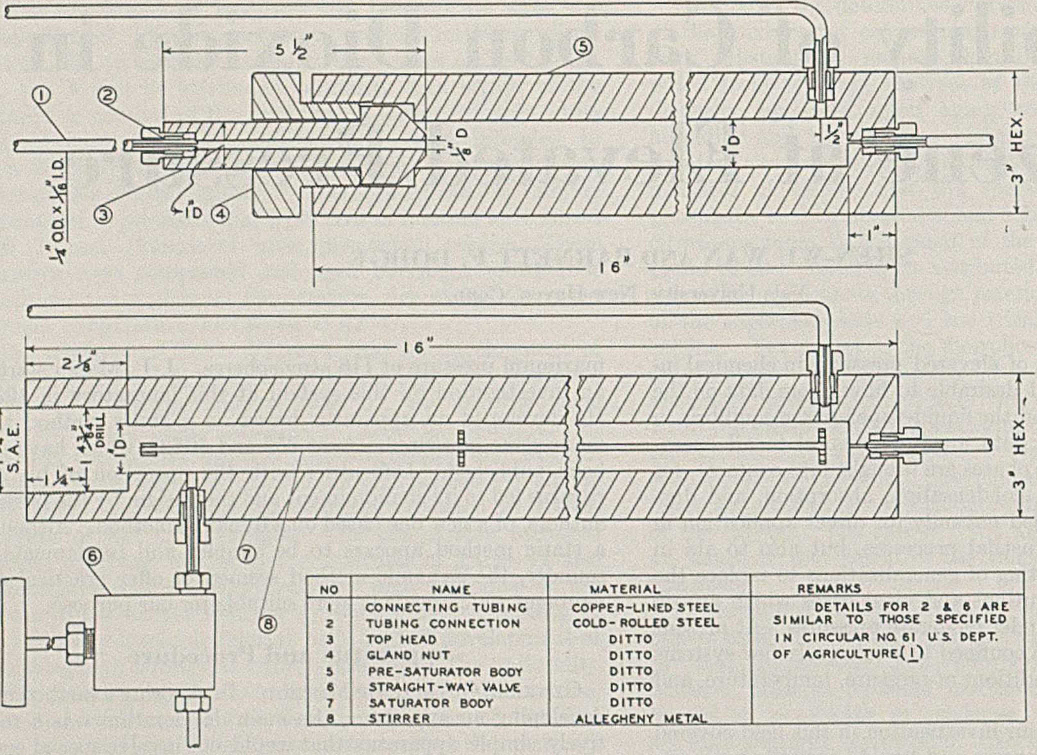

Figure 2. Details of Saturators and Equilibrium Vessel

NO	NAME	MATERIAL	REMARKS
1	CONNECTING TUBING	COPPER-LINED STEEL	DETAILS FOR 2 & 6 ARE SIMILAR TO THOSE SPECIFIED IN CIRCULAR NO. 61 U.S. DEPT. OF AGRICULTURE (1)
2	TUBING CONNECTION	COLD-ROLLED STEEL	
3	TOP HEAD	DITTO	
4	GLAND NUT	DITTO	
5	PRE-SATURATOR BODY	DITTO	
6	STRAIGHT-WAY VALVE	DITTO	
7	SATURATOR BODY	DITTO	
8	STIRRER	ALLEGHENY METAL	

and Krase (*2*) in their study of the system water-nitrogen at elevated pressures and temperatures, but with important differences in detail.

Procedure. With the particular dynamic method used, the liquid phase is continually exposed to more gas and is bound to come to equilibrium if sufficient time is allowed. The situation is different in the case of the gas phase because it makes a single pass through a given column of liquid and must become saturated with the less volatile component during this relatively short time of contact. It was believed that the best procedure was to over-saturate the gas relative to the equilibrium temperature by maintaining the first presaturator 10° higher than the desired equilibrium temperature, and to depend on the other saturator and the equilibrium vessel to reduce the concentration of benzene to the proper value for equilibrium. This scheme was followed in most runs but some at 30° C. were made with an approach from the low-temperature side. Both procedures gave substantially checking results.

A series of runs was made on a given filling of liquid, first at increasing pressure steps and then with decreasing ones. Pressures and flow rates were controlled manually. At least 2 hours were allowed to elapse before any samples were taken. Samples of both phases were taken at 1-hour intervals and immediately analyzed. A given run was completed when two consecutive liquid samples agreed within the limit of experimental error.

The amount of benzene in the sample was obtained from the increase in weight of the U-tubes. The carbon dioxide absorbed in the standard sodium hydroxide solution was determined by the usual procedure of precipitating the carbonate with barium chloride and titrating the solution with standard acid and phenolphthalein indicator.

The carbon dioxide was the usual commercial grade supplied as a liquid in cylinders and it was employed without further purification. The benzene was Merck's c. p., thiophene-free which was partially frozen, filtered, and then distilled over P_2O_5; only that portion was retained which boiled between 79.9° and 80.1° C. Before charging into the apparatus it was boiled to remove dissolved gases.

The working out of a satisfactory procedure for liquid sampling required considerable experimentation. Direct expansion from the equilibrium vessel to an analytical train gave inconsistent results. Possibly the gas evolved when the pressure was released failed to carry along all the liquid that belonged with it. This led to the development of a separate pressure sampler, which gave consistent results only after many trials had evolved a special technique. The main features of this technique were very slow sampling and flushing of the contents of the sampler.

Some trouble was at first encountered in vapor-phase sampling because of the presence of considerable liquid in the line, until it was realized that the solubility of carbon dioxide in benzene was so great at the high pressures that the volume of the liquid phase had expanded to several times the volume of the original benzene. When allowance was made for this increase in volume, no further trouble with gas-phase samples was encountered.

Results

The runs at 10°, 15°, and 20° C. and 150 pounds per square inch pressure gave erratic liquid-phase samples with no trend of any kind discernible. We were inclined to attribute this to the presence of two liquid phases, but no proof was obtained and the experiments of Sander at 20° C. and at pressures up to 700 pounds per square inch did not indicate any such phenomenon. (Sander worked in glass and hence could have observed the formation of more than one liquid phase.) Since our apparatus was not adapted to the investigation of a system containing two liquid phases, no further work was done at these temperatures. The results for 30°, 40°, 50°, and 60° C. are shown in the form of pressure-composition isotherms in Figure 3.

A considerable number of check runs was made to test the reproducibility of the whole procedure as finally developed, and the maximum deviation in the composition of any two liquid phases was 0.4 mole per cent carbon dioxide. In the majority of cases the difference was of the order of 0.1 per cent.

Figure 3 shows that the agreement with Marsh's data at 50° C. is quite good. We are loath to attempt any comparison with Marsh's data at 25° C. because of the uncertainty of extrapolating data in this region so close to the critical

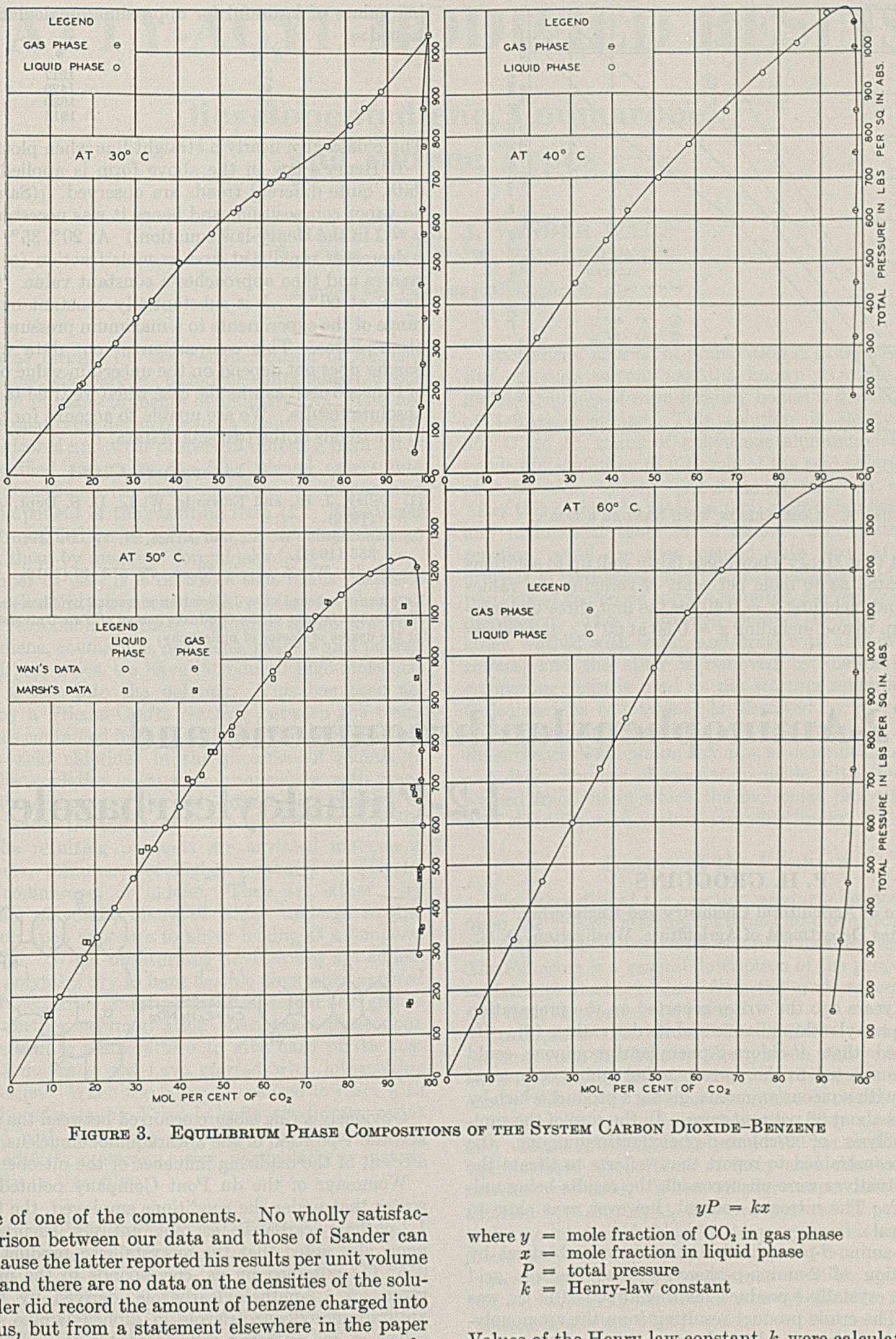

Figure 3. Equilibrium Phase Compositions of the System Carbon Dioxide–Benzene

temperature of one of the components. No wholly satisfactory comparison between our data and those of Sander can be made because the latter reported his results per unit volume of solution, and there are no data on the densities of the solutions. Sander did record the amount of benzene charged into his apparatus, but from a statement elsewhere in the paper one would infer that his figures on volume of solvent are only approximate. Accepting his value for benzene volume, we calculated his results to our basis and found poor agreement as shown in Figure 4. Sander's results are reported for 20°, 35°, 60°, and 100° C., and the results in Figure 4 were obtained by graphical interpolation.

It is of interest to see how well the results follow a simple solubility law such as Henry's law which may be expressed in the form,

$$yP = kx$$

where y = mole fraction of CO_2 in gas phase
x = mole fraction in liquid phase
P = total pressure
k = Henry-law constant

Values of the Henry-law constant, k, were calculated from the experimental data and are as follows:

Mole Fraction CO₂ in Liquid	Henry-Law Constant at: 30° C.	40° C.	50° C.	60° C.
0.10	1240	1420	1670	1860
0.20	1230	1430	1650	1918
0.30	1208	1440	1605	1940
0.40	1190	1395	1605	1935
0.50	1169	1360	1588	1910
0.60	1102	1303	1535	1840
0.70	1045	1255	1492	1742

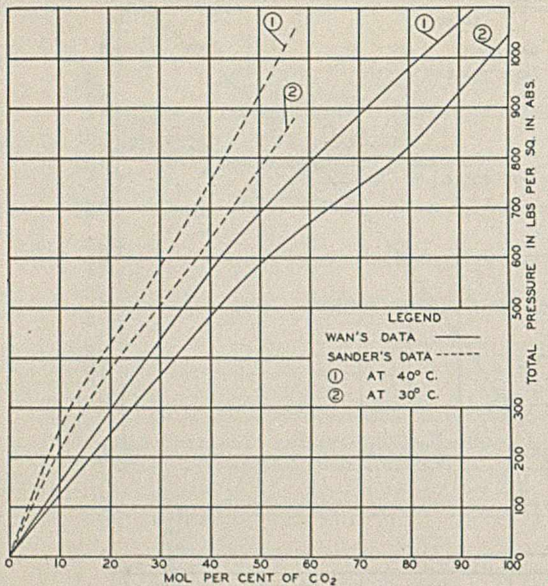

FIGURE 4. COMPARISON WITH SANDER'S DATA

It is evident that Henry's law holds fairly well up to solutions as concentrated as 40 mole per cent. Averaging the values of k up to and including $x = 0.40$ for the first three temperatures, and up to and including $x = 0.50$ at 60° C., the following values of k, useful for approximate calculations, are obtained:

t° C.	k
30	1217
40	1420
50	1630
60	1913

These data give nearly a straight line when plotted.

If Henry's law in the above form is applied to Sander's data, quite different trends are observed. (Sander reported no vapor compositions and hence it was necessary to assume $y = 1$ in the Henry-law equation.) At 20°, 35°, and 100° C., k decreases rapidly at first as mole fraction (or pressure) increases and then approaches a constant value. On the other hand, at 60° C., k is substantially constant over the whole range of the experiments to a maximum pressure of about 100 atmospheres. This comparison of our data with those of Sander does not depend on the uncertain value of the volume of benzene used as was the case when we tried to compare the absolute results. We are unable to account for the difference in the trends of the two sets of data.

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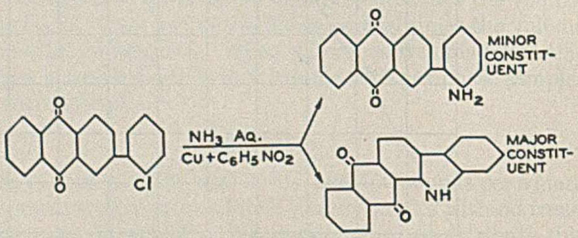
THIS paper is based on a dissertation presented by Shen-wu Wan in June, 1935, to the faculty of the Graduate School of Yale University in candidacy for the degree of doctor of philosophy.

2-Aminophenylanthraquinone and 1,2-Phthaloylcarbazole

P. H. GROGGINS
Bureau of Agricultural Chemistry and Engineering,
United States Department of Agriculture, Washington, D. C.

A FEW years ago the writer reported on the preparation of β-phenylanthraquinone and its derivatives (*2*). He showed that 4′-chloro-β-phenylanthraquinone could readily be converted to the corresponding amino compound by reacting with aqueous ammonia, giving a product which by titration was about 98 per cent pure. In the case of the similar ammonolysis of 2-chloro-β-phenylanthraquinone, the author was constrained to report that "efforts to titrate the 2-amino derivatives were unsuccessful, the results being uniformly low". The nitrogen content, however, was close to the theoretical.

When 2′-amino-β-phenylanthraquinone was obtained by the cyclization of 2-amino-*p*-phenyl-*o*-benzoylbenzoic acid (*3*), a brown crystalline product, melting at 200–201° C., was obtained. The crude product resulting from the ammonolysis of 2′-chloro-β-phenylanthraquinone with aqueous ammonia containing nitrobenzene and a copper catalyst also gave evidence of the presence of some amine, either by titration with sodium nitrite or by diazotizing and coupling with R salt. When this crude product was recrystallized from toluene and *o*-dichlorobenzene, long, silky, orange-colored needles (melting at 255° C.) were obtained. This crystalline product is not 2-amino-β-phenylanthraquinone, but 1,2-phthaloylcarbazole:



Obviously a ring closure occurred between the amino group and the 1 position of the anthraquinone nucleus, probably as a result of the oxidizing influence of the nitrobenzene.

Weinmayr of the du Pont Company pointed out to the writer that under the conditions employed, the formation of 1,2-phthaloylcarbazole is not entirely surprising. Weinmayr also noted that the recrystallized product (melting at 255° C.) obtained by us, corresponds to the melting point given for 1,2-phthaloylcarbazole, derived by heating 1-α-anthraquinonylbenzotriazole in diphenylamine (*1*). It dissolves in concentrated sulfuric acid with a deep blue color and shows an instantaneous color change when a drop of nitric acid is added to the sulfuric acid solution; this is a reaction characteristic of the carbazole structure.

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FATTY-ACYL-MODIFIED RESINS

Dicyclopentadiene, Coumarone, and Indene Types

A. W. RALSTON, R. J. VANDER WAL,
S. T. BAUER, AND E. W. SEGEBRECHT
Armour and Company, Chicago, Ill.

THE resins formed by the polymerization of dicyclopentadiene-, coumarone-, or indene-containing fractions are useful in many branches of industry (*1*). The use of phenol as a modifying agent results in resins with increased solubility in alcohol and with properties differing from those of the unmodified resins (*2*, *5*). The phenol enters into chemical combination with the coumarone or indene and becomes a component of the resulting resin (*4*). Staudinger (*6*) produced modified resins by hydrogenation, and Kessler (*3*) produced them by means of formaldehyde.

For a number of uses it is desirable that resins possess a high degree of flexibility, combined with resistance to chemical attack and a reasonable hardness. In order to prepare from dicyclopentadiene, coumarone, or indene, resins which possess these general properties, we have introduced high-molecular weight acyl groups into the polymer. This has been accomplished by a Friedel-Crafts reaction between the resin-forming bodies contained in the fractions and high-molecular-weight fatty acid chlorides in the presence of aluminum chloride. The acylation occurs simultaneously with some degree of polymerization of the resin-forming components of the distillate under the influence of the catalysts used in the reaction. The resulting products are acylated monomers, dimers, trimers, tetramers, or higher polymers of dicyclopentadiene, coumarone, or indene. They are either very viscous liquids or solids, many of which undergo further polymerization upon exposure to air or baking at a temperature of 100° C. When unsaturated acyl groups are added, the acylated polymers dry to hard flexible films when exposed to the air. When either unsaturated or saturated acyl groups are present, further polymerization often takes place upon heating at moderate temperatures to give hard plastic materials. In some cases we have started with low-melting coumarone resins. When the latter are caused to react with fatty acid chlorides under Friedel-Crafts conditions, resins are produced with properties differing from those characterizing unmodified coumarone resins, particularly as regards their flexibility in thin films.

Methods of Preparation

Two types of starting material were used: (*a*) the crude solvent naphthas containing as a major constituent coumarone, indene, or dicyclopentadiene, respectively, together with lesser quantities of the other two, and (*b*) a commercial coumarone resin produced by the polymerization of a coumarone-containing fraction. The resin contents of the fractions[1] employed in this work, based upon the yield of comparatively soft resin which could be obtained, were as follows: coumarone fraction, 39 per cent; indene fraction, 74; dicyclopentadiene fraction, 60. The coumarone resin used had a melting point of 94° C. (ball and ring).

The general method of preparation is as follows: A quantity of crude solvent naphtha known to contain approximately 0.1 mole of resin-forming bodies is dissolved in 25 cc. of tetrachloroethane. This solution is slowly added at 25° C. to 15 grams of anhydrous aluminum chloride suspended in a solution of 0.1 mole of the acid chloride in 75 cc. of tetrachloroethane. The time of addition is 2 hours. After this period the reaction temperature is raised to 50° C. and maintained there for 2 hours. The contents of the reaction vessel are then poured onto ice. After the hydrolysis is completed, the tetrachloroethane and unreactive portions of the crude solvent naphtha are removed by steam distillation. The hydrolyzed product is then dissolved in ether, washed with water, and dried with anhydrous sodium sulfate, and the ether is removed by distillation. When coumarone resin is used as the starting material, 0.1 mole (calculated as coumarone) is dissolved in 25 cc. of tetrachloroethane and caused to react with fatty acid chlorides in the presence of aluminum chloride, as described above.

A large number of runs were made with the above described fractions in which the molecular proportions of the acid chlorides were varied over wide limits.

Nature of the Products

The properties of the reaction products depend somewhat upon the type of starting materials employed and upon the molecular ratio of fatty acid chlorides used for the acylation. The following is a general description of the properties of the acylated products obtained from the crude solvent naphthas and from the coumarone resin:

COUMARONE FRACTION. Friedel-Crafts products were prepared from this fraction by acylation with various molecular proportions of stearoyl chloride, oleoyl chloride, and linolenoyl chloride by the method previously described. (These acid chlorides are prepared from the fatty acids of linseed oil.) In the following description "100 per cent" means that equimolecular proportions of fatty acid chlorides and coumarone were used. Where smaller proportions of the acid chloride were employed, they are reported as percentages of that amount of acid chloride necessary for this equimolecular mixture.

Stearoylation of the coumarone fraction by the use of 100, 67, 33, and 10 per cent of stearoyl chloride, respectively, resulted in a series of soft solids. A blank sample prepared by subjecting the coumarone fraction to similar conditions also gave a soft solid. These samples were then heated at 100° C. for 65 hours, which was selected as a convenient period. (The polymerization undoubtedly could be accomplished in a shorter time.) This process resulted in the formation of hard resins except when 67 and 100 per cent of equimolecular proportions of stearoyl chloride were used. The heat-treated stearoylated resins were decidedly less brittle than the heat-treated unmodified sample. The

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[1] Obtained from the Pennsylvania Industrial Chemical Corporation, Clairton, Penna.

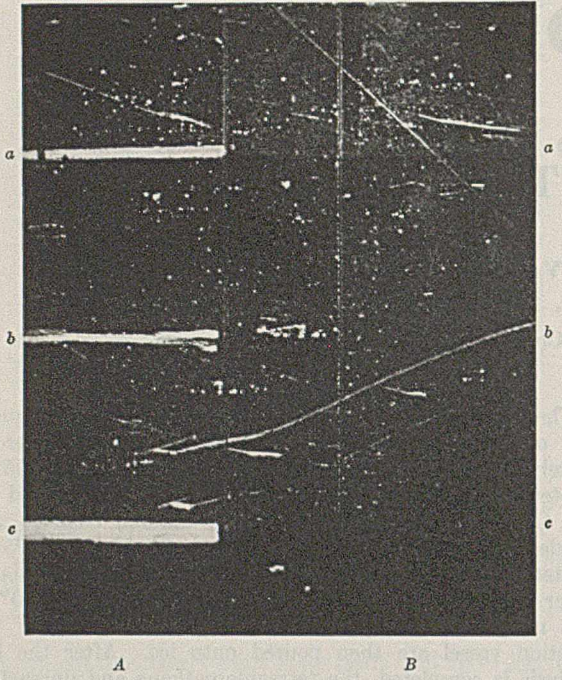


FIGURE 1. TIN PLATE COATED WITH BAKED MODIFIED, *B*, AND UNMODIFIED RESIN, *A* (× 3)

molecular weights of these coumarone–stearoyl chloride reaction products as determined by the cryoscopic method in benzene are shown in the following table:

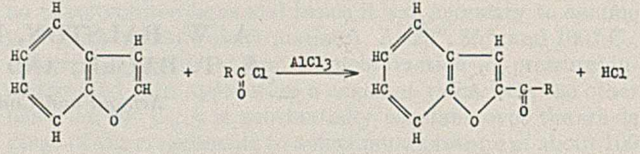
Compn., % Equimolecular Proportion of Stearoyl Chloride	Molecular Weight
0	306.5
10	317.8
33	351.4
67	357.4
100	416.6

The molecular weights of the acylated coumarone polymers obtained under these conditions tend to indicate that the products are essentially mixtures of dimers and trimers. Acylation with stearoyl chloride is accompanied by a decreased tendency towards polymerization of the coumarone. In the product prepared from equimolecular proportions of coumarone and stearoyl chloride, the molecular weight determination shows that only a small amount of polymerization takes place. When these products were heated for 24 hours at 100° C., all of them underwent further polymerization.

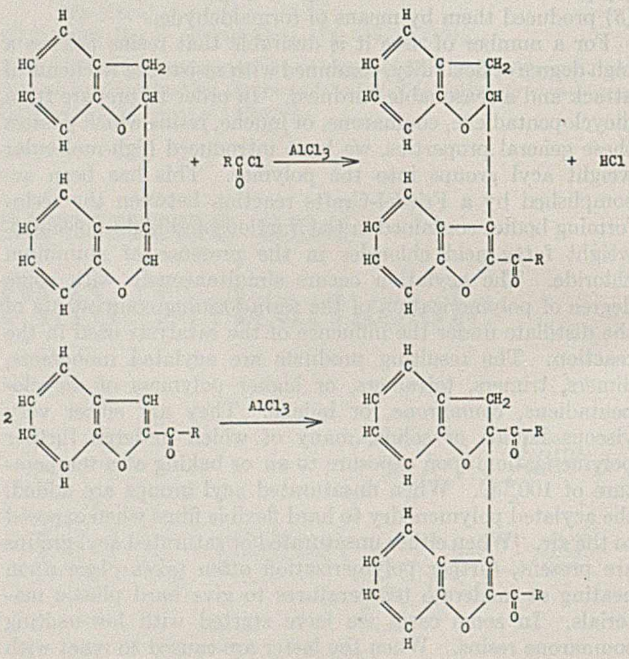
The coumarone fraction was acylated with oleoyl chloride using 10, 33, and 67 per cent of an equimolecular proportion of the oleoyl chloride. The products were all soft solids which further polymerized to hard resins when baked for 65 hours at 100° C. The molecular weight of the sample prepared from 67 per cent of the amount of oleoyl chloride necessary for an equimolecular mixture was 584.2. This molecular weight corresponds closely to that of an acylated dimer.

Acylation of the coumarone fraction with linolenoyl chloride resulted in products ranging from very viscous liquids to soft solids. All of the linolenoylated coumarones formed hard resins when heated at 100° C. for several hours. Some of these products also possessed the property of air drying, since samples exposed to atmospheric conditions formed films after varying periods of time. The samples prepared from 10 and from 100 per cent of the theoretical amount of linolenoyl chloride had molecular weights of 335.3 and 506.0, respectively. Upon baking at 100° C. for 40 hours, the molecular weight of the former increased to 564.2.

Determination of the free acid content of one of the 100 per cent acylated coumarones showed that by far the larger portion of the acid chloride had been used in the acylation. Under the mild conditions employed and in view of the molecular weights obtained, it seems unlikely that more than one acyl group is attached to each nucleus. Monomeric coumarone probably reacts as follows:



Several possible methods for the formation of acylated polymers exist. Acylated polymers may be formed either by acylation of unacylated polymers or by polymerization of an acylated molecule with one or more acylated or unacylated molecules. Reactions of the following type probably predominate:



These in turn can again polymerize with coumarone, monomeric acylated coumarone, and polymeric mono- or polyacylated coumarone to produce higher polymers. The acylated products probably consist of mixtures of substances of the above nature. These are further polymerized upon heating to give higher polymers.

INDENE FRACTION. The products from the acylation of this fraction with 10, 33, 67, and 100 per cent of the theoretical amount of stearoyl chloride for an equimolecular reaction were highly viscous liquids or soft solids. When heated at 100° C. for several hours, the 10 and 33 per cent stearoylated products polymerized further to hard resins. The others were not affected by this treatment. The product prepared from 67 per cent of the theoretical amount of stearoyl chloride had a molecular weight of 448.7 which indicates that it contains considerable amounts of the stearoylated dimer.

Acylation of the indene fraction with oleoyl chloride resulted in all cases in the formation of highly viscous oils which, when heated for several hours at 100° C., gave hard resins.

The reaction products of the indene fraction and linolenoyl chloride under the conditions described were viscous oils; all of them polymerized upon heating to give hard resins. Samples were prepared from 10, 33, 67, and 100 per cent of the theoretical amount of linolenoyl chloride. The last three dried upon exposure to atmospheric conditions. The 10 per cent product had a molecular weight of 234.7, which indicated it to be a partially linolenoylated dimer. This molecular weight increased to 596.3 upon heating for 40 hours at 100° C. The sample prepared from equimolecular proportions of indene and linolenoyl chloride (100 per cent) had a molecular weight of 1500. Upon heating, this product became insoluble in benzene so that a molecular weight could not be obtained by our method.

DICYCLOPENTADIENE FRACTION. The dicyclopentadiene fraction when condensed with stearoyl chloride produced solids in the case of the 10 and 33 per cent runs. These further polymerized upon heating to give hard solids. Samples prepared from higher proportions of stearoyl chloride were liquids which showed little tendency to polymerize further upon heating. Oleoyl chloride and dicyclopentadiene yielded products ranging from solids to viscous liquids as the percentage of oleoyl chloride was increased. All of these products changed to hard, flexible resins upon heating. The fraction was acylated with 33 and 67 per cent of the theoretical amount of linolenoyl chloride. The first product was a viscous liquid and the latter a hard resin. Both samples further polymerized in air and, when heated, formed hard resins.

TABLE I. ACYLATED PRODUCTS OF COUMARONE RESIN

Acid Chloride	Theoretically Equivalent Quantity (Acid Chloride), %	Product	
		Friedel-Crafts	Heat-Treated
Stearoyl chloride	0	Hard resin	Hard resin
	16	Resin	Hard resin
	33	Soft solid	Hard resin
	50	Viscous liquid	Hard resin
	67	Viscous liquid	Semisolid
	83	Viscous liquid	Semisolid
	100	Viscous liquid	Viscous liquid
Oleoyl chloride	10	Solid	Hard resin
	33	Solid	Hard resin
	67	Solid	Fairly hard resin
	100	Viscous liquid	Fairly hard resin
Linolenoyl chloride	10	Solid	Hard resin
	33	Solid	Hard resin
	67	Solid	Hard resin
	100	Viscous liquid	Hard resin

COUMARONE RESIN. The coumarone resin used had a melting point of 94° C. (ball and ring). It was acylated in the same manner as that used for the resin-containing fractions. The type of products obtained is shown in Table I.

The molecular weight of the product formed by the use of equimolecular proportions of stearoyl chloride and the coumarone resin was 971.6.

Properties and Uses

These high-molecular-weight acyl-modified resins are of particular interest because of their high flexibility. Their hardness is in many cases similar to that of the unmodified resins. Those prepared by the use of unsaturated fatty acid chlorides are of interest in the varnish industry because of their ability to form hard films upon exposure to air. These modified resins can be baked upon metallic surfaces to give thin, protective films which are flexible and adhere tenaciously to the metal. Figure 1 shows a photomicrograph of a piece of tin plate coated with an unmodified coumarone resin, *A*, and with a resin prepared by acylation of the same fraction with oleoyl chloride, *B*. After baking and cooling, the plate was bent at points *a*, *b*, and *c*. In the case of the unmodified resin the resin film ruptured at the bends, whereas the modified resin film followed the bends without breaking. Because of the water resistance and flexibility of films of these modified resins, they would be useful for waterproofing leather, textiles, cellulose products, and similar materials where flexibility of the protective film is required.

The solubilities of the Friedel-Crafts reaction products both before and after heat polymerization were determined in ethyl alcohol, ether, carbon tetrachloride, benzene, kerosene, turpentine, acetone, and isopropyl alcohol. The reaction products before heat polymerization are, in general, soluble in ether, carbon tetrachloride, benzene, turpentine, kerosene, and acetone, mostly insoluble in cold ethyl or isopropyl alcohols, and only slightly soluble in hot ethyl or isopropyl alcohols. After heat polymerization for 40 hours at 100° C. the solubility varies, depending upon the specific sample, but in general is considerably less than for the unheated product. Baked samples are insoluble in hot ethyl and hot isopropyl alcohols.

The stabilities of the polymerized resins in water, 18 per cent hydrochloric acid solution, and 20 per cent sodium hydroxide solution were determined. This was accomplished by sealing samples of several of the resins together with the various solutions in test tubes and examining them after definite time intervals for signs of decomposition. Observations were made after 5-day contact with the solvents at room temperature; then the tubes were heated for 24 hours at 90° C. and again examined. The following resins were used in this test: 10 and 33 per cent linolenoylated dicyclopentadiene fraction, 10 and 67 per cent linolenoylated indene fraction, 10 and 67 per cent linolenoylated coumarone fraction, and 10 and 67 per cent stearoylated indene fraction. None of the resins showed significant change in any of the solvents at room temperature. At the higher temperature water and the 18 per cent hydrochloric acid solution were without effect. Treatment with the hot 20 per cent sodium hydroxide solution resulted in a slight decomposition in the case of the 10 per cent acylated resins. The resins possessing a higher degree of acylation were not affected.

An attempt is now under way to improve the color of these resins. The effect of catalysts upon the polymerization and drying of those prepared from the higher unsaturated chlorides will be studied. More quantitative data as regards their comparative flexibilities will also be obtained.

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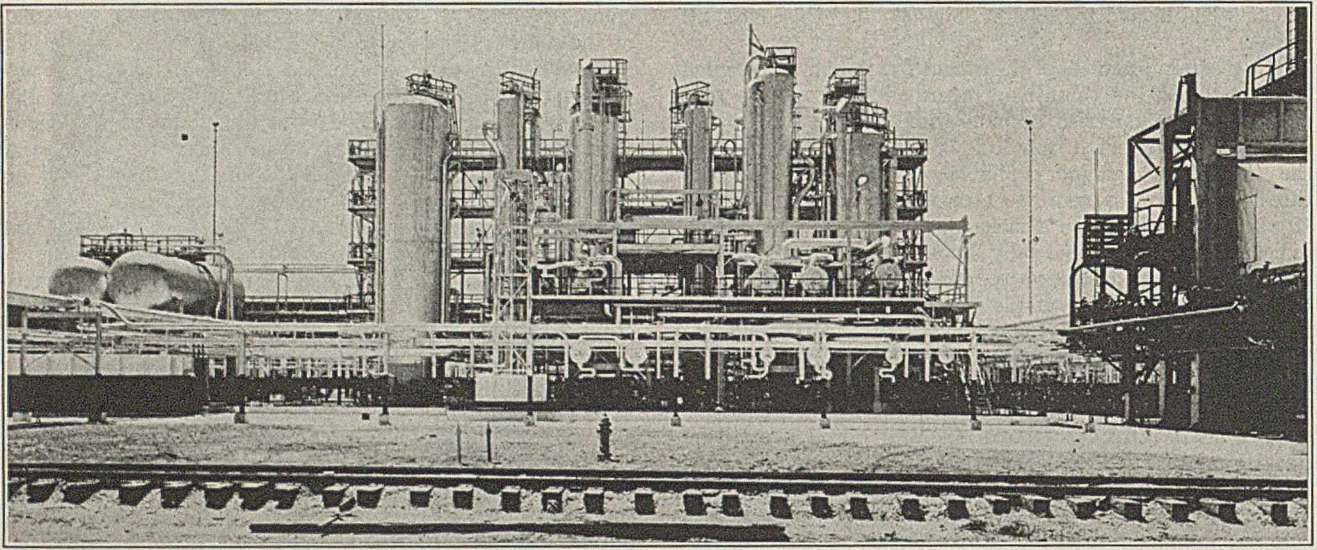


Phenol Solvent-Extraction Plant for the Production of Lubricating Oils of High Viscosity Index

Viscosity Index of Lubricating Oils

E. W. DEAN, A. D. BAUER, and J. H. BERGLUND
Standard Oil Development Company,
New York, N. Y.

THE viscosity index scale for petroleum oils, as proposed by Dean and Davis (*3*) and subsequently revised by Davis, Lapeyrouse, and Dean (*2*), was based on Saybolt Universal viscosities. The constants used in making the calculations did not extend below 40 seconds Saybolt Universal viscosity at 210° F.

A need exists for basic constants in kinematic as well as Saybolt units and for the extension of the scale to lower values. The present paper reports the preparation and availability of a table of kinematic constants covering the range of 2.0–75.0 centistokes (equivalent to 32.8–349 Saybolt seconds) at 210° F. The new table, except for a slight revision in the range corresponding to 40–50 seconds Saybolt at 210° F., is equivalent to that previously published (*2*) according to the relation between kinematic and Saybolt viscosities that has been approved by the American Society for Testing Materials (*1, 4*). The constants covering the range from 2.0–4.2 centistokes at 210° F. are new material (Table I).

Definition of Viscosity Index

The viscosity index of an oil is a figure calculated from known viscosities at 100° and 210° F. according to one of the following equations:

$$\text{V. I.} = \frac{L - U}{L - H} \times 100 \qquad (1)$$

$$\text{V. I.} = \frac{L - U}{D} \times 100 \qquad (2)$$

where U is the viscosity of the oil at 100° F., and L and H are basic constants representing viscosities at 100° F. of hypothetical oils having the same viscosity at 210° F. as the oil in question. Hypothetical oil L has a viscosity index of zero and hypothetical oil H has a viscosity index of 100. D is equal to $L - H$, and Equation 2 is simply a conveniently usable equivalent of Equation 1.

Derivation of Basic Constants

The general nature of the basic constants for the viscosity index scale is indicated by Figure 1. The L and H curves were originally located by Dean and Davis (*3*) through actual tests of blends of finished lubricating oils derived, respectively, from the extreme types of commercial oils with which the senior author was familiar at the time. However, the use of these data as a basis for the scale was arbitrary, and we did not attempt to characterize the numerical values in terms of specific types of crude oil. The two important considerations were, first, to establish a scale which within reasonable limits would give the same viscosity indices for oils of similar origin but different viscosity and, secondly, to define the scale precisely.

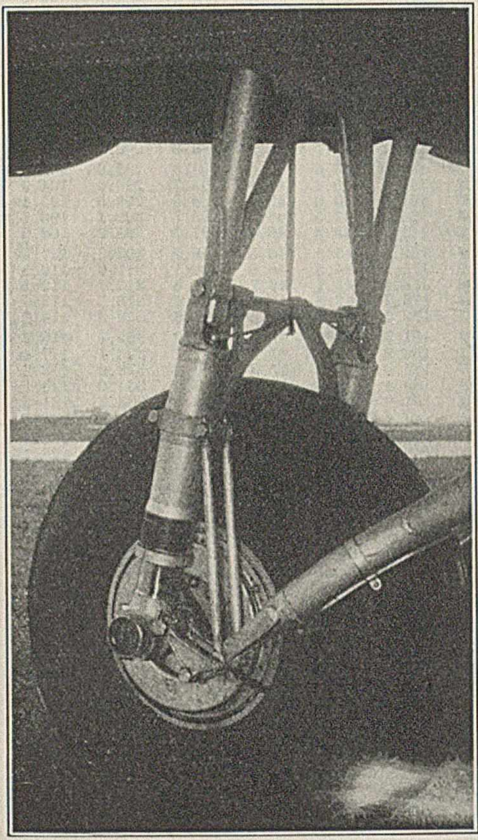
The two curves were defined in terms of the published equations (*3*):

$$\text{For 100 V. I.: } Y = 0.0408X^2 + 12.568X - 475.4 \qquad (3)$$

$$\text{For 0 V. I.: } Y = 0.2160X^2 + 12.070X - 721.2 \qquad (4)$$

where Y = Saybolt viscosity at 100° F.
X = Saybolt viscosity at 210° F.

The lowest experimentally determined points for the H and L curves were, respectively, 49.0 and 42.0 seconds Saybolt at 210° F. The extrapolation of the equations below about 50 seconds proved to be unjustifiable although extensions in the other direction have yielded consistent results for viscosities much higher than those of the heaviest oils actually used by Dean and Davis in deriving their equations. The inconsist-



RETRACTABLE OLEO LANDING GEAR OF A MODERN AIRPLANE

This device must operate under widely varying temperature conditions and requires an oil of high viscosity index.

TABLE I. VISCOSITY INDICES OF OILS FROM CRUDES (NOT REFINED BY SOLVENT EXTRACTION)

No.	Source[a]	Description	Centistokes 210° F.	Centistokes 100° F.	Viscosity Index	Kinematic Viscosity Index (Fenske)
		From Pennsylvania Crudes				
1	1	Commercial 300 oil	1.592	4.686	99.2	...
2	2	300 oil distillate	1.636	4.904	97.3	...
3	1	Commercial 300 oil	1.640	4.89	100.0	46.2
4	1	Lab. dist., dewaxed, narrow cut	1.846	5.834	101.1	...
5	1	Lab. dist., dewaxed, narrow cut	1.858	5.981	95.3	...
6	1	Lab. dist., dewaxed, broad cut	1.859	5.917	99.8	...
7	3	Lab. dist., not dewaxed	1.86	5.80	107.6	...
8	1	Lab. dist., dewaxed, broad cut	1.949	6.411	97.0	...
9	1	Lab. dist., dewaxed, broad cut	2.080	7.068	98.3	...
10	1	Lab. dist., dewaxed, narrow cut	2.121	7.420	91.5	...
11	1	Lab. dist., dewaxed, broad cut	2.215	7.904	93.4	...
12	3	Lab. dist., not dewaxed	2.39	8.50	110.9	...
13	1	Lab. dist., dewaxed, broad cut	2.398	8.930	95.0	...
14	1	Lab. dist., dewaxed, narrow cut	2.425	9.158	92.3	...
15	2	Commercial spindle oil	2.544	10.03	87.2	120.5
16	1	Lab. dist., dewaxed, broad cut	2.600	10.19	94.3	...
17	1	Lab. dist., dewaxed, broad cut	2.842	11.75	95.3	...
18	1	Lab. dist., dewaxed, narrow cut	2.881	12.16	91.0	...
19	1–4	Lab. blend, commercial oils	2.926	12.02	104.0	138.9
20	3	Lab. dist., not dewaxed	3.13	13.30	107.4	139.1
21	1	Lab. dist., dewaxed, broad cut	3.216	14.27	98.8	...
22	1	Pressed dist., filtered	3.225	14.29	99.9	...
23	1	Pressed dist., unfiltered	3.267	14.74	96.6	...
24	2	Commercial spindle oil	3.325	15.57	87.8	115.7
25	2–4	Lab. blend, commercial oils	3.356	15.47	95.5	123.0
26	1	Lab. dist., dewaxed, broad cut	3.552	16.83	99.3	...
27	1	Lab. dist., dewaxed, narrow cut	3.376	15.78	92.1	...
28	1	Lab. dist., dewaxed, broad cut	3.948	20.03	101.1	...
29	1	Lab. dist., dewaxed, narrow cut	4.060	21.38	95.1	...
30	1–4	Lab. blend, commercial oils	4.186	21.59	108.1	122.1
31	3	Lab. dist., not dewaxed	4.33	22.60	111.1	123.2
32	1	Lab. dist., dewaxed, broad cut	4.417	24.13	101.6	...
33	2–4	Lab. blend, commercial oils	4.470	24.58	102.1	112.2
34	4	Commercial motor oil	6.121	41.22	103.0	103.9
		From Texas and Louisiana Crudes				
35	1	Commercial spindle oil	2.613	10.343	91.9	126.6
36	5	Commercial spindle oil	2.951	12.51	95.0	128.1
37	1	Commercial spindle oil	3.745	18.927	89.9	111.8
38	5	Commercial spindle oil	3.933	20.21	96.0	114.7
39	5	Transformer oil	3.970	20.84	91.1	109.9

[a] Sources of oils: 1, refinery No. 1; 2, refinery No. 2; 3, Pennsylvania crude fractionated by Dean and Lane, U. S. Bureau of Mines; 4, commercial motor oil, believed not to be refined by solvent extraction; 5, refinery No. 3.

TABLE II. BASIC CONSTANTS IN THE RANGE 40–50 SECONDS SAYBOLT UNIVERSAL AT 210° F.

Viscosity at 210° F.		Former Constants			New Constants					
		H	*L*	*D*	*H*		*L*		*D*	
Saybolt	Kinematic	Saybolt	Saybolt	Saybolt	Saybolt	Kinematic	Saybolt	Kinematic	Saybolt	Kinematic
40	4.20	107	138	31	107.1	22.280	137.9	29.360	30.8	7.080
41	4.51	120	161	41	119.3	25.136	157.9	33.883	38.6	8.747
42	4.82	133	185	52	132.7	28.184	181.7	39.208	49.0	11.024
43	5.13	147	210	63	146.9	31.408	208.4	45.088	61.5	13.680
44	5.43	161	237	76	161.5	34.588	236.5	51.030	75.0	16.442
45	5.75	176	265	89	176.3	37.980	265.1	57.430	88.8	19.450
46	6.06	191	293	102	191.3	41.266	293.9	63.630	102.6	22.364
47	6.37	206	322	116	206.2	44.559	322.4	69.830	116.2	25.271
48	6.68	222	353	131	222.0	47.992	352.3	76.302	130.3	28.310
49	6.99	239	386	147	239.0	51.697	386.2	83.672	147.2	31.975
50	7.29	257	422	165	255.1	55.161	422.0	91.398	166.9	36.237

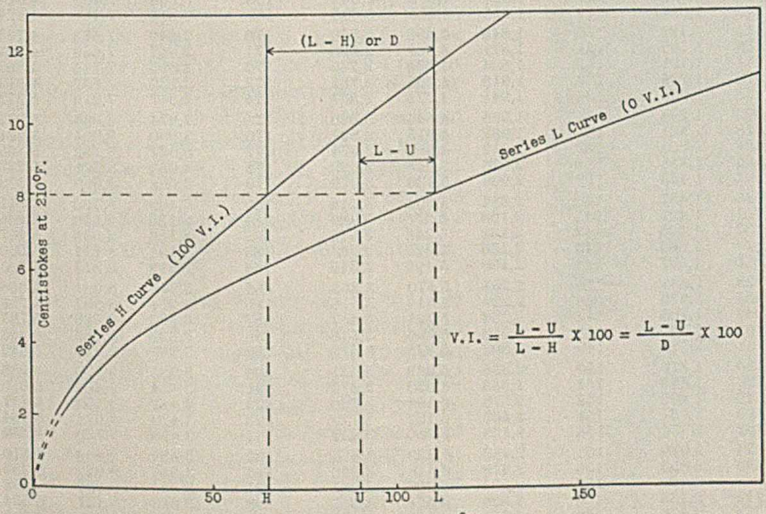


FIGURE 1. GENERAL BASIS OF THE VISCOSITY INDEX SCALE

encies in the range of 40 to 50 seconds at 210° F. were rectified by Davis, Lapeyrouse, and Dean (*2*) who published some empirical constants that have been proved by subsequent experience to be reasonably satisfactory. Some further slight changes in this specific range have, however, been found necessary in the tables described in this report, as the empirical figures do not fall on a smooth curve.

The low viscosity extension just adopted and covering the range below 4.20 centistokes (40 seconds Saybolt) at 210° F. is defined in terms of the following equations:

For 100 V. I.: $Y = 1.4825X + 0.91375X^2$ (5)

For 0 V. I.: $Y = 1.655X + 1.2625X^2$ (6)

where Y = kinematic viscosity at 100° F.

X = kinematic viscosity at 210° F.

Saybolt Universal viscosities are not desirable for this low range, and the extension is in centistokes only.

TABLE III. SPECIMEN PAGES FROM TABLES OF CONSTANTS FOR CALCULATING VISCOSITY INDEX FROM KNOWN KINEMATIC OR SAYBOLT VISCOSITY (AT 210° F.)

Kinematic Viscosity								Saybolt Viscosity							
Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*
4.00	20.550	26.820	6.270	4.50	25.040	33.720	8.680	40.0	107.1	137.9	30.8	45.0	176.3	265.1	88.8
4.01	20.635	26.944	6.309	4.51	25.136	33.883	8.747	40.1	108.3	139.7	31.4	45.1	177.9	268.1	90.2
4.02	20.720	27.068	6.348	4.52	25.232	34.046	8.814	40.2	109.4	141.5	32.1	45.2	179.3	270.9	91.6
4.03	20.805	27.192	6.387	4.53	25.328	34.209	8.881	40.3	110.6	143.4	32.8	45.3	180.7	273.6	92.9
4.04	20.890	27.316	6.426	4.54	25.424	34.372	8.948	40.4	111.9	145.4	33.5	45.4	182.4	276.6	94.2
4.05	20.975	27.440	6.465	4.55	25.520	34.535	9.015	40.5	113.1	147.3	34.2	45.5	183.8	279.4	95.6
4.06	21.060	27.564	6.504	4.56	25.616	34.698	9.082	40.6	114.3	149.3	35.0	45.6	185.2	282.2	97.0
4.07	21.145	27.688	6.543	4.57	25.712	34.861	9.149	40.7	115.6	151.4	35.8	45.7	186.8	285.2	98.4
4.08	21.230	27.812	6.582	4.58	25.808	35.024	9.216	40.8	116.8	153.5	36.7	45.8	188.2	288.0	99.8
4.09	21.315	27.936	6.621	4.59	25.904	35.187	9.283	40.9	118.0	155.7	37.7	45.9	189.8	290.9	101.1
4.10	21.400	28.060	6.660	4.60	26.000	35.350	9.350	41.0	119.3	157.9	38.6	46.0	191.3	293.9	102.6
4.11	21.488	28.190	6.702	4.61	26.098	35.521	9.423	41.1	120.7	160.1	39.4	46.1	192.7	296.6	104.9
4.12	21.576	28.320	6.744	4.62	26.196	35.692	9.496	41.2	122.0	162.6	40.6	46.2	194.2	299.6	105.4
4.13	21.664	28.450	6.786	4.63	26.294	35.863	9.569	41.3	123.3	164.8	41.5	46.3	195.7	302.4	106.7
4.14	21.752	28.580	6.828	4.64	26.392	36.034	9.642	41.4	124.6	167.1	42.5	46.4	197.2	305.2	108.0
4.15	21.840	28.710	6.870	4.65	26.490	36.205	9.715	41.5	125.9	169.4	43.5	46.5	198.7	308.2	109.5
4.16	21.928	28.840	6.912	4.66	26.588	36.376	9.788	41.6	127.2	171.7	44.5	46.6	200.1	311.0	110.9
4.17	22.016	28.970	6.954	4.67	26.686	36.547	9.861	41.7	128.6	174.3	45.7	46.7	201.6	313.7	112.1
4.18	22.104	29.100	6.996	4.68	26.784	36.718	9.934	41.8	129.9	176.7	46.8	46.8	203.1	316.5	113.4
4.19	22.192	29.230	7.038	4.69	26.882	36.889	10.007	41.9	131.3	179.1	47.8	46.9	204.6	319.3	114.7
4.20	22.280	29.360	7.080	4.70	26.980	37.060	10.080	42.0	132.7	181.7	49.0	47.0	206.2	322.4	116.2
4.21	22.370	29.497	7.127	4.71	27.080	37.238	10.158	42.1	134.1	184.2	50.1	47.1	207.7	325.1	117.4
4.22	22.460	29.634	7.174	4.72	27.180	37.416	10.236	42.2	135.5	186.8	51.3	47.2	209.2	328.0	118.8
4.23	22.550	29.771	7.221	4.73	27.280	37.594	10.314	42.3	136.8	189.4	52.6	47.3	210.9	331.0	120.1
4.24	22.640	29.908	7.268	4.74	27.380	37.772	10.392	42.4	138.2	191.9	53.7	47.4	212.3	333.8	121.5
4.25	22.730	30.045	7.315	4.75	27.480	37.950	10.470	42.5	139.7	194.7	55.0	47.5	214.0	337.0	123.0
4.26	22.820	30.182	7.362	4.76	27.580	38.128	10.548	42.6	141.1	197.3	56.2	47.6	215.6	339.9	124.3
4.27	22.910	30.319	7.409	4.77	27.680	38.306	10.626	42.7	142.5	199.9	57.4	47.7	217.1	342.8	125.7
4.28	23.000	30.456	7.456	4.78	27.780	38.484	10.704	42.8	144.0	202.8	58.8	47.8	218.9	346.1	127.2
4.29	23.090	30.593	7.503	4.79	27.880	38.662	10.782	42.9	145.4	205.5	60.1	47.9	220.5	349.2	128.7
4.30	23.180	30.730	7.550	4.80	27.980	38.840	10.860	43.0	146.9	208.4	61.5	48.0	222.0	352.3	130.3
4.31	23.272	30.875	7.603	4.81	28.082	39.024	10.942	43.1	148.4	211.3	62.9	48.1	223.7	355.6	131.9
4.32	23.364	31.020	7.656	4.82	28.184	39.208	11.024	43.2	149.8	213.9	64.1	48.2	225.4	358.8	133.4
4.33	23.456	31.165	7.709	4.83	28.286	39.392	11.106	43.3	151.3	216.8	65.5	48.3	227.0	362.0	135.0
4.34	23.548	31.310	7.762	4.84	28.388	39.576	11.188	43.4	152.7	219.7	67.0	48.4	228.6	365.2	136.6
4.35	23.640	31.455	7.815	4.85	28.490	39.760	11.270	43.5	154.2	222.4	68.2	48.5	230.3	368.5	138.2
4.36	23.732	31.600	7.868	4.86	28.592	39.944	11.352	43.6	155.7	225.2	69.5	48.6	232.1	372.2	140.1
4.37	23.824	31.745	7.921	4.87	28.694	40.128	11.434	43.7	157.1	227.9	70.8	48.7	233.7	375.5	141.8
4.38	23.916	31.890	7.974	4.88	28.796	40.312	11.516	43.8	158.6	230.9	72.3	48.8	235.5	379.1	143.6
4.39	24.008	32.035	8.027	4.89	28.898	40.496	11.598	43.9	160.0	233.7	73.7	48.9	237.4	382.8	145.4
4.40	24.100	32.180	8.080	4.90	29.000	40.680	11.680	44.0	161.5	236.5	75.0	49.0	239.0	386.2	147.2
4.41	24.194	32.334	8.140	4.91	29.104	40.869	11.765	44.1	163.1	239.6	76.5	49.1	240.7	389.8	149.1
4.42	24.288	32.488	8.200	4.92	29.208	41.058	11.850	44.2	164.6	242.3	77.7	49.2	242.4	393.6	151.2
4.43	24.382	32.642	8.260	4.93	29.312	41.247	11.935	44.3	166.0	245.2	79.2	49.3	244.0	397.1	153.1
4.44	24.476	32.796	8.320	4.94	29.416	41.436	12.020	44.4	167.5	248.1	80.6	49.4	245.7	400.6	154.9
4.45	24.570	32.950	8.380	4.95	29.520	41.625	12.105	44.5	168.9	250.9	82.0	49.5	247.2	404.2	157.0
4.46	24.664	33.104	8.440	4.96	29.624	41.814	12.190	44.6	170.5	253.9	83.4	49.6	248.9	407.8	158.9
4.47	24.758	33.258	8.500	4.97	29.728	42.003	12.275	44.7	172.0	256.7	84.7	49.7	250.5	411.4	160.9
4.48	24.852	33.412	8.560	4.98	29.832	42.192	12.360	44.8	173.5	259.3	85.8	49.8	252.0	415.0	163.0
4.49	24.946	33.566	8.620	4.99	29.936	42.381	12.445	44.9	175.0	261.5	86.5	49.9	253.6	418.6	165.0

TABLE IV. BASIC VALUES FOR CALCULATING VISCOSITY INDEX FROM SAYBOLT VISCOSITIES (AT 210° F.)

Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*
40	107.1	137.9	30.8	80	791	1,627	836	120	1,620	3,838	2,218	160	2,580	6,740	4,160
41	119.3	157.9	38.6	81	810	1,674	864	121	1,643	3,902	2,259	161	2,606	6,821	4,215
42	132.7	181.7	49.0	82	829	1,721	892	122	1,665	3,966	2,301	162	2,631	6,903	4,272
43	146.9	208.4	61.5	83	849	1,769	920	123	1,688	4,031	2,343	163	2,657	6,985	4,328
44	161.5	236.5	75.0	84	868	1,817	949	124	1,710	4,097	2,387	164	2,683	7,068	4,385
45	176.3	265.1	88.8	85	888	1,865	977	125	1,733	4,163	2,430	165	2,709	7,151	4,442
46	191.3	293.9	102.6	86	907	1,914	1,007	126	1,756	4,229	2,473	166	2,735	7,234	4,499
47	206.2	322.4	116.2	87	927	1,964	1,037	127	1,779	4,296	2,517	167	2,761	7,318	4,557
48	222.0	352.3	130.3	88	947	2,014	1,067	128	1,802	4,363	2,561	168	2,788	7,403	4,615
49	239.0	386.2	147.2	89	966	2,064	1,098	129	1,825	4,430	2,605	169	2,814	7,488	4,674
50	255.1	422.0	166.9	90	986	2,115	1,129	130	1,848	4,498	2,650	170	2,840	7,573	4,733
51	271.7	456.1	184.4	91	1,006	2,166	1,160	131	1,871	4,567	2,696	171	2,867	7,659	4,792
52	288.4	490.5	202.1	92	1,026	2,217	1,191	132	1,894	4,636	2,742	172	2,893	7,745	4,852
53	305.3	525.2	219.9	93	1,046	2,270	1,224	133	1,918	4,705	2,787	173	2,920	7,832	4,912
54	322.2	560.5	238.3	94	1,066	2,322	1,256	134	1,941	4,775	2,834	174	2,947	7,919	4,972
55	339.2	596.0	256.8	95	1,087	2,375	1,288	135	1,965	4,845	2,880	175	2,974	8,006	5,032
56	356.4	632.3	275.9	96	1,107	2,428	1,321	136	1,988	4,915	2,927	176	3,000	8,094	5,094
57	373.5	668.6	295.1	97	1,128	2,481	1,353	137	2,012	4,986	2,974	177	3,027	8,182	5,155
58	390.8	705.5	314.7	98	1,148	2,536	1,388	138	2,036	5,058	3,022	178	3,054	8,271	5,217
59	408.2	742.8	334.6	99	1,168	2,591	1,423	139	2,060	5,130	3,070	179	3,082	8,360	5,278
60	425.6	780.6	355.0	100	1,189	2,646	1,457	140	2,084	5,202	3,118	180	3,109	8,450	5,341
61	443.1	818.9	375.8	101	1,210	2,701	1,491	141	2,108	5,275	3,167	181	3,136	8,540	5,404
62	460.6	857.4	396.8	102	1,231	2,757	1,526	142	2,132	5,348	3,216	182	3,163	8,630	5,467
63	478.4	896.5	418.1	103	1,252	2,814	1,562	143	2,156	5,422	3,266	183	3,191	8,721	5,530
64	496.1	936.2	440.1	104	1,273	2,870	1,597	144	2,180	5,496	3,316	184	3,218	8,813	5,595
65	514.0	976.1	462.1	105	1,294	2,928	1,634	145	2,205	5,570	3,365	185	3,246	8,904	5,658
66	531.8	1,016.3	484.5	106	1,315	2,985	1,670	146	2,229	5,645	3,416	186	3,274	8,997	5,723
67	549.8	1,057.1	507.3	107	1,337	3,043	1,706	147	2,254	5,721	3,467	187	3,302	9,089	5,787
68	567.8	1,098.3	530.5	108	1,358	3,102	1,744	148	2,278	5,796	3,518	188	3,329	9,182	5,853
69	586.1	1,140.1	554.0	109	1,379	3,161	1,782	149	2,303	5,873	3,570	189	3,357	9,276	5,919
70	604	1,182	578	110	1,401	3,220	1,819	150	2,328	5,949	3,621	190	3,385	9,370	5,985
71	623	1,225	602	111	1,422	3,280	1,858	151	2,353	6,026	3,673	191	3,414	9,464	6,050
72	641	1,268	627	112	1,444	3,340	1,896	152	2,378	6,104	3,726	192	3,442	9,559	6,117
73	660	1,311	651	113	1,466	3,400	1,934	153	2,403	6,182	3,779	193	3,470	9,654	6,184
74	678	1,355	677	114	1,488	3,462	1,974	154	2,428	6,260	3,832	194	3,498	9,750	6,252
75	697	1,399	702	115	1,510	3,523	2,013	155	2,453	6,339	3,886	195	3,527	9,846	6,319
76	716	1,444	728	116	1,532	3,585	2,053	156	2,478	6,418	3,940	196	3,555	9,942	6,387
77	734	1,489	755	117	1,554	3,648	2,094	157	2,503	6,498	3,995	197	3,584	10,039	6,455
78	753	1,534	781	118	1,576	3,711	2,135	158	2,529	6,578	4,049	198	3,613	10,137	6,524
79	772	1,580	808	119	1,598	3,774	2,176	159	2,554	6,659	4,105	199	3,641	10,235	6,594
												200	3,670	10,333	6,663

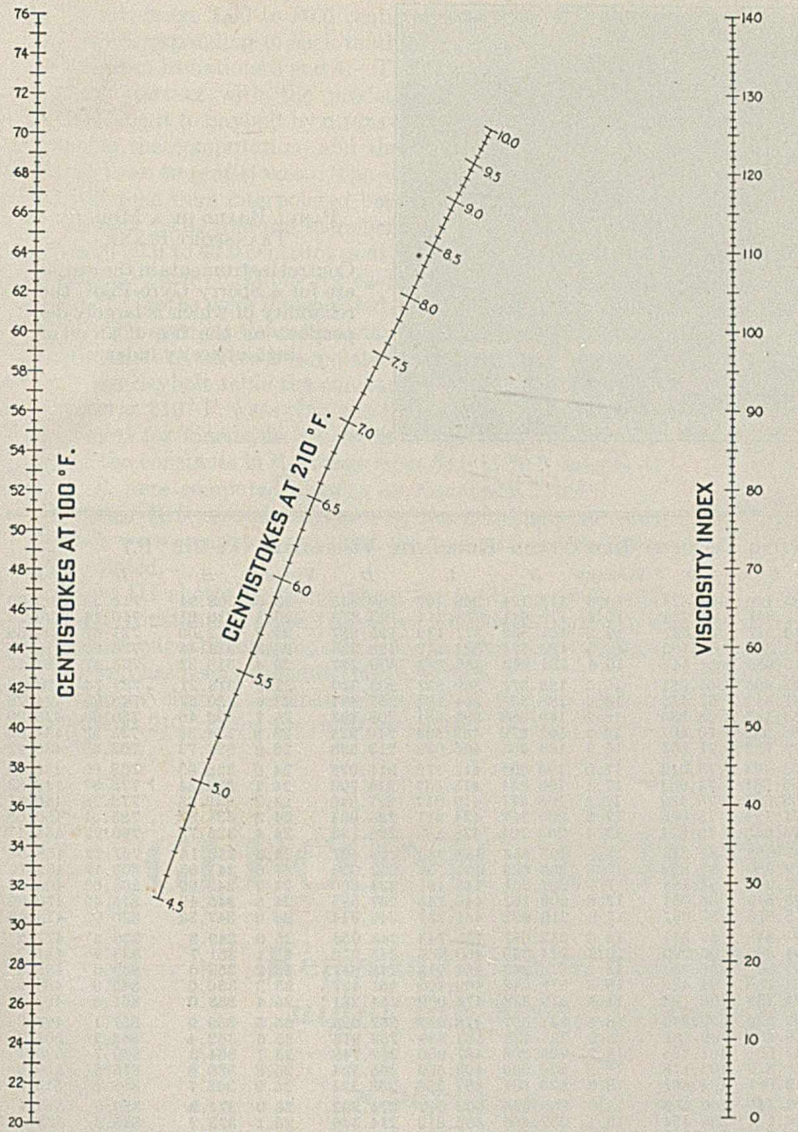


Figure 2. Nomographic Chart for Estimation of Viscosity Index

Although Equations 5 and 6 extend down to zero viscosity, they cannot be used in the range where the oils they represent have vapor pressures that are too high to permit accurate viscosity determinations at 210° F. The lower limit of the table that has been prepared is 2.0 centistokes at 210° F., which, according to the A. S. T. M. viscosity conversion table, is equivalent to 32.8 seconds Saybolt. With this extension, the viscosity index scale now covers all ordinary lubricating oils.

We selected these constants for the low viscosity range after plotting available data for low-viscosity commercial oils produced by operating subsidiaries of the Standard Oil Company of New Jersey. Products refined by solvent extraction processes were excluded. The extension is admittedly arbitrary, as were the constants for the higher range, but it has been demonstrated that the use of the new values permits viscosity indices to be obtained for "light" oils which correspond closely to those of more viscous products refined by the same processes from the same stocks.

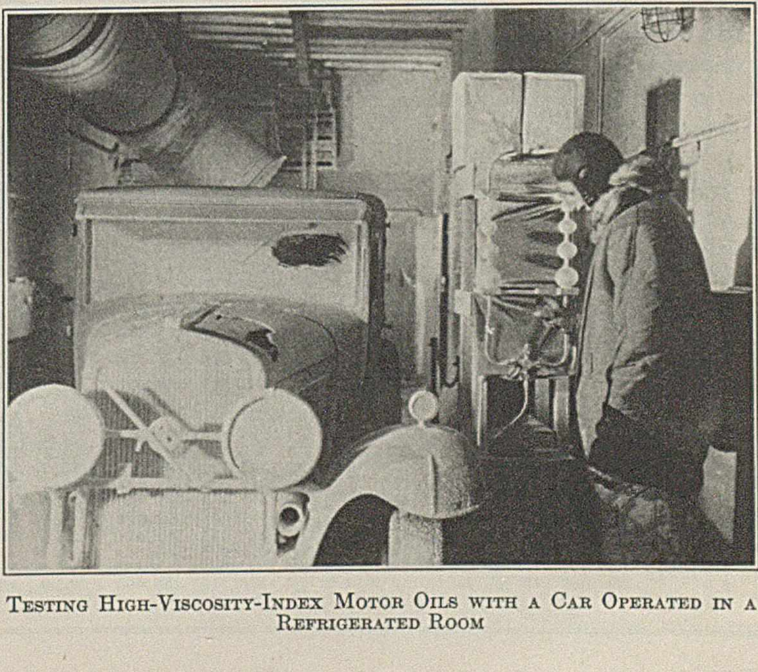
The constants in the range 40 to 50 seconds Saybolt (4.20 to 7.29 centistokes) at 210° F. are shown in Table II in comparison with those which they supersede (*2*). In the majority of cases the differences are not more than 1 second Saybolt. No change was made in the constants for the range above 50 seconds Saybolt (7.29 centistokes) at 210° F. except that some of the tabulated values show fractional seconds instead of being rounded off to even seconds, Saybolt.

Computation of Tables

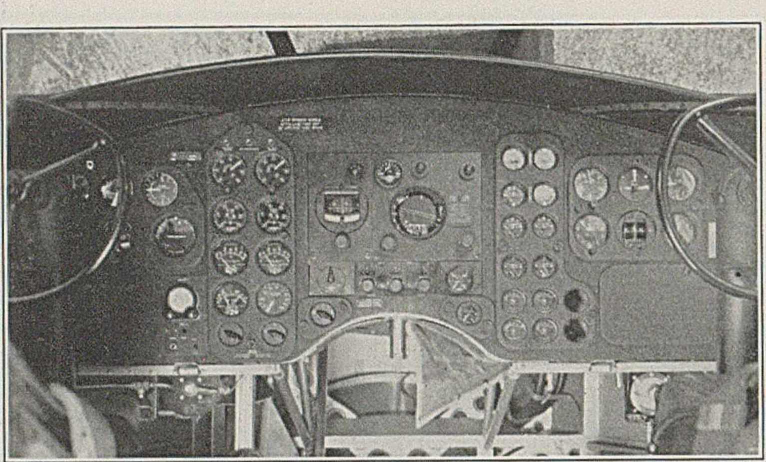
The older published table shows values of *L*, *H*, and *D* for each even second Saybolt at 210° F. The relatively large magnitude of the increments made it necessary to interpolate when high accuracy was desired, or even moderate accuracy in the lower ranges of viscosity. The new tables were computed with the following increments:

Range of Viscosity	Increments in Viscosity
2.00 to 29.99 centistokes	0.01 centistoke
30.0 to 39.9	0.1
40.0 to 75.0	0.5
40.0 to 159.9 seconds Saybolt	0.1 second Saybolt
160.0 to 350.0	1.0

Each individual set of constants in the range 2.00 to 3.99 centistokes at 210° F. was calculated from Equations 5 and 6. Throughout the range 4.00 to 7.29 centistokes the *H* and *L* values were obtained by a special method of calculation which was equivalent to graphic interpolation on a greatly magnified scale. In this range of viscosity the constants are not defined by equations.



Testing High-Viscosity-Index Motor Oils with a Car Operated in a Refrigerated Room



Panel Board of a Modern Transport Plane

Control instruments in the center are for a Sperry Gyro-Pilot, the reliability of which is largely dependent on the use of an oil of high viscosity index.

Table V. Basic Values for Calculating Viscosity Index from Kinematic Viscosities (at 210° F.)

Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*	Viscosity	*H*	*L*	*D*
2.0	6.620	8.360	1.740	9.0	76.352	135.176	58.824	16.0	178.174	369.107	190.933	23.0	308.34	711.24	402.90
2.1	7.143	9.043	1.900	9.1	77.617	137.841	60.224	16.1	179.841	373.214	193.373	23.1	310.21	716.44	406.23
2.2	7.684	9.752	2.068	9.2	78.880	140.517	61.637	16.2	181.552	377.439	195.887	23.2	312.09	721.67	409.58
2.3	8.243	10.485	2.242	9.3	80.184	143.284	63.100	16.3	183.224	381.577	198.353	23.3	314.44	728.22	413.78
2.4	8.821	11.244	2.423	9.4	81.448	145.989	64.541	16.4	184.942	385.729	200.787	23.4	316.32	733.47	417.15
2.5	9.417	12.028	2.611	9.5	82.714	148.695	65.981	16.5	186.577	389.897	203.320	23.5	318.21	738.74	420.53
2.6	10.031	12.838	2.807	9.6	83.986	151.411	67.425	16.6	188.300	394.184	205.884	23.6	320.57	745.35	424.78
2.7	10.664	13.672	3.008	9.7	85.262	154.147	68.885	16.7	189.983	398.381	208.398	23.7	322.46	750.66	428.20
2.8	11.315	14.532	3.217	9.8	86.575	156.982	70.407	16.8	191.670	402.594	210.924	23.8	324.36	755.98	431.62
2.9	11.984	15.417	3.433	9.9	87.856	159.722	71.866	16.9	193.401	406.929	213.528	23.9	326.73	762.65	435.92
3.0	12.671	16.328	3.657	10.0	89.178	162.494	73.316	17.0	195.094	411.172	216.078	24.0	328.63	768.00	439.37
3.1	13.377	17.263	3.886	10.1	90.458	165.361	74.903	17.1	196.831	415.537	218.706	24.1	330.54	773.37	442.83
3.2	14.101	18.224	4.123	10.2	91.814	168.303	76.489	17.2	198.571	419.917	221.346	24.2	332.45	778.76	446.31
3.3	14.843	19.210	4.367	10.3	93.128	171.194	78.066	17.3	200.357	424.421	224.064	24.3	334.83	785.51	450.68
3.4	15.603	20.222	4.619	10.4	94.461	174.075	79.614	17.4	202.104	428.832	226.728	24.4	336.75	790.92	454.17
3.5	16.382	21.258	4.876	10.5	95.825	177.068	81.243	17.5	203.853	433.260	229.407	24.5	339.14	797.72	458.58
3.6	17.179	22.320	5.141	10.6	97.152	179.980	82.828	17.6	205.605	437.704	232.099	24.6	341.05	803.17	462.12
3.7	17.994	23.407	5.413	10.7	98.492	182.907	84.415	17.7	207.361	442.161	234.800	24.7	342.99	808.63	465.64
3.8	18.828	24.520	5.692	10.8	99.818	185.849	86.031	17.8	209.162	446.745	237.583	24.8	345.40	815.49	470.09
3.9	19.680	25.657	5.977	10.9	101.206	188.873	87.667	17.9	210.923	451.237	240.314	24.9	347.33	820.99	473.66
4.0	20.550	26.820	6.270	11.0	102.537	191.848	89.311	18.0	212.687	455.743	243.056	25.0	349.3	826.5	477.2
4.1	21.400	28.060	6.660	11.1	103.909	194.899	90.990	18.1	214.350	460.266	245.916	25.1	351.7	833.4	481.7
4.2	22.280	29.360	7.080	11.2	105.305	197.966	92.661	18.2	216.268	464.915	248.647	25.2	353.6	839.0	485.4
4.3	23.180	30.730	7.550	11.3	106.721	201.150	94.429	18.3	218.042	469.469	251.427	25.3	356.0	845.9	489.9
4.4	24.100	32.180	8.080	11.4	108.100	204.238	96.138	18.4	219.818	474.039	254.221	25.4	358.0	851.5	493.5
4.5	25.040	33.720	8.680	11.5	109.493	207.339	97.846	18.5	221.597	478.625	257.028	25.5	359.9	857.1	497.2
4.6	26.000	35.350	9.350	11.6	110.887	210.468	99.581	18.6	223.423	483.339	259.916	25.6	362.4	864.1	501.7
4.7	26.980	37.060	10.080	11.7	112.273	213.601	101.328	18.7	225.208	487.956	262.748	25.7	364.3	869.7	505.4
4.8	27.980	38.840	10.860	11.8	113.711	216.829	103.118	18.8	226.996	492.590	265.594	25.8	366.8	876.8	510.0
4.9	29.000	40.680	11.680	11.9	115.114	219.981	104.867	18.9	228.831	497.352	268.521	25.9	368.7	882.5	513.8
5.0	30.040	42.570	12.530	12.0	116.507	223.145	106.638	19.0	230.625	502.017	271.392	26.0	371.2	889.6	518.4
5.1	31.090	44.500	13.410	12.1	117.948	226.412	108.464	19.1	232.466	506.812	274.346	26.1	373.2	895.3	522.1
5.2	32.150	46.460	14.310	12.2	119.438	229.784	110.346	19.2	234.354	511.739	277.385	26.2	375.1	901.0	525.9
5.3	33.210	48.440	15.230	12.3	120.883	233.078	112.195	19.3	236.201	516.568	280.367	26.3	377.6	908.1	530.5
5.4	34.270	50.430	16.160	12.4	122.330	236.392	114.062	19.4	238.052	521.413	283.361	26.4	379.6	913.9	534.3
5.5	35.330	52.430	17.100	12.5	123.781	239.713	115.932	19.5	239.906	526.274	286.368	26.5	382.1	921.1	539.0
5.6	36.390	54.430	18.040	12.6	125.274	243.136	117.862	19.6	241.806	531.247	289.441	26.6	384.0	926.9	542.9
5.7	37.450	56.430	18.980	12.7	126.730	246.482	119.752	19.7	243.666	536.164	292.498	26.7	386.5	934.1	547.6
5.8	38.510	58.430	19.920	12.8	128.189	249.842	121.653	19.8	245.529	541.075	295.546	26.8	388.5	939.9	551.4
5.9	39.570	60.430	20.860	12.9	129.689	253.305	123.616	19.9	247.440	546.120	298.680	26.9	391.0	947.2	556.2
6.0	40.630	62.430	21.800	13.0	131.153	256.690	125.537	20.0	249.31	551.07	301.76	27.0	393.0	953.1	560.1
6.1	41.690	64.430	22.740	13.1	132.658	260.180	127.522	20.1	251.18	555.96	304.78	27.1	395.0	958.9	563.9
6.2	42.750	66.430	23.680	13.2	134.166	263.684	129.518	20.2	253.10	561.12	308.02	27.2	397.5	966.3	568.8
6.3	43.810	68.430	24.620	13.3	135.716	267.293	131.577	20.3	254.98	566.12	311.14	27.3	399.5	972.2	572.7
6.4	44.880	70.430	25.550	13.4	137.230	270.824	133.594	20.4	256.86	571.13	314.27	27.4	402.0	979.6	577.6
6.5	45.970	72.460	26.490	13.5	138.745	274.369	135.624	20.5	258.79	576.28	317.49	27.5	404.0	985.5	581.5
6.6	47.080	74.550	27.470	13.6	140.270	277.964	137.694	20.6	260.59	581.08	320.49	27.6	406.0	991.4	585.4
6.7	48.220	76.740	28.520	13.7	141.784	281.498	139.714	20.7	262.39	585.90	323.51	27.7	408.5	998.9	590.4
6.8	49.390	79.040	29.650	13.8	143.348	285.177	141.829	20.8	264.64	591.94	327.30	27.8	410.6	1,004.9	594.3
6.9	50.590	81.440	30.850	13.9	144.874	288.776	143.902	20.9	266.45	596.80	330.35	27.9	413.1	1,012.4	599.3
7.0	51.820	83.920	32.100	14.0	146.402	292.388	145.986	21.0	268.26	601.66	333.40	28.0	415.1	1,018.4	603.3
7.1	52.980	86.460	33.480	14.1	147.933	296.014	148.081	21.1	270.08	606.55	336.47	28.1	417.7	1,025.9	608.2
7.2	54.150	89.040	34.890	14.2	149.507	299.749	150.242	21.2	272.35	612.67	340.32	28.2	419.7	1,032.0	612.3
7.3	55.273	91.660	36.387	14.3	151.043	303.402	152.359	21.3	274.17	617.59	343.42	28.3	422.2	1,039.5	617.3
7.4	56.473	94.095	37.622	14.4	152.582	307.069	154.487	21.4	275.99	622.52	346.53	28.4	424.3	1,045.6	621.3
7.5	57.699	96.528	38.859	14.5	154.124	310.749	156.625	21.5	278.27	628.70	350.43	28.5	426.3	1,051.7	625.4
7.6	58.873	98.958	40.085	14.6	155.708	314.540	158.832	21.6	280.10	633.67	353.57	28.6	428.9	1,059.4	630.5
7.7	60.063	101.398	41.335	14.7	157.255	318.247	160.992	21.7	281.93	638.65	356.72	28.7	430.9	1,065.5	634.6
7.8	61.305	103.925	42.620	14.8	158.804	321.968	163.164	21.8	284.22	644.89	360.67	28.8	433.5	1,073.2	639.7
7.9	62.513	106.388	43.875	14.9	160.396	325.801	165.405	21.9	286.06	649.91	363.85	28.9	435.5	1,079.3	643.8
8.0	63.723	108.859	45.136	15.0	161.950	329.549	167.599	22.0	287.90	654.94	367.04	29.0	438.1	1,087.0	648.9
8.1	64.969	111.419	46.450	15.1	163.548	333.410	169.862	22.1	290.21	661.24	371.03	29.1	440.2	1,093.2	653.0
8.2	66.251	114.067	47.816	15.2	165.190	337.385	172.195	22.2	292.05	666.30	374.25	29.2	442.8	1,101.0	658.2
8.3	67.501	116.650	49.149	15.3	166.793	341.275	174.482	22.3	293.90	671.38	377.48	29.3	444.8	1,107.2	662.4
8.4	68.753	119.306	50.553	15.4	168.399	345.179	176.780	22.4	296.22	677.75	381.53	29.4	446.9	1,113.5	666.6
8.5	70.041	121.926	51.885	15.5	170.007	348.881	178.874	22.5	298.08	682.86	384.78	29.5	449.5	1,121.3	671.8
8.6	71.296	124.528	53.232	15.6	171.660	353.131	181.471	22.6	299.96	687.98	388.02	29.6	451.6	1,127.6	676.0
8.7	72.542	127.153	54.611	15.7	173.274	357.078	183.804	22.7	302.28	694.41	392.13	29.7	454.2	1,135.5	681.3
8.8	73.793	129.786	55.993	15.8	174.891	361.039	186.148	22.8	304.13	699.57	395.44	29.8	456.2	1,141.8	685.6
8.9	75.089	132.515	57.426	15.9	176.552	365.117	188.565	22.9	306.00	704.74	398.74	29.9	458.3	1,148.1	689.8
												30.0	460.9	1,156.0	695.1

In the range 7.30 to 30.0 centistokes at 210° F. the constants corresponding to each tenth of a centistoke were computed from Equations 3 and 4. The actual calculation necessitated starting with the predetermined kinematic value, translating it to Saybolt by means of the A. S. T. M. table, performing the computation, and then translating the Saybolt result back to centistokes. The constants for hundredths of a centistoke were interpolated between the computed values for tenths, using uniform increments in these narrow ranges.

From 30.0 to 40.0 centistokes at 210° F. the constants were computed from equations for each fifth of a centistoke and those for tenths were interpolated. From 40.0 to 75.0 centistokes the even centistoke constants were computed and the half-centistoke values interpolated.

In the Saybolt table the constants in the range 40 to 50.0 seconds at 210° F. were obtained by the same special method employed for kinematic constants of equivalent magnitude. All of the constants in the range from 50.0 to 70.0 seconds at 210° F. were computed directly by Equations 2 and 3. In the range 70.0 seconds and above, the constants for even seconds were computed and those for tenths of a second were interpolated.

Table III shows specimen pages for both kinematic and Saybolt constants. (The full series of tables, numbering forty-four pages of the same size, is too lengthy for the present paper and has been printed in pamphlet form, *5*.)

Table IV shows constants corresponding to even seconds Saybolt at 210° F. for the range 40 to 200. Table V covers the range 2.0 to 30.0 centistokes at 210° F. with increments of one-tenth centistoke. The use of these tables, with interpolation when necessary, gives results approximately equal to those obtainable by use of the more complete tables (*5*).

Nomographic Charts

Viscosity indices can be estimated conveniently by the use of nomographic charts of the type shown as Figure 2. A series of these charts has been prepared and printed.

(Single copies of the pamphlet or charts will be supplied without charge. Larger supplies may be purchased at approximately the cost of printing. Requests or orders should be addressed to Standard Inspection Laboratory, Standard Oil Development Company, 26 Broadway, New York.)

Acknowledgment

Acknowledgment is made of the assistance rendered by G. H. B. Davis of the Esso Laboratories, Standard Oil Development Company, and F. H. Garner of the Esso European Laboratory, Anglo American Oil Company, Ltd.

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GLUCONIC ACID PRODUCTION

Repeated Use of Submerged *Aspergillus niger* for Semicontinuous Production

N. PORGES, T. F. CLARK, AND E. A. GASTROCK

Agricultural By-Products Laboratory, Ames, Iowa[1]

Calcium gluconate has been produced semicontinuously through the utilization of the floating mycelial growth from previous fermentations. Thirteen successive fermentations have shown no decrease in activity. A saving of time has resulted by the elimination of the lag period, the elimination of other than the initial pregerminated inoculum for a series of fermentations, and the maintenance of high rates of oxidation of glucose to gluconic acid. This process should be of industrial interest.

THE production of gluconic acid from glucose by the cultivation of *Aspergillus niger* under agitation, aeration, and pressure in rotary aluminum fermenters on both laboratory and semiplant scale has been reported (*1*, *3*, *5*). Yields up to 95 per cent of theoretical were obtained from fermentation media containing 15 grams of glucose per 100 cc. in a fermentation period of 24 hours. All fermentations were conducted as single-batch processes and were seeded with the fungus which had been previously cultivated for 24 hours in a germination solution (*3*).

Since these fermentations exhibited prolonged lag periods, followed by a fairly rapid conversion of glucose to gluconic acid, it was considered probable that the process might be hastened by re-use of the developed active fungal growth. This hastening could result from a decrease or elimination of the lag period, accompanied by a greater over-all rate of oxidation, and the avoidance of the preparation of fresh inoculum for each subsequent fermentation. The practicability of such a method was indicated in a preliminary experiment (*1*), and the present paper is concerned with further investigations of this process for rapid fermentations.

Two methods for the re-use of the mycelia were investigated: (*a*) transference of an aliquot of the actively fermenting solution with its proportionate amount of fungal growth to a second drum containing freshly prepared medium, and (*b*) retention, with a portion of the solution, of the greater part of the mycelia following a period of flotation at the com-

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[1] Established by the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture, in cooperation with the Iowa State College.

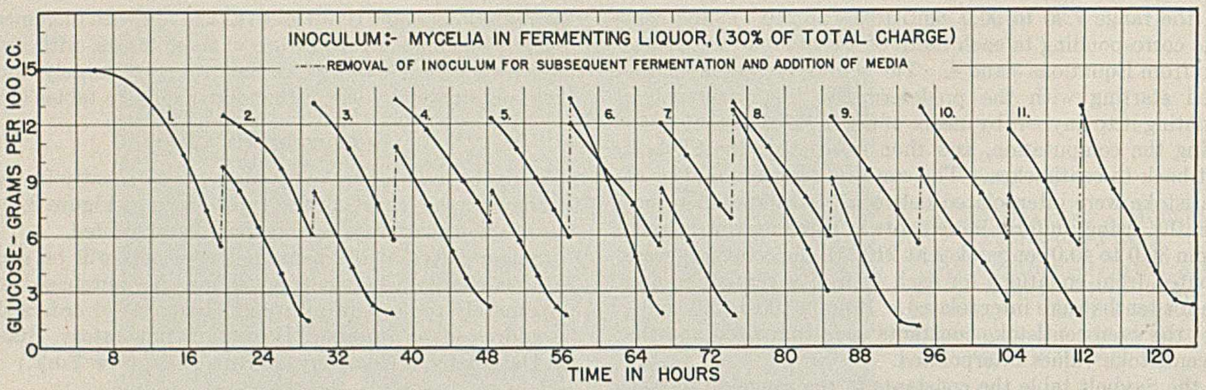

Figure 1. Continuous Conversion, in Two Fermenters, of Glucose to Gluconic Acid by *A. niger*

For inoculum, a portion of the fermenting liquor was transferred during high activity; this was replaced by fresh solution.

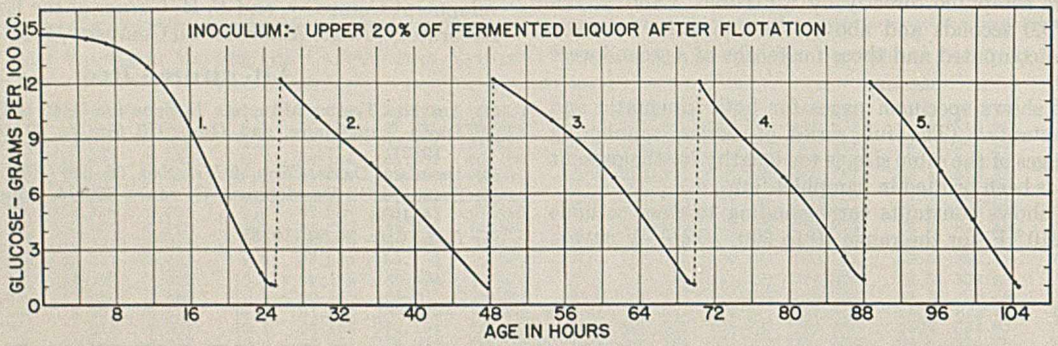

Figure 2. Semicontinuous Conversion of Glucose by *A. niger* to Yield 15 Grams Gluconic Acid per 100 Cc.

Inoculum, a portion of the final fermented liquor containing floating mycelia; transfer time, 35 minutes.

pletion of the fermentation. A third method, the noncontaminated retention by filtration of the mycelial growth for subsequent fermentations, is being studied.

General Technique

These investigations were conducted in laboratory-size rotary aluminum drums (*1*, *2*) and in a semiplant-size fermenter (*1*, *4*). Operating conditions during the fermentations were as follows:

Air pressure	30 lb./sq. in. gage (155 cm. Hg)
Air flow	375 cc./liter/min.
Speed of rotation	9.5 r. p. m.
Temperature	30° C.

As fermenting agent, the fungus *Aspergillus niger*, strain 67, was used throughout these studies. The germinated inoculum added at the start of a series of fermentations amounted to one thirty-second of the volume of the initial charge in the fermenter. To arrive at the amounts of fungus present in the fermentation solutions, 300-cc. portions were treated with 15 to 25 cc. of concentrated hydrochloric acid and filtered; the residue was washed, dried at a maximum temperature of 80° C., and weighed. The limitations of this method are realized, but it gives an indication of the trend of the fungal growth. Other analytical procedures and the media were described previously (*1*, *3*). The course of a fermentation was followed by analyzing samples withdrawn at intervals. Identification ratios (*1*) were determined for each fermentation and showed the presence of calcium gluconate only.

Laboratory-Scale Fermentations

Two-Fermenter Processes. Fermentations involving the repeated use of the mycelia at an active stage were conducted in two small rotary drums. The greatest activity in fermentation solutions containing 15 grams of glucose and 2.65 grams of calcium carbonate per 100 cc. occurred, as indicated by the rate of glucose utilization, shortly after the pH started to decrease (*1*). When sufficient gluconic acid was formed to react with all of the calcium carbonate, clarification of the solution resulted. At this point an aliquot equal to 30 per cent of the next charge was transferred, under agitation, to a second drum to serve as inoculum for the subsequent fermentation. Results of a series of fermentations showed that the mycelia retained activity throughout successive transfers and also that the quantity of gluconic acid recovered was low because of the large volume of fermenting solution removed for inoculum.

A second series of fermentations was conducted in a similar manner, except that sterile solutions containing glucose equivalent to that originally present in the aliquots were used to replace the volumes withdrawn as inocula. The results are presented in Figure 1. The broken lines represent the periods during which the fermentations were interrupted to remove the inocula and to add fresh solutions. The variations in the glucose concentration after replenishing the solutions are caused to some extent by the difference in size of the drums and the differences in glucose concentration of the replacement solutions. All fermentations, including the initial fermentation subsequent to the prolonged lag period, maintained a fair rate of glucose conversion and, with the exception of the first fermentation, were completed in an average time of 18.25 hours.

Single-Fermenter Processes. Semicontinuous processes requiring single fermenters have distinct advantages. These advantages can be realized provided that for inocula the greater portions of the mycelia can be recovered at the completion of fermentations, in contrast to the small quantities of mycelia available in a portion of fermenting liquor as transferred in the foregoing experiments. Upon completion of a fermentation the solution was transferred to a sterile, calibrated, inverted Pyrex bottle in order to observe the separation of the solution into two strata under atmospheric pressure. After 25 minutes the upper layer amounted to about 20 per cent of the total volume and contained the greater portion of the fungal growth; this upper layer was returned to the rotary drum as inoculum for the succeeding charge. The elapsed time between fermentations, including the flotation period, was approximately 35 minutes.

In this method the yields of gluconic acid for all fermentations except the final in any series were 80 per cent of the capacity of the fermenter. The addition of the inoculum diluted the fermentation medium and resulted in lowered glucose concentration and increased gluconic acid content at the beginning of a subsequent fermentation, but the total molecular equivalents remained approximately constant throughout an entire series of fermentations. Typical results of a few laboratory-scale experiments using this technique are presented in Figures 2, 3, and 4.

Yields of 15 Grams Gluconic Acid per 100 Cc. Fermentation media containing 15 grams of glucose per 100 cc. were found satisfactory in the single-batch process (*1*, *3*); hence, similar media were tried for the semicontinuous or multibatch fermentations (Figure 2). Fermentations 2 and 3 were noticeably longer than subsequent fermentations in this series. These slower rates of glucose conversion have been attributed to the formation of calcium gluconate crystals in fermentations 1 and 2. These crystals hindered the satisfactory separation of the mycelia so that the active fungal growth in the inocula for fermentations 2 and 3 was materially lessened. Results of this series of fermentations indicated that under the conditions of this experiment there were no decided advantages over the single-batch method if previously sterilized media were used in both methods.

Yields of 10 Grams Gluconic Acid per 100 Cc. Increased rates of glucose conversion might be expected from media containing a lower concentration of glucose, provided the amount of active mycelia produced would approximate that found in the fermentations using the higher glucose concentrations. The amount of gluconic acid formed would necessarily be less, and for this reason the calcium carbonate content should be reduced in order to avoid the presence of undissolved calcium carbonate at the completion of the fermentation and to assure the separation of mycelium during the period of flotation. Therefore 2.25 grams of calcium carbonate per 100 cc., an amount sufficient to neutralize the gluconic acid produced from 8.1 grams of glucose, were used in the series presented in Figure 3. These fermentations, with the exception of the initial one, were completed in an average time of 7 hours. The average over-all rate of glucose conversion was more than twice that of the over-all rate in the initial fermentation (namely, 0.97 gram per 100 cc. per hour as compared to 0.43 gram) and was the result of the elimination of the lag period and the maintenance or increase of the activity throughout the series.

Yields of 12 and 11 Grams Gluconic Acid per 100 Cc. To assure the elimination of the lag period and maintenance of high rates of glucose oxidation, it is essential to have sufficient free acid for easy and rapid separation of the mycelia at the completion of each fermentation. In the series of fermentations shown in Figure 4, the maximum amount of calcium carbonate advisable (2.65 grams per 100 cc.) was used (*1*). The media used in the first seven fermentations contained 12 grams of glucose per 100 cc. The fermentations after the initial lag period were completed fairly rapidly, with an average rate of glucose conversion of 0.93 gram per 100 cc. per hour.

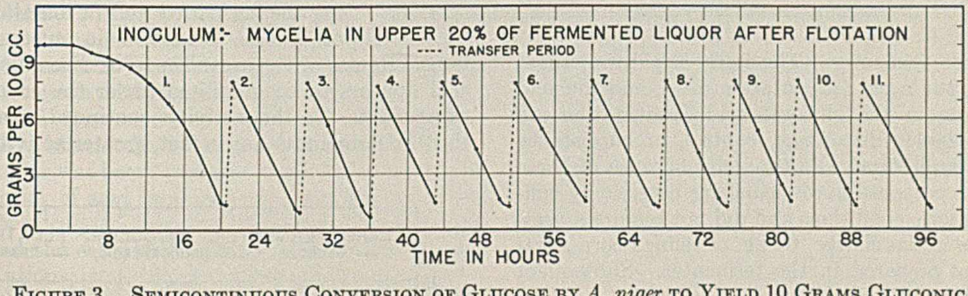

Figure 3. Semicontinuous Conversion of Glucose by *A. niger* to Yield 10 Grams Gluconic Acid per 100 Cc.

Inoculum, a portion of the final fermented liquor containing floating mycelia; transfer time, 35 minutes; calcium carbonate equivalent to 8.1 grams acid per 100 cc.

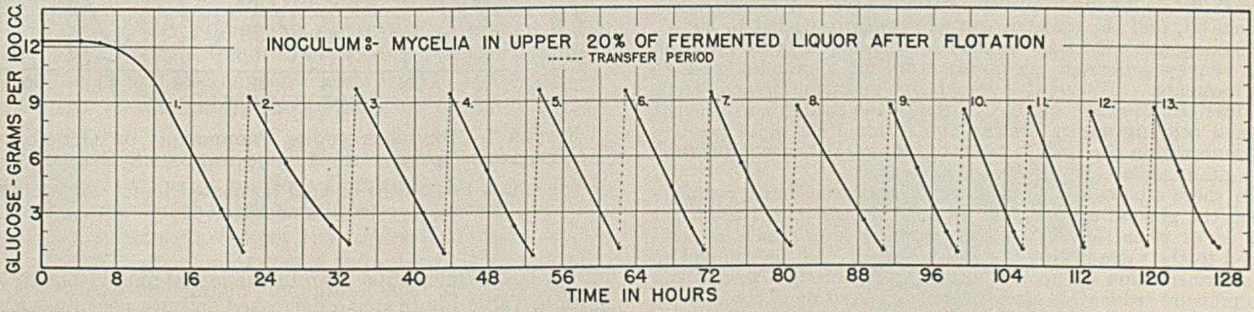

Figure 4. Semicontinuous Conversion of Glucose by *A. niger* to Yield 12 and 11 Grams Gluconic Acid per 100 Cc.

Inoculum, a portion of the final fermented liquor containing floating mycelia; transfer time, 35 minutes; calcium carbonate equivalent to 9.56 grams acid per 100 cc.

In the remaining six fermentations the glucose concentration in the media was decreased to 11 grams per 100 cc. The average rate of glucose conversion increased to 1.08 grams per 100 cc. per hour with a consequent shortening of the fermentation periods. In this double series the separation of the mycelia was rapid and distinct; analyses indicated that satisfactory separations occurred only after the pH had dropped below 4.5. Such an acid condition may be obtained either by increasing the glucose concentration or by decreasing the quantity of calcium carbonate, and in many fermentations favors the reutilization of practically all of the mycelia with the elimination of the lag period.

Semiplant-Scale Experiments

The experiments conducted in laboratory-scale equipment showed semicontinuous or multibatch production of gluconic acid to have advantages over the single-batch method. However, additional equipment was necessary for the preparation and noncontaminated transference of fermentation media to the large fermenter. The fairly rapid growth of *Aspergillus niger*, the rapid fermentation rates, and the acid condition occurring in the gluconic acid fermentation are factors which evidently discourage, control, or outdistance most chance contamination. Fortunately, because of these characteristics the preparation of media was possible by boiling under atmospheric conditions and did not require a pressure cooker. The initial charge, 64 kg. of refined corn sugar in 530 liters, was prepared in the fermenter. Subsequent charges were prepared as follows:

Table I. Semicontinuous Production of Gluconic Acid from Glucose by *A. niger*[a] in Large Fermenter

Fermentation No.	1	2	3	4	5
Refined corn sugar charged, kg.	66.9	53.5	53.5	53.5	53.5
At Beginning of Fermentation					
Glucose, grams/100 cc.	12.1	9.1	9.6	9.4	9.4
Gluconic acid, grams/100 cc.[b]	0.3	1.6	1.8	1.8	1.9
pH	6.8	5.6	5.6	5.7	5.6
Fungus, grams/liter[c]	0.27	0.41	0.70	1.26	1.88
At Completion of Fermentation					
Age, hours	16.4	9.0	8.4	8.2	7.8
Glucose, residual, grams/100 cc.	1.2	0.9	1.0	1.0	0.9
Gluconic acid, grams/100 cc.[b]	11.8	10.1	10.5	9.8	9.9
Free gluconic acid, grams/100 cc.[d]	0.5	0.8	0.9	1.4	1.3
Av. glucose conversion, grams/100 cc./hour	0.66	0.91	1.02	1.02	1.09
pH	4.8	4.2	4.2	3.9	4.0
Fungus, grams/liter[c]	0.70	0.79	1.32	2.12	2.89

[a] Inoculum for subsequent fermentations was upper two tenths of fermented solution after a flotation period of 35 minutes.

[b] Calculated from calcium determination.

[c] Dried at 80° C.

[d] Determined by direct titration.

> Refined corn sugar and nutrient salts equivalent to 80 per cent of the initial charge were dissolved in approximately 475 liters of water in a covered aluminum tank. Heating and maintenance at boiling were effected by means of steam passed through aluminum coils submerged in the solution. Boiling was continued (1.5 to 2 hours) until the water in excess of 424 liters was driven off, and the medium was subsequently cooled to 30° C. by passing water through the coils. When required, this medium was conveyed through previously sterilized aluminum pipes to the fermenter. During this preparation and transference, sterile air was continuously bubbled through the medium to prevent intense coloring during heating and to maintain slight positive pressure within the tank in order to minimize chance infiltration of contaminants.
>
> In these studies the fermentations were considered complete when the glucose content had dropped to less than 1 gram per 100 cc. or when the rates of conversion were negligible as compared to the rates during the active stages. At the completion of a fermentation the rotary fermenter was brought to rest and the pressure reduced to atmospheric. Separation of the mycelia was allowed to take place within the fermenter under atmospheric pressure for 35 minutes and was followed by removal of the underlying liquor (80 per cent of the charge) and then by recharging with fresh medium from the aluminum tank.

Results of this series of fermentations are presented in Table I and in Figure 5.

The reduction of pressure was essential for proper separation of mycelia, as was indicated by the amount of fungus found at the beginning of the second fermentation. At the end of the initial fermentation, pressure was not released until a portion of the underlying liquor was withdrawn and a part of the growth lost. Upon release of pressure the remaining mycelia floated to the top. This phenomenon can be explained from the fact that, upon release of the pressure, the air and dissolved gases evidently come out of solution as minute bubbles; some of them attach themselves to strands of mycelia, carry these strands to the surface of the solution, and thus cause rapid stratification.

Outstanding results of these investigations are that, in a series of fermentations, pregerminated inocula other than for initial fermentations are needless, that subsequent lag periods are completely eliminated, and that the rate of glucose conversion in subsequent fermentations is practically constant. An average time of 8.4 hours was required for fermentation as compared to an estimated 13 hours (calculated from the first glucose curve in Figure 5) which was required to convert a similar quantity of glucose in the initial fermentation. These results were possible because separation of mycelia by flotation permitted the retention of over 85 per cent of the active mycelia. These amounts, greater than those present in the pregerminated inocula, immediately promoted the oxidation of glucose to gluconic acid in subsequent fermentations with the consequent elimination of the lag period.

Discussion

The results of these studies show that the reutilization of the submerged mycelia of the fungus *Aspergillus niger* is highly successful in eliminating the lag period and in maintaining high rates of glucose oxidation in successive fermentations. Re-use of the organism to oxidize glucose to gluconic acid appears to be unlimited under the conditions of these experiments, as the activity continued unabated through thirteen fermentations; in fact, greater activity was observed in the last fermentation than in the initial one, although the data in Table I indicated a decreased activity per unit weight of fungus for successive fermentations. This suggests that the activity was not a direct function of the total mass of mycelia but was related to the young, actively growing fungus.

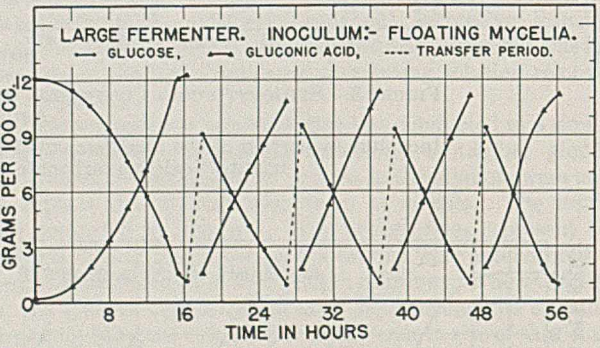

Figure 5. Semicontinuous Production of Gluconic Acid from Glucose by *A. niger* in Large Fermenter

Inoculum, two-tenths of final fermented liquor containing floating mycelia; transfer time, 95 minutes.

Table II. Comparison of Semicontinuous, or Multibatch, and Single-Batch Methods for the Production of Gluconic Acid by *A. niger*[a]

Method Used	Approx. Glucose Concn.	Av. Gluconic Acid in Final Liquors	Estd. Over-all Process Time	Glucose in Original Media	Glucose in Final Liquors	Total Gluconic Acid in Final Liquors	Acid Produced per Fermenter per Hr.
	G./100 cc.	*G./100 cc.*	*Hr.*	*Kg.*	*Kg.*	*Kg.*	*Kg.*
Single-batch:							
Without auxiliary sterilizer	15	15.5	341	874	29	904	2.65
With sterilizer	15	15.5	284	874	29	904	3.18
Two fermenters, inoculum, active fermenting solution	15	15.1	128	874	111	882	3.45
One fermenter, inoculum, floated mycelia	15	15.3	215	715	47	745	3.46
	10	10.0	111	477	57	487	4.39
	12 and 11	12.0	127	551	49	584	4.62
	11.5	11.4	120	548	48	554	4.62

[a] Calculations based on eleven fermentations.

Microscopic examinations of the mycelia throughout the fermentations showed that the periods of active vegetative growth coincided with increased rates of conversion of glucose to gluconic acid. These conversion rates decreased with spore formation. The optimum concentration of glucose in the original fermentation medium appears to be approximately 11 to 12 grams per 100 cc. Fermentations exclusive of the initial are completed in slightly over 9 hours; shorter periods of fermentation have been attained with lower glucose concentrations, but the efficiencies of production were considerably lower.

A direct comparison of the semicontinuous or multibatch with the single-batch method is of interest. Eleven fermentations are being used as the basis of comparison, as three of the five series reported here have had at least this number. Results of the calculations are presented in Table II. The estimated over-all process time (third column) includes the 6 hours which were required for the preparation of the initial charge, the 1 hour for the final discharging of the fermenter, and the 95 minutes for intermediate transfers. However, there are two exceptions in the above estimates: In the single-batch method in which no auxiliary equipment was used, the time between fermentations is estimated as 7 hours (1 hour for unloading and 6 hours for preparation). In the two-fermenter method intermediate transfer time is not included, since one fermenter was being prepared while the other was in use. The quantity of acid produced per fermenter per hour (last column) is calculated from the total gluconic acid in the final liquors and the estimated over-all process time for the eleven fermentations; these figures give an indication of the relative efficiencies of the various methods considered.

The process requiring two fermenters and using 30 per cent of the fermenting liquor as inoculum has marked advantages over the single-batch method reported earlier (*1*) but only a slight advantage over the single-batch method employing separately prepared media. However, if the large fermenter is inoculated directly with spores, the fermentation time for the single-batch methods requires more than 30 hours instead of 24 hours (*1*), and the semicontinuous method has the distinct advantage of eliminating the germination period in the fermenter.

The processes requiring a single fermenter and utilizing the developed mycelia of previous fermentations have decided advantages under the best conditions. When solutions containing 15 grams glucose per 100 cc. are used, the only gain appears to be the elimination of the subsequent pregermination periods, for similar amounts of acid are produced per fermenter per hour as in the previous method. However, as more dilute glucose solutions are used, greater amounts of gluconic acid are produced per fermenter per hour. The multibatch method employing the optimum glucose concentration (approximately 11 to 12 grams per 100 cc.) yields over 45 per cent more gluconic acid per hour than the single-batch method using separately sterilized media and approximately 75 per cent more than the single-batch method described in the earlier publication (*1*).

These studies show that in the production of gluconic acid by fermentation the lag period is eliminated through the reutilization of the developed mycelia, and that semicontinuous or multibatch methods of fermentation are feasible; the resulting economies are enhanced by selection of proper sugar concentrations.

Summary and Conclusions

1. Gluconic acid was produced semicontinuously by the reutilization of submerged growths of *Aspergillus niger*. Several methods involving the transfer of these submerged growths were studied.

2. Gluconic acid production per fermenter per hour showed no marked variation when glucose concentrations of 15 grams per 100 cc. were used, regardless of the stage at which transfers were made.

3. Gluconic acid production per fermenter per hour was greatly increased when the glucose content in the original fermentation medium was reduced to 10–12 grams per 100 cc.; best results were obtained with glucose concentrations of approximately 11.5 grams per 100 cc., when transfers of the greater portion of fungal growth with 20 per cent of the fermented liquors were made after a period of flotation. The yields of gluconic acid per hour were approximately 45 per cent greater than in the single-batch method using previously sterilized media and approximately 75 per cent greater than in the single-batch method described in an earlier publication (*1*).

4. The semicontinuous or multibatch methods were studied with the use of pregerminated inoculum in the initial fermentation; however, it is possible to eliminate the equipment, time, and effort required in pregermination procedure.

5. The re-use of the fungal growths from the fermented liquors eliminated the lag period prevalent in the single-batch fermentations and maintained a relatively high rate of oxidation of glucose to gluconic acid throughout a series of fermentations; economies resulted which should be of industrial interest.

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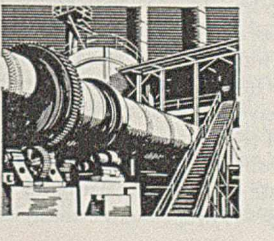


Chalking of Titanium Dioxide Pigmented Exterior Finishes

SYNTHETIC ENAMELS

D. H. DAWSON AND R. D. NUTTING
Krebs Pigment & Color Corporation, Baltimore, Md.

The results of a lengthy study of the chalking characteristics of titanium dioxide pigments in enamel vehicle systems show that Florida and Delaware exposures, in general, undergo similar types of initial film failure. The degree of correlation in chalking, fading, and loss of gloss between Florida and Delaware exposures is such that the usually faster Florida results may be accepted as representative. Differences due to variation in weather conditions during the course of the year at a given northern location usually are greater than between locations. Accelerated cabinet exposures of enamel films of the definitely chalking type also show satisfactory correlation with actual outside exposures. In all cases, however, differences due to uncontrollable variables are such that standard enamels should be included for purposes of comparison.

RECENT years have shown a marked increase in the use of exterior enamels. This has been brought about to a considerable degree through the development of the synthetic resins, and particularly to the drying-oil-modified alkyds or glycerol-phthalate type.

The pigmentation of such enamels has presented definite problems. Because of reactivity limitations, inert pigments are normally required, and in order to obtain high luster, a further restriction to the pigments of high hiding and opacity which will allow low pigmentation must be made. Further, since the alkyd enamels fail most commonly by chalking or by checking-cracking, it is important that the manufacturer so select a pigment or combination of pigments that these types of failure are avoided or at least minimized for a reasonable length of time.

The chalking-type failure usually starts with a rapid decrease in the gloss of the finish, followed by a disintegration of the film into a more or less loosely adherent chalk on the enamel surface. Chalking failure is particularly undesirable in tints because of the resultant faded appearance. The chalk may generally be removed by polishing, although the ease with which the original luster can be restored by such means will vary widely.

Checking-cracking failure is generally slower in starting, but once it has set in, the base material beneath the enamel is exposed to the action of the weather through myriads of narrow but deep fissures.

Although it is of the utmost importance for the enamel manufacturer to know what types of pigments to use in order to obtain the best results, it is frequently undesirable to await the outcome of long-time exposure tests under the conditions of actual use. On the other hand, the paint industry, in general, seems to have reached no definite agreement concerning the usefulness of the accelerated type of exposure.

The "Symposium on Correlation between Accelerated Laboratory Tests and Service Tests on Protective and Decorative Coatings" (*1*) represented many shades of opinion on the subject. The conclusions offered ranged all the way from such expressions as "useless" to a "fairly satisfactory correlation" between accelerated and northern test-fence exposures.

The general conclusion, as stated earlier by Armstrong and Fuller (*2*) is that accelerated weathering cycles are too severe. Chalking differences were telescoped so that differences were minimized, whereas checking-cracking failure was so greatly accelerated that significant differences could scarcely be appreciated.

In the course of an extensive study of the chalking characteristics of titanium dioxide pigments in alkyd enamel systems, numerous exposure tests have been made under severe weather conditions in Florida and in an accelerated cabinet of customary design; identical enamels were also placed on exposure in the milder climate of Delaware.

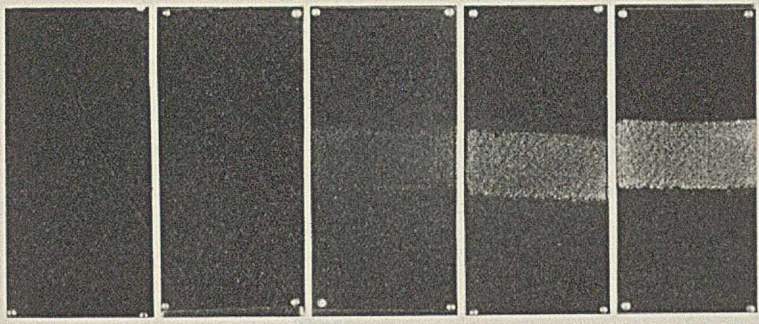
Preparation of Exposure Panels

The enamels used in this study were prepared by grinding the pigments in a drying-oil-modified alkyd solution having the following characteristics:

Resin in solution, %	50
Solvent, %	
Petroleum spirits	25
Xylene	75
Viscosity	
MacMichael	3000
G-H	Z_1–Z_2
Acid No.	3–4
Specific gravity	0.960
Color (Paint & Varnish Inst. Glass Stds.)	2–3

The pigments were mixed with the resin solution at a ratio of pigment to nonvolatile resin of 260 to 100, and ground one pass through a laboratory five-roll mill at a setting of approximately 0.001 inch to return good enamel gloss and fineness. The ground mill base was reduced by the addition of more resin solution to give the desired ratio of pigment to nonvolatile. Cobalt naphthenate drier to the amount of 0.03 per cent metal on the nonvolatile, along with xylene-petroleum thinners, was added to the reduction. The enamel was tinted gray with 5 parts of lamp black (ground separately in the resin) per 100 parts of white pigment. After aging overnight, the enamel was reduced with xylene to a viscosity of 18 seconds through the 10-F Parlin cup for spraying.

The weight ratio of pigment to binder was maintained at 0.75 to 1.00 for all titanium dioxide pigments. With other less opaque pigments, the ratio of pigment to binder was increased to give an enamel having close to the same hiding power. Where the pigmentation was principally a low-opacity pigment such as antimony oxide, equal hiding could not be used because of the degradation of other properties, notably gloss.



Slight Considerable Bad Very bad Extreme

FIGURE 1. CHALKING SCALE

The enamel was sprayed on 4 × 12 inch steel panels primed with a commercial short-oil alkyd primer surfacer and well sanded and tacked before application. Two full coats of enamel, with sanding between coats, were applied at intervals of several days to allow thorough drying. The panels for accelerated exposure measured 2.75 × 5.75 inches and were prepared in an identical manner.

Exposure of Panels

The prepared panels were exposed at an angle of 45° to the south in both Delaware and Florida. In the accelerated exposure cabinet the panels were exposed alternately to the light from a carbon arc filtered through a Pyrex No. 9200 PX globe at a distance of 15 inches and to a mild mistlike water spray. At intervals a heavy water spray, simulating rain, was applied to the panels. A "day" in the accelerated cabinet was divided into the following operations:

1. Seventeen hours of exposure to the carbon arc; for 90 seconds in every 20 minutes the panels were wet with the fine spray of water.
2. Three hours of exposure to a heavy water spray without the carbon arc.
3. Four hours for examination of the panels, etc.

The carbon arc was operated at 14–17 amperes and 220 volts, and approximately 53 kilowatt-hours were consumed in one exposure day. The spectral distribution of the light reaching the panels is compared with June sunlight at Washington, D. C., in the following table:

Wave length, mμ	279–290	290–320	320–360	360–480	480–600	600–1400	1400–4200	4200–12,000
Arc light, filtered through Pyrex globe	0.05	4.6	6.2	15.0	8.3	14.9	21.3	30.65
June sunlight	0.0	2.0	2.8	12.6	21.9	38.9	21.4	0.4

All panels were examined frequently, and their condition was noted. The degree to which the panel had faded was estimated by polishing a section and observing the contrast in whiteness between the faded and polished portions. A scale of gradings was set up, designated as slight, considerable, bad, very bad, and extreme fading.

In order to estimate the amount of chalk held on the surface of the enamel film, a narrow piece of black velvet was rubbed firmly across the exposed face of the panel. The degree of contrast between the adhering particles of white chalk and the black velvet was used to establish a scale, practically identical with the fading scale, for estimating the stage of chalking to which the panel had progressed. Figure 1 illustrates this scale in various stages of chalking failure.

Results in Alkyd Enamels

The degree of correlation afforded by exposure in the accelerated cabinet, in Florida, and in Delaware for rapidly chalking enamels is illustrated by Figure 2. Curves *D* and *B* represent enamels pigmented with pure titanium dioxide in whose manufacture deliberate processing variations were made; the third curve is "Ti-Pure" CR. The agreement between all types of exposures is generally good.

With the more chalk-resistant pigments, including the new chalk-resistant titanium dioxides such as "Ti-Pure" Y-CR and "Ti-Pure" O, the agreement between accelerated and normal exposure conditions is not so good (Figure 3). Here the Florida exposures indicate a distinct superiority for "Ti-Pure" Y-CR over a 50/50 combination of titanium dioxide and antimony oxide, and a slight advantage during the early stages of exposure over a 25/75 mixture. These results are at variance with the more normal exposures in Delaware which indicate early equality between "Ti-Pure" Y-CR and the 50/50 mixture of titanium dioxide and antimony oxide. It is somewhat surprising, perhaps, that in this series of exposures the accelerated cabinet results fall more nearly in line with those obtained from the panels exposed in Delaware than from the ones exposed in Florida.

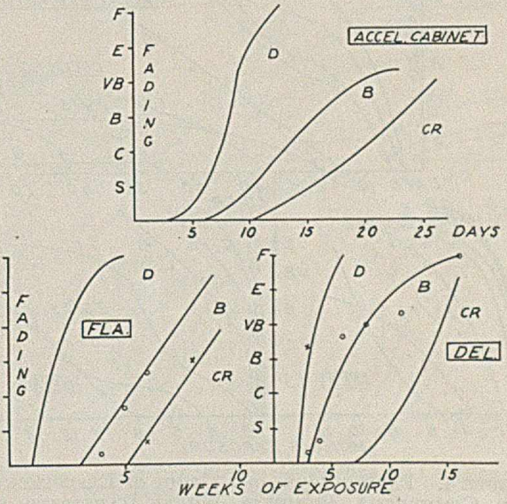


FIGURE 2. FADING RATES OF RAPIDLY CHALKING ALKYD ENAMELS

In spite of certain discrepancies, we have found the accelerated cabinet exposures and Florida exposures to be of definite value, particularly in our search for a definitely chalk-resistant type of titanium dioxide. Figure 4 represents a number of experimental pigments (*C*, *E*, *G*, and *I*) which were various steps in the development of the chalk-resistant titanium dioxide, "Ti-Pure" O. Although several of the panels in the accelerated cabinet started checking after 50 to 60 days, all of the panels failed eventually by chalking when exposed to

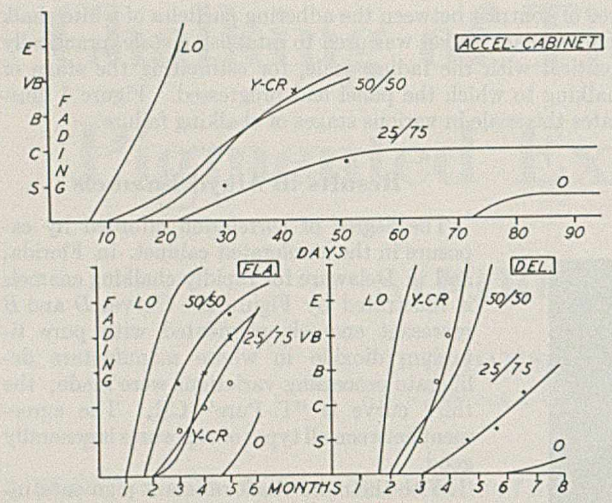


Figure 3. Fading Rates of Relatively Chalk-Resistant Alkyd Enamels

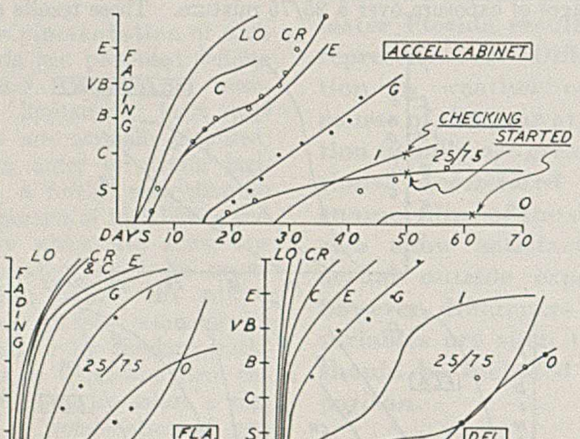


Figure 4. Fading Rates of a Group of Experimental and Commercial Pigments Which Illustrate the Utility of Accelerated Devices for Prediction of Pigment Performance

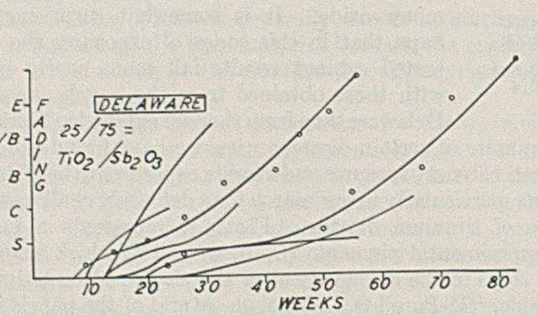


Figure 5. Fading Rates of Identical Enamels Exposed in Delaware at Different Seasons

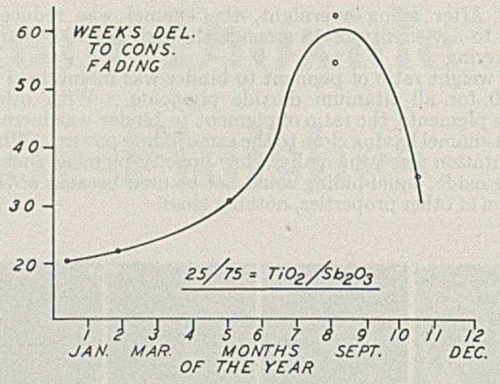


Figure 6. Effect of Time of Exposure on Rapidity of Fading in Delaware

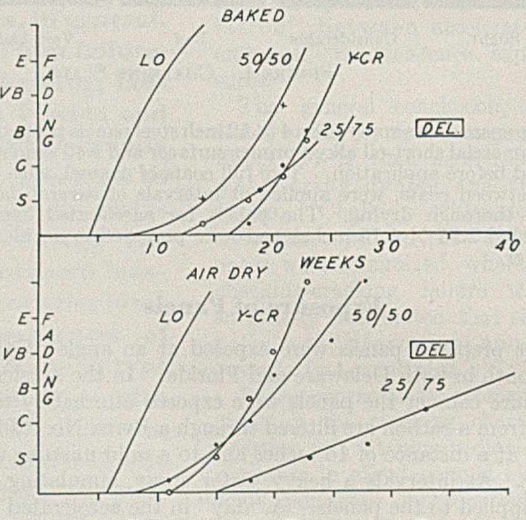


Figure 7. Effect of Air Drying and Baking on Fading

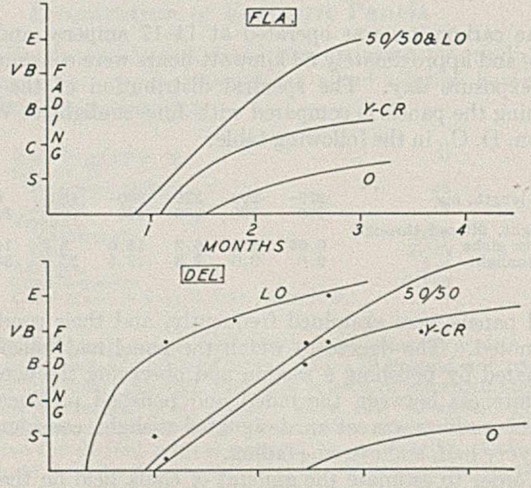


Figure 8. Fading Rates of Commercial Pigments in a Modified Phenolic Varnish

the weather, both in Florida and in Delaware. In spite of this irregularity, we were able to eliminate from further consideration, on the basis of cabinet exposures, pigments *C*, *E*, and *G*, since they were not so effective as the 25/75 mixture of titanium dioxide and antimony oxide. The inclusion of this control pigment assured us that the checking was probably illusory, for it was known that this mixture fails eventually by slow chalking and not by checking in the formulation used.

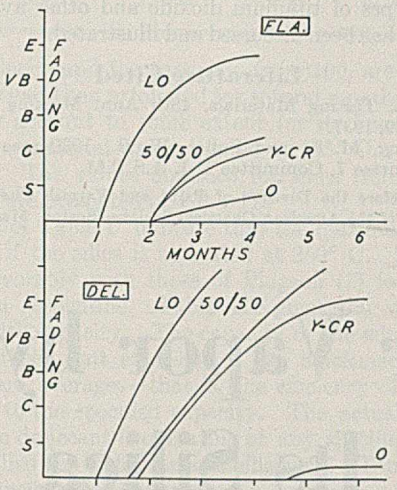


FIGURE 9. FADING RATES OF COMMERCIAL PIGMENTS IN A LONGER OIL MARINE-TYPE ALKYD

Importance of Control Panels

The necessity of including control enamels in every series of exposures is emphasized by this group. To emphasize further the importance of including controls, Figure 5 shows the 25/75 titanium dioxide/antimony oxide exposure curves in Delaware, taken from a large number of different exposure series. Depending upon the time of the year at which the exposures were started and upon the character of the weather during the life of the panel, wide variations in fading characteristics are obtained. It is apparent that these variations are greater than those between accelerated and normal exposures, although the reversal of relationships between pigments previously noted has never been found to occur. It is interesting to note that there is usually a 5–6 month "incubation" period before chalking begins. Figure 6 shows that exposures started in December, having the full quota of summer weather, fail much more rapidly than exposures started in August; the latter must wait until February for the end of the "incubation" period and several months longer, of course, until the more severe chalking weather sets in.

Effect of Film Application

Variations in film application may also notably affect the manner in which various pigmented enamels behave on exposure. In Figure 7 the two groups of pigments were ground in the same enamel liquids in identical fashion, the only difference being that one group was applied as an air-dry finish to the panels, whereas in the other group the enamels were formulated without drier and were baked. In the baked enamel "Ti-Pure" Y-CR appears to definite advantage over the 25/75 mixture of titanium dioxide/antimony oxide in the early stages of exposure and is decidedly superior to the 50/50 mixture. In the air-dry formulation, however, the 25/75 mixture is much more fade resistant than "Ti-Pure" Y-CR, which is here about equal to the 50/50 mixture during the early stages of failure.

Results in Vehicles Other Than Alkyds

Attention has been directed solely to finishes of the alkyd type. However, the same general agreement appears between pigments having various degrees of chalk resistance in other enamel vehicles, such as a modified phenolic type in Figure 8 and a long-oil alkyd marine type in Figure 9.

Effect of Pigment Combinations

Four titanium dioxide pigments, varying in their resistance to chalking in the following order of increasing resistance, have been discussed: "Ti-Pure" LO, "Ti-Pure" CR, "Ti-Pure" Y-CR, and "Ti-Pure" O.

By a suitable combination of these pigments it is possible to cover practically all the variations in the degree of chalking and fading required by enamel manufacturers. Figure 10 represents a family of curves obtained by mixing varying amounts of "Ti-Pure" Y-CR and "Ti-Pure" O. The percentage of "Ti-Pure" Y-CR in each mixture is indicated by a number adjacent to the appropriate curve. The fading resistance increases regularly as the percentage of "Ti-Pure" Y-CR in the mixture is decreased and the amount of "Ti-Pure" O is increased. The ratios of "Ti-Pure" Y-CR to "Ti-Pure" O used in formulating these enamels were: 100/0, 70/30, 50/50, 30/70, 10/90, and 0/100. These results are in good correlation in all three types of exposure.

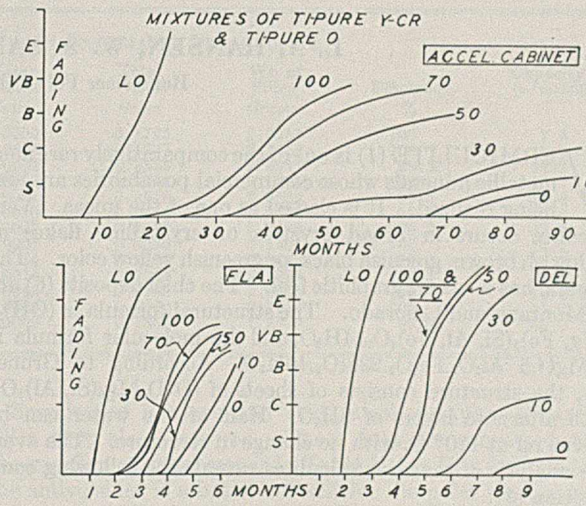


FIGURE 10. FADING RATES OF MIXTURES OF COMMERCIAL TITANIUM DIOXIDE PIGMENTS

Because of their superior hiding power, it is now possible to utilize the special chalk-resistant grades of "Ti-Pure" to effect substantial savings in pigment costs and at no sacrifice in the chalk and fade resistance of the finished enamel. By eliminating much or all of the less opaque pigments, lower ratios of pigment to binder can be utilized to effect substantial improvements in gloss.

The savings in pigment cost through the use of the chalk-resistant grades of "Ti-Pure" are estimated at between 20 and 50 per cent and pigmentation (ratio of pigment to binder) can be reduced in the same order and at the same time equal film hiding power and equal resistance to chalking and fading can be maintained.

Summary

Extended exposure tests show that within the field of alkyd enamels:

1. Accelerated cabinet exposures show excellent correlation with Florida and Delaware exposures in rapidly chalking enamel films.
2. In more chalk-resistant films of the type most widely used commercially, the correlation between accelerated cabinet and normal exposures is definitely poorer; however, the technique may still be used to estimate gross chalking differences with proper precautions.
3. In the more chalk-resistant films, the accelerated cabinet cycles used in this study yielded definitely misleading results with respect to checking type failure.
4. Even normal exposures may show reversals between pigments in chalking rate, depending on whether the film is air-dried or baked, and in some cases depending on location.

The necessity for reporting chalking rates in relative rather than absolute terms is emphasized by the large differences obtainable at varying periods with the same enamels.

The relation between the chalking rates of the new chalk-resistant types of titanium dioxide and other available pigmentations has been discussed and illustrated.

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Presented before the Division of Paint and Varnish Chemistry at the 98th Meeting of the American Chemical Society, Boston, Mass.

Sorption of Water Vapor by Vermiculite and Its Silica

L. A. HANSEN, W. S. SAMUEL, JR., AND P. A. FORNI
Rensselaer Polytechnic Institute, Troy, N. Y.

VERMICULITE (*1*) is one of the comparatively rare nonmetallic minerals whose commercial possibilities are just being realized. It is classed as one of the micas. Vermiculite occurs in broad crystals or crystalline flakes of yellowish brown, greenish black, or greenish yellow color. The mineral has a soapy, graphitic feel. The chief deposits (*6*) are in Montana and Colorado. The structural formula is $(OH)_2$-$(Mg, Fe)_3(Si, Al, Fe)_4O_{10}.4H_2O$, and the molecular formula is $22MgO.5\ Al_2O_3.Fe_2O_3.22SiO_2.40H_2O$. According to Gruner (*2*), the structure consists of sheets of $(OH)_4Mg_6(Si, Al)_8O_{20}$ with alternate layers of $8H_2O$. Half of the water can be driven off at 110° C. with no change in structure. The average analysis of seven vermiculites reveals the following composition (*2*):

	Av. Analysis, %	Theoretical Composition
SiO_2	35.04	36.71 = $22SiO_2$
Al_2O_3	14.55	14.15 = $5Al_2O_3$
Fe_2O_3	5.13	4.43 = Fe_2O_3
FeO	0.59	
NiO	2.44	
MgO	21.71	24.62 = 22MgO
CaO	0.46	
H_2O	19.99	20.09 = $40H_2O$
Total	99.91	100.00

The most remarkable property of vermiculite is its great expansion when heated (*1*). On exfoliation the expansion occurs only at right angles to the cleavage planes, and the sheets spread apart into an accordionlike structure, the color meanwhile changing to a silvery or golden brown (*4*).

The freshly exfoliated vermiculite has been reported as being a powerful desiccant (*5*). According to Guthrie and Wilbor (*3*), a silica of excellent sorbing properties can be prepared from the mineral.

Silica can be separated from the other oxides by treating vermiculite with acids such as sulfuric and hydrochloric. After the reaction is complete, the remaining silica is washed thoroughly and dried. The yield of silica was found to be 99 per cent of the theoretical. The silica prepared from exfoliated vermiculite was a chalky white material; that prepared from the unexfoliated vermiculite had a silvery white color. The density of the silica is about 0.1.

There is apparently little, if any, information in the literature on the desiccating or adsorbing properties of either exfoliated vermiculite or its silica. This report consists of the results of a preliminary study of these properties. A more thorough investigation is under way.

The silica was prepared from both the exfoliated and the unexfoliated vermiculite by treatment with hot dilute sulfuric acid (1:3) for about 3 hours. The silica was filtered in a Büchner funnel, washed with dilute sulfuric acid and finally with distilled water, and dried in an oven at 105° C.

The apparatus (*8*) used is sketched in Figure 1. Air obtained from the laboratory line was first passed through tube 1 containing fuller's earth. The pressure was regulated by means of tube 2 containing water, the height of which was controlled by the position of bottle 3. The air next passed through saturators 4, 5, and 6, the latter having a sintered glass dispersing disk to ensure saturation with water vapor. The saturated air then passed through tube 7 containing the sorbent and through tubes 8 and 9 containing phosphoric anhydride. The volume of air was determined by allowing water to flow from bottle 10 into container 12 and keeping the water in the two limbs of manometer 11 at the same height. The volume of air corresponds to the volume of water displaced from bottle 10. The saturators and the tube containing the sorbent were immersed in a constant temperature bath held at 25° C. The rate of flow of saturated air was usually adjusted so as to be between 0.5 and 1.0 liter per hour per gram of desiccant. To determine the amount of water adsorbed, the tube of desiccant was weighed before and after a run, as was also the first tube containing phosphoric anhydride. The gain in weight of the two tubes measured the total amount of water vapor. Measurements were made only at 100 per cent relative humidity.

The results for exfoliated vermiculite are given in Table I.

TABLE I. EFFICIENCY OF EXFOLIATED VERMICULITE

Water Adsorbed, x	Water Passed	Total Water	Wt. of Desiccant, m	Efficiency	Capacity, $(x/m)100$
Gram	*Gram*	*Gram*	*Gram*	%	
0.0278	0.0146	0.0424	4.0217	65.5	0.69
0.0322	0.0496	0.0818	3.4009	39.4	0.95
0.0276	0.0174	0.0450	3.3181	61.4	0.83

The efficiency and the capacity, $(x/m)100$, are low. This vermiculite had been exfoliated for several months before use which may account to some extent for its low desiccating power. The material was activated at 115° C. for 48 hours before use. The values obtained for silica from exfoliated vermiculite are presented in Table II.

The data of Table I indicate that the maximum capacity is obtained if the silica is activated at 250° C. The results compare favorably with those of Pidgeon (7) for silica obtained from serpentine. Table III gives the variation of efficiency with capacity. The capacity of the silica is about 13.4 at 100 per cent efficiency. The efficiencies listed in Table III are averages—that is, the efficiency of the water removal up to the specified capacity. The actual efficiency at which the desiccant is operating at any specified capacity might be called the instantaneous efficiency. Table IV lists these efficiencies as calculated.

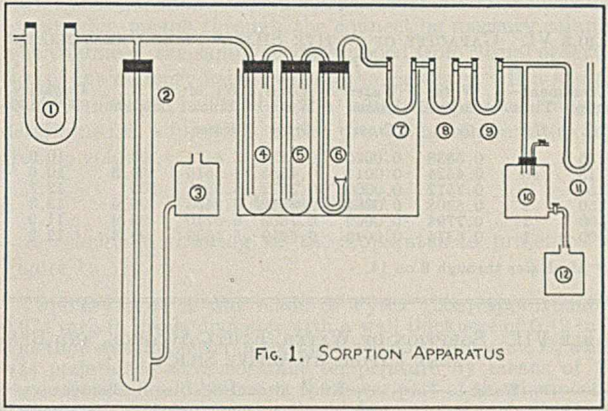

FIG. 1. SORPTION APPARATUS

A few runs were made to determine the capacity of the silica upon reactivation; they indicate that there is a slight loss in capacity, as shown in Table V.

The silica prepared from unexfoliated vermiculite is slightly inferior to the silica obtained from the exfoliated mineral. The results are collected in Table VI for silica prepared from the unexpanded mineral. Activation at 250° C. again appears to be best.

TABLE II. CAPACITY OF ACTIVE SILICA FROM EXFOLIATED VERMICULITE

Treatment		Size Mesh		Water Adsorbed	Water Passed	Total Water	Wt. of Silica	Efficiency	Capacity, $(x/m)100$
Temp.	Time	Through	On						
° *C.*	*Hr.*			*Gram*	*Gram*	*Gram*	*Grams*	%	
115	48	8	14	0.1725	0.0000	0.1725	2.3257	100	7.4
115	48	8	14	0.1776	0.0001	0.1777	2.5956	100	6.8
250	1	8	14	0.3520	0.0004	0.3524	2.3941	99.8	14.7
250	1	8	14	0.3384	0.0000	0.3384	2.1594	100	15.7
250	74	8	14	0.2498	0.0021	0.2519	2.0562	99.3	12.2
350	1	8	14	0.2814	0.0030	0.2844	2.0633	99.0	13.6
500	0.5	8	14	0.2690	0.0007	0.2697	2.2423	99.7	12.0
500	1	8	14	0.3019	0.0001	0.3020	2.1405	100	14.1
500	1	14	20	0.2705	0.0034	0.2739	2.0413	99.0	13.3
500	1	20	..	0.2940	0.0014	0.2954	2.1291	99.5	13.8
500	2	8	14	0.2698	0.0042	0.2740	2.0911	98.4	12.9
500	18	8	14	0.3060	0.0000	0.3060	2.7311	100	11.2
1000	0.2	14	20	0.1862	0.0002	0.1864	1.8579	99.9	10 0

TABLE III. VARIATION OF EFFICIENCY WITH CAPACITY OF ACTIVE SILICA[a] FROM EXFOLIATED VERMICULITE

Water Adsorbed, x	Total Water	Capacity, (x/m)-100	Efficiency	Water Adsorbed, x	Total Water	Capacity, (x/m)-100	Efficiency
Gram	*Gram*		%	*Gram*	*Gram*		%
0.2940	0.2954	13.8	99.5	0.3720	0.4912	17.4	75.8
0.3318	0.3481	15.6	95.2	0.3900	0.5435	18.3	71.9
0.3429	0.3985	16.1	86.0	0.3986	0.5910	18.7	67.4
0.3604	0.4566	16.9	78.9	0.4102	0.6501	19.2	63.1

[a] Weight of silica used was 2.1291 grams.

TABLE IV. INSTANTANEOUS EFFICIENCY OF ACTIVE SILICA[a] FROM EXFOLIATED VERMICULITE

Capacity, $(x/m)100$	Adsorbed Water	Water Passed	Total Water	Efficiency
	Gram	*Gram*	*Gram*	%
Up to 13.4	0.2853	0.0000	0.2853	100
13.4–14.0	0.0132	0.0030	0.0162	81
14.0–15.0	0.0212	0.0103	0.0315	67
15.0–16.0	0.0213	0.0204	0.0417	51
16.0–17.0	0.0213	0.0405	0.0618	34
17.0–18.0	0.0213	0.0603	0.0816	26
18.0–19.0	0.0214	0.1243	0.1457	15

[a] Weight of silica used was 2.1291 grams.

TABLE V. EFFECT OF REACTIVATION

Original Activation			Reactivation		
Treatment		Capacity, $(x/m)100$	Treatment		Capacity, $(x/m)100$
Temp.	Time		Temp.	Time	
°*C.*	*Hr.*		°*C.*	*Hr.*	
250	74	12.2	250	1	12.0
250	1	14.7	250	1	12.6
500	1	14.1	115	48	11.6

Sorption of benzene and ethyl alcohol vapors by active silica were also measured. These data are compared with the sorption of water vapor in Table VII. It is evident that the active silica is a better sorbent for the polar alcohol than

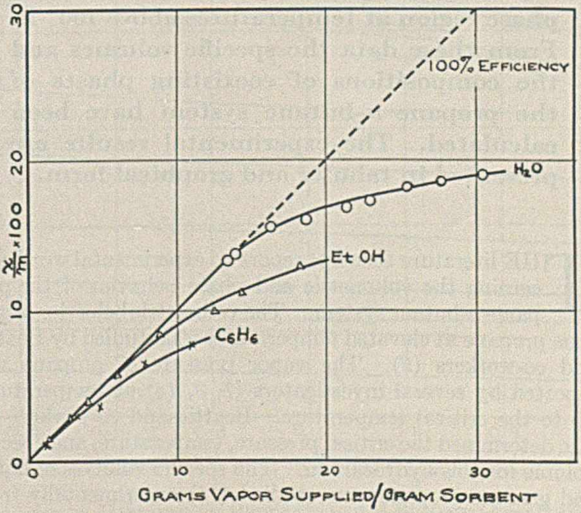

FIGURE 2. SORPTION OF VAPORS BY ACTIVE SILICA

TABLE VI. CAPACITY OF ACTIVE SILICA[a] FROM UNEXFOLIATED VERMICULITE

Treatment Temp. °C.	Treatment Time Hr.	Water Adsorbed Gram	Water Passed Gram	Total Water Gram	Wt. of Silica Grams	Efficiency %	Capacity, $(x/m)100$
115	48	0.5838	0.0000	0.5838	5.8474	100	10.0
115	48	0.4524	0.0011	0.4535	4.2516	99.8	10.6
250	1	0.7572	0.0000	0.7572	5.9541	100	12.7
250	1	0.8308	0.0004	0.8312	6.2406	99.9	13.3
500	1	0.7794	0.0009	0.7803	6.5710	99.9	11.9
500	1	0.6376	0.0043	0.6419	5.1606	99.3	12.3

[a] Mesh size through 8 on 14.

TABLE VII. SORPTION OF WATER, ETHYL ALCOHOL, AND BENZENE VAPORS BY ACTIVE SILICA

Water		Ethyl Alcohol		Benzene	
$\frac{x}{m}$	G. supplied/ g. silica	$\frac{x}{m}$	G. supplied/ g. silica	$\frac{x}{m}$	G. supplied/ g. silica
0.134	0.134	0.002	0.002	0.004	0.004
0.138	0.139	0.014	0.014	0.011	0.012
0.156	0.163	0.028	0.028	0.030	0.032
0.161	0.187	0.039	0.040	0.036	0.044
0.169	0.214	0.057	0.059	0.064	0.078
0.174	0.230	0.084	0.087	0.076	0.109
0.182	0.255	0.100	0.124		
0.186	0.277	0.112	0.143		
0.191	0.305	0.130	0.182		

for the nonpolar benzene. Figure 2 compares the sorbability of these organic vapors with that of water.

Silica obtained from vermiculite by removal of the other oxides seems to have the characteristics of a good desiccating agent. Its chief disadvantage is its low density which would require a large volume of desiccating material.

Acknowledgment

The authors desire to express their thanks to F. E. Schundler and Company, Inc., for supplying the crude and exfoliated vermiculite used in this investigation.

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Phase Equilibria in Hydrocarbon Systems

The Propane–*n*-Butane System in the Critical Region[1]

C. N. NYSEWANDER, B. H. SAGE, AND W. N. LACEY
California Institute of Technology, Pasadena, Calif.

The volumetric and phase behavior of six mixtures of propane and *n*-butane have been investigated throughout the two-phase region at temperatures above 160° F. From these data the specific volumes and the compositions of coexisting phases of the propane–*n*-butane system have been calculated. The experimental results are presented in tabular and graphical form.

THE literature seems to report no experimental work concerning the volumetric and phase behavior of the propane–*n*-butane system. The volumetric behavior of gaseous propane at elevated temperatures was studied by Beattie and co-workers (*2*). The vapor pressure of propane was reported by several investigators (*7, 8, 14*) at temperatures up to the critical temperature. Beattie and co-workers (*3*) also determined the critical pressure, temperature, and specific volume for this hydrocarbon. The specific volumes of liquid and gaseous propane were studied (*14*) experimentally from 70° F. to the critical temperature. These data suffice to establish the volumetric and phase behavior of propane with sufficient accuracy for present purposes.

The vapor pressure of *n*-butane has been measured from below the atmospheric boiling point to the critical state (*4, 5, 7, 15, 16*). The critical constants of *n*-butane were determined by Seibert and Burrell (*16*), but more recently Beattie and co-workers (*4*) reported the following values: critical temperature, 305.6° F.; critical pressure, 550.7 pounds per square inch; critical volume, 0.071 cubic foot per pound. These latter measurements were employed to establish the critical behavior of *n*-butane in connection with this investigation. The specific volumes of the saturated liquid and the saturated gas were determined (*15*) at temperatures between 70° and 250° F., and Beattie (*4*) studied the volumetric behavior in the vicinity of the critical state and also measured the vapor pressure of this hydrocarbon at several temperatures. These data are sufficient, therefore, to establish the volumetric and phase behavior of *n*-butane throughout the temperature range of the present investigation.

Materials and Method

The propane used in this investigation was obtained from the Phillips Petroleum Company whose special analysis

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[1] This is the twenty-seventh paper in this series. Previous articles appeared during 1934 to 1939, inclusive.

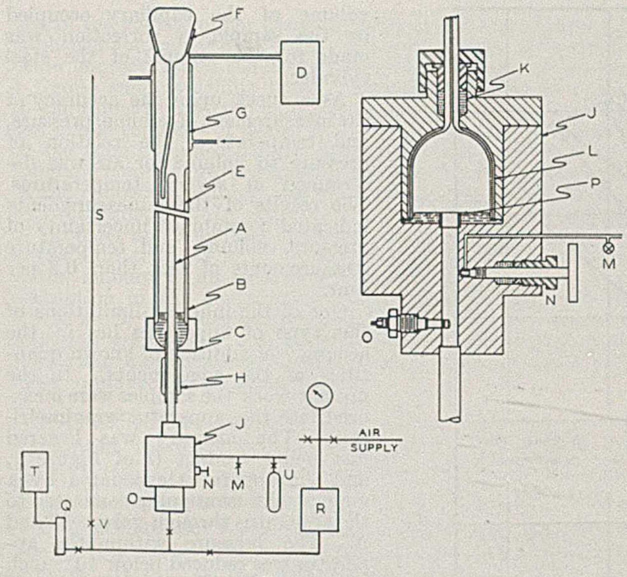

FIGURE 1. DIAGRAM OF APPARATUS

indicated that this hydrocarbon contained less than 0.05 mole per cent impurities. The material was further purified in a column approximately 1/2 inch in diameter and 4 feet long, packed with glass rings. The middle fraction from this distillation was condensed at liquid air temperatures at a pressure less than 10^{-4} inch of mercury. This fractionation and partial condensation were repeated twice, and the final product was collected in an evacuated steel weighing bomb.

The *n*-butane was obtained from the Phillips Petroleum Company and originally contained approximately 0.3 mole per cent isobutane. This hydrocarbon was also subjected to two distillations and partial condensations. The purified material exhibited less than 0.1 pound per square inch change in vapor pressure due to isothermal condensation from dew point to bubble point at a temperature of 160° F. It is believed that the propane and the *n*-butane used in this investigation contained less than 0.1 mole per cent impurities.

The method employed was similar to that used by Young and co-workers (*13*) in their classical investigations of the volumetric behavior of the paraffin hydrocarbons. A similar type of apparatus was also employed by Bahlke and Kay (*1*, *9*) in their studies of hydrocarbon mixtures.

In general, the method involves the use of a transparent capillary tube, closed at one end, within which the sample is confined over mercury. This tube is placed inside a constant temperature bath so arranged as to permit visual observation of the capillary. The effective volume of the tube is varied by the addition or withdrawal of mercury. The pressure existing within the capillary is measured by suitable means through the connecting mercury column. The volume of the sample is determined from visual observation of the mercury height within the capillary. If a sample of known weight is added to the tube, the pressure may be determined as a function of the prevailing temperature and specific volume.

Apparatus

A schematic drawing of the apparatus is presented in Figure 1:

Capillary tube *A* was made of Pyrex glass, approximately 0.074 inch in inside diameter with a wall thickness of 0.12 inch. The tube was immersed in the glass-walled thermostat, *B*, which was maintained at a constant temperature by means of the vapor from a liquid boiling in the lower part of the thermostat. Energy was supplied to this liquid from the electric heater *C*. To maintain a constant temperature, the pressure within the thermostat was maintained at a constant value by means of manostat *D*.

The vapor from the thermostat chamber was condensed by the water-cooled jacket *G*. In order to avoid undue energy losses from it, thermostat *B* was provided with an integral vacuum jacket, *E*. The interior surfaces of the vacuum jacket were silvered except for a narrow strip along its axis. This arrangement reduced the condensation on the wall of the thermostat and also kept the temperature more uniform (within 0.04° F.) in all parts of the thermostat.

The temperature was measured by means of a multilead copper-constantan thermocouple, one junction of which was carried into the thermostat through the ground-glass seal, *F*. The other junction was immersed in an ice bath. The voltage of the thermocouple was measured by means of a White potentiometer with an uncertainty of not more than 0.02 per cent. The thermocouple was calibrated against a strain-free platinum resistance thermometer which had been recently standardized by the National Bureau of Standards. It is believed that the temperature within the thermostat was known within 0.2° F. relative to the international platinum scale throughout the entire range of temperatures in this investigation. To avoid high temperatures at the lower part of the capillary tube outside of the thermostat, a water-cooled jacket, *H*, was provided. A series of liquids of different boiling points was used in the thermostat in order that the pressure within the thermostat might be kept between 5 and 15 pounds per square inch absolute, throughout the temperature range investigated.

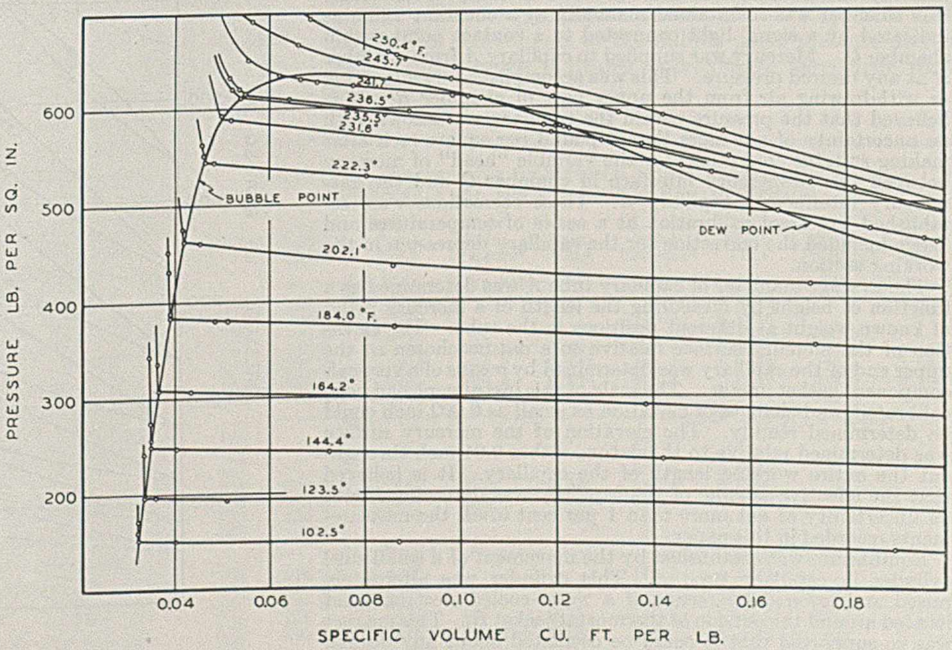

FIGURE 2. EXPERIMENTAL RESULTS FOR A MIXTURE OF PROPANE AND *n*-BUTANE CONTAINING 69.8 MOLE PER CENT PROPANE

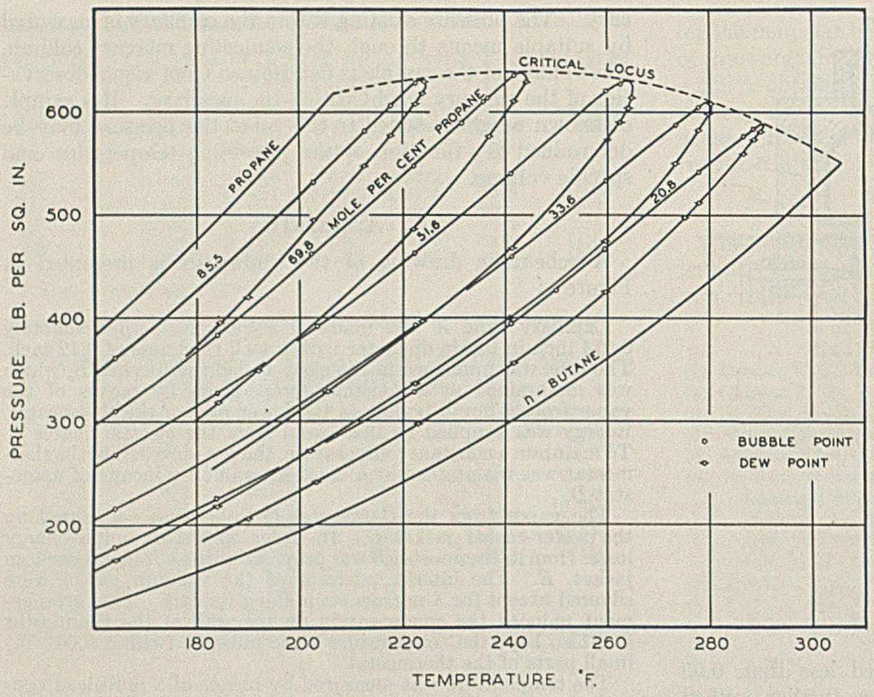

Figure 3. Pressure-Temperature Diagram for the Propane-*n*-Butane System

The capillary tube was attached to steel block *J* by means of packing gland *K*. Within chamber *J* the end of the capillary was expanded into vessel *L*. Valves *M* and *N* were connected to a mercury diffusion pump and weighing bomb *U*, respectively. Electric contact *O* permitted the maintenance of a constant mercury level below valves *M* and *N* during evacuation and the addition of samples. Vertical tube *P* in chamber *J* was extended somewhat above the lower edge of glass vessel *L* in order to provide a mercury seal within chamber *J*.

The pressure within the capillary was determined by means of a fluid pressure balance, *T*, having a sensitivity of 1 pound per square inch at pressures above 300 pounds per square inch and a sensitivity of 0.1 pound at lower pressures. The balance was connected to the mercury within the capillary through the oil-mercury interface in chamber *Q*. The mercury level within this chamber was maintained manually at a constant value as indicated by a signal light connected to a contact point within chamber *Q*. Mercury was supplied to capillary *A* from chamber *R* at any desired pressure. This was accomplished by admitting or withdrawing air from the upper part of chamber *R*. It is believed that the pressure within the capillary was known with an uncertainty of not more than 1 pound per square inch after making suitable corrections for the variable "head" of mercury between the oil-mercury interface in chamber *Q* and the gas-mercury interface in capillary *A*. These corrections were established by direct calibration at a series of temperatures and hence included the correction for the capillary depression in the working section.

The average diameter of capillary tube *A* was determined as a function of height by measuring the length of a mercury pellet of known weight at different positions in the tube. The elevation of the mercury surface relative to a datum chosen at the upper end of the capillary was determined by means of a vertical-component cathetometer. The scale of this instrument had been calibrated, and changes of elevation as small as 0.002 inch could be determined readily. The elevation of the mercury surface was determined relative to the datum within 0.01 inch throughout the entire working length of the capillary. It is believed that the effective volume of the capillary was determined with an uncertainty of not more than 1 per cent in all the measurements recorded in this paper.

Equilibrium was established by the movement of a small steel cylinder in capillary tube *A*. This cylinder was alternately raised and lowered by means of a water-cooled electromagnet located around the outside of thermostat jacket *B*. This magnet was so supported that it could be oscillated about any desired point in the tube. The frequency and length of the oscillations could be varied over wide limits in order to obtain the best agitation of the contents of the tube. In the evaluation of the volume of the capillary occupied by the sample, a correction was made for the volume of the steel cylinder.

As a check upon the accuracy of the measurement of volume, pressure, and temperature, the relation of pressure to volume for air was determined at several temperatures. The results of these measurements indicated a combined uncertainty of pressure, volume, and temperature measurements of less than 0.3 per cent.

One of the inherent limitations of this type of apparatus lies in the accuracy of addition of known quantities of the components. In the present work the samples were measured into the apparatus gravimetrically. The mercury was lowered just below contact *O* of Figure 1, and the apparatus evacuated by a mercury diffusion pump connected to the apparatus through valves *M* and *N*. The pressure within the apparatus was reduced below 10^{-5} inch of mercury. As a check, valve *N* was closed, the mercury was allowed to rise in the capillary, and the pressure necessary to bring the mercury nearly to the top of the capillary was determined by means of manometer *S* which was connected to chamber *J* through valve *V*. In effect, this procedure used the apparatus as a McLeod gage and permitted the direct estimation of the pressure existing within the apparatus before the addition of the sample. The desired amount of *n*-butane was distilled into the apparatus with the mercury level below valve *N*. The upper end of the capillary was then cooled by means of liquid air which condensed nearly all of the *n*-butane in the upper end of the capillary tube. The mercury was then allowed to rise in the capillary, and the weight of *n*-butane added to the apparatus was checked by the determina-

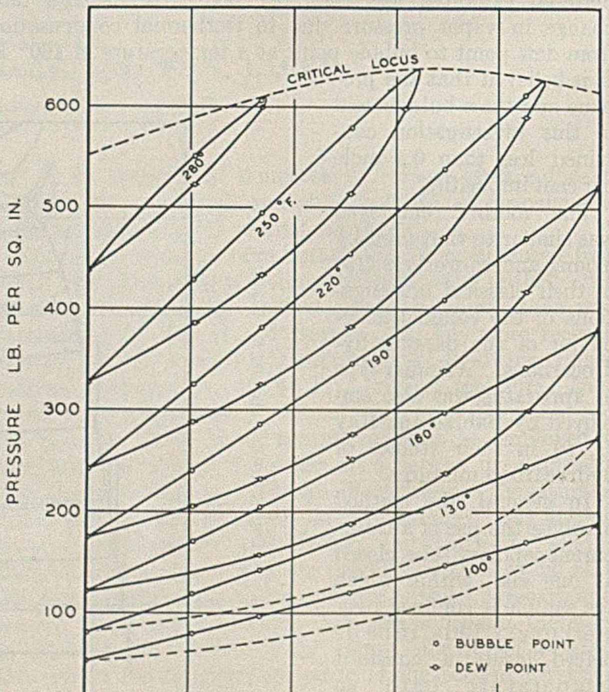

Figure 4. Pressure-Composition Diagram for the Propane-*n*-Butane System

tion of the volume under known conditions and comparison with published volumetric data (*15*). The mercury was again lowered below contact *O*, and the desired amount of propane added from a second small weighing bomb. Liquid air was again applied to the upper end of the capillary, and the mercury allowed to rise above the level of heater *C*. To avoid the loss of material in the tubing connecting the weighing bomb to valve *N*, the weighing bombs were immersed in liquid air, and the hydrocarbon in the connecting tubing was condensed in the bomb before it was disconnected. In general, it was found that the samples of propane and *n*-butane could be added with an uncertainty of not more than 1.1×10^{-6} pound (0.5 mg.). This uncertainty would amount to an error of approximately 1 per cent in the estimation of the composition of the sample. Although this leaves much to be desired in the way of accuracy, it is believed that the gravimetric method is nearly as satisfactory as the somewhat more elaborate volumetric procedures which have been employed in this connection (*9*).

It is difficult to ascertain with accuracy the absolute uncertainties involved in measurements of this nature. In general, it is believed that the bubble point and dew point pressures were ascertained with an uncertainty of not more than 2 pounds per square inch throughout the greater portion of this work. The temperatures were determined within 0.2° F. relative to the international platinum scale. The compositions of the mixtures were known within 1.5 per cent, and the specific volumes probably do not involve an absolute uncertainty greater than 3 per cent. In the case of this particular system, relatively high precision is required in the measurement of bubble point and dew point pressures for the establishment of the phase behavior since the vapor pressures of the components are not greatly different from one another. It is hoped, however, that these data will establish the critical behavior of this system with an accuracy sufficient for most purposes and permit the estimation of the volumetric and phase behavior of the system at temperatures above 160° F. well enough for engineering design requirements.

Experimental Results

Figure 2 presents the results obtained for a mixture containing 63.3 weight per cent propane. The experimental points indicated are representative of the density of data obtained for five other mixtures of propane and *n*-butane. In each case it was impossible to carry the dew point measurements much below 180° F. because of the large specific volume of the dew point gas under these conditions. In general, the bubble point and dew point pressures as determined by visual observation agreed within small limits (1 pound per square inch) with those determined by locating the sudden changes in the isothermal pressure-volume relation. The distinctness of these breaks at the bubble point and at the dew point is indicated by the isotherms in Figure 2. A somewhat larger uncertainty was involved in the establishment of the pressure at dew point than that at the bubble point as a result of the smaller discontinuous change in $(\partial V/\partial P)_T$ in the latter case. Also in the case of dew point measurements, for which the volume of the system was much larger, there was somewhat greater difficulty in obtaining equilibrium throughout the length of the tube.

Figure 3 presents a pressure-temperature diagram for the propane–*n*-butane system, including the mixtures which were studied experimentally. The circled points represent the experimentally determined dew and bubble points. The bubble point and dew point pressures and the specific volumes for each of these mixtures are recorded in Table I for a series of temperatures. The values of pressure, temperature, and specific volume corresponding to the critical point and the point of maximum temperature of the two-phase region—i. e., the cricondentherm (*6*)—are recorded in Table II.

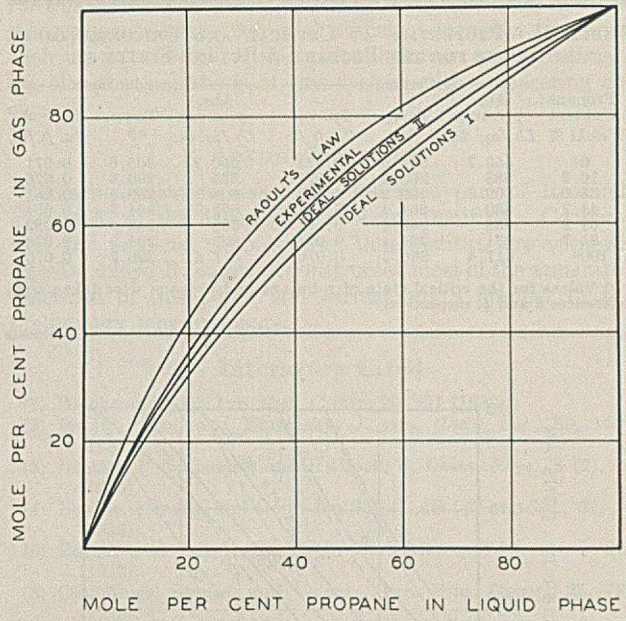

FIGURE 5. LIQUID-GAS COMPOSITION DIAGRAM FOR THE PROPANE–*n*-BUTANE SYSTEM AT 190° F.

From the data in Table I a number of diagrams illustrating the volumetric and phase behavior of this system may be drawn. Figure 4 is a pressure-composition diagram for this system at temperatures above 100° F. The behavior is similar to that found by Kay (*9*) for the ethane-heptane system except that the pressures within the two-phase region which are in excess of the critical pressure of either of the components cover a much smaller range; this is limited in the case of the propane–*n*-butane system to approximately 25 pounds per square inch. The dotted curve in the upper part of Figure 4 is the locus of the critical pressures for this system. The nearly linear relation of the composition of the bubble point liquid to the bubble point pressure at the lower temperatures indicates approximate agreement with Raoult's law.

TABLE I. PROPERTIES OF BUBBLE POINT LIQUID AND DEW POINT GAS FOR THE PROPANE–*n*-BUTANE SYSTEM

Temp., ° F.	Bubble Point Pressure[a]	Bubble Point Vol.[b]	Dew Point Pressure[a]	Dew Point Vol.[b]	Bubble Point Pressure[a]	Bubble Point Vol.[b]	Dew Point Pressure[a]	Dew Point Vol.[b]
	16.2 Weight % Propane				28.0 Weight % Propane			
100	80.5	0.0296	...	...	97.5	0.0302	...	...
130	119.0	0.0308	...	...	140.5	0.0316	...	...
160	170.5	0.0322	...	...	205.0	0.0333	156.2	...
190	239.5	0.0344	206.3	0.48	286.0	0.0361	234.0	0.423
220	327.0	0.0368	289.2	0.327	384.0	0.0398	327.5	0.284
250	430.5	0.0429	386.5	0.225	496.5	0.0445	434.0	0.197
280	552.0	0.0504	524.5	0.126	609.0[c]	0.078[c]	600.2	0.093
	44.7 Weight % Propane				62.0 Weight % Propane			
100	...	....	...	...	137.5	....	...	...
130	...	....	...	...	203.5	....	...	...
160	...	....	...	...	283.5	0.0360	...	...
190	347.0	0.0382	277	0.392	386.5	0.0400	...	...
220	455.0	0.0429	384	0.254	510.5	0.0460	...	...
250	564.0	0.0492	514.0	0.162	...	....	...	...
280	...	....	...	...	...	....	...	...
	63.3 Weight % Propane				81.7 Weight % Propane			
100	148.0	0.0320	...	...	172.0	0.0325	...	...
130	211.9	0.0335	...	...	248.5	0.0346	...	...
160	298.0	0.0362	...	...	345.5	0.0376	...	...
190	408.4	0.0398	341.5	0.294	473.0	0.0428	430	0.220
220	539.2	0.0459	473.8	0.178	615.3	0.0545	593	0.111
250	...	....	...	...	...	....	...	...
280	...	....	...	...	...	....	...	...

[a] Pounds per square inch absolute. [b] Cubic feet per pound. [c] Retrograde dew point.

Table II. Properties at Critical and Cricondentherm States for the Propane–*n*-Butane System

Propane Content *Weight %*	Critical: Abs. pressure *Lb./sq. in.*	Critical: Temp. *°F.*	Critical: Sp. vol. *Cu. ft./lb.*	Cricondentherm: Abs. pressure *Lb./sq. in.*	Cricondentherm: Temp. *°F.*	Cricondentherm: Sp. vol. *Cu. ft./lb.*
0[a]	550.7	305.6	0.071	550.7	305.6	0.071
16.2	588	290.4	0.071	585	290.6	0.076
28.0	609	280.2	0.072	604	280.5	0.081
44.7	630	264.4	0.072	622	264.9	0.084
63.3	638	243.5	0.071	630	243.9	0.082
81.7	631	224.4	0.071	626	224.6	0.076
100[a]	617.4	206.3	0.070	617.4	206.3	0.070

[a] Values for the critical state of *n*-butane and propane were taken from references *3* and *4*, respectively.

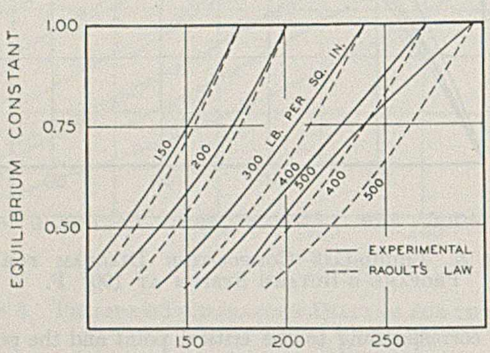

Figure 6. Equilibrium Constant for *n*-Butane in the Propane–*n*-Butane System

For some purposes it is of interest to compare the compositions of the gas phase and the coexisting liquid phase. Figure 5 shows the composition of the gas phase as a function of the mole fraction of propane in the liquid phase for a temperature of 190° F. For comparison, values obtained upon the assumption of Raoult's law and of two other generalizations have been included. Raoult's law involves the equivalent of the assumption of perfect gas behavior for the gas phase and the neglect of the volume of the liquid phase. In the case indicated as "ideal solutions I", the deviation of the gas phase from the perfect gas laws and the volume of the liquid phase have been taken into account; but it has been assumed that at the temperature in question the partial volume of each component in each phase at every pressure is equal to the specific volume of the pure component in the same type of phase and at the same pressure. This type of behavior is the basis of the fugacity relation proposed by G. N. Lewis (*10*), which was applied to hydrocarbon behavior by Souders and co-workers (*17*). For the curve denoted "ideal solutions II", the partial volume of the component in the liquid phase was neglected (i. e., the fugacity of the component in the liquid phase was assumed to be independent of pressure), but the deviation of the gas phase from the perfect gas laws was taken into account. Again it was assumed that the partial volume of each component in the gas phase was equal to the specific volume of the component at every pressure for the temperature in question. This type of generalization was proposed by W. K. Lewis (*11*, *12*) and in the present instance appears to approximate the experimental data somewhat better than does the more general application of the concept of ideal solutions to hydrocarbon behavior proposed by Souders and coworkers. However, in certain regions the actual behavior falls closer to that predicted on the basis of Raoult's law than it does to either of the other generalizations.

For many purposes it is convenient to employ the "equilibrium constant"—i. e., the ratio of the mole fraction of a given component in a gas phase, to its mole fraction in a coexisting liquid phase—as a measure of its phase distribution in a system. Figure 6 depicts the equilibrium constants for *n*-butane as a function of temperature for several pressures. The increased deviation of the experimental data at the higher pressures from that predicted by Raoult's law is clearly indicated. Equilibrium constants for propane and *n*-butane in the propane–*n*-butane system are recorded in Table III as functions of pressure and temperature. Owing to the rather low accuracy obtained in the original experimental data, uncertainties as great as 5 per cent may be involved in the equilibrium constants recorded in Table III.

Owing to the rapid variation in the equilibrium constants with pressure, it is often convenient to plot the product of the equilibrium constant and the pressure against the pressure. Figure 7 presents such a diagram for propane and for *n*-butane in this system. The variation of the *KP* product indicates, in a way, the deviations of the system from the laws of Raoult and Dalton. If these relations were valid, the value of *KP* could be determined for each of the com-

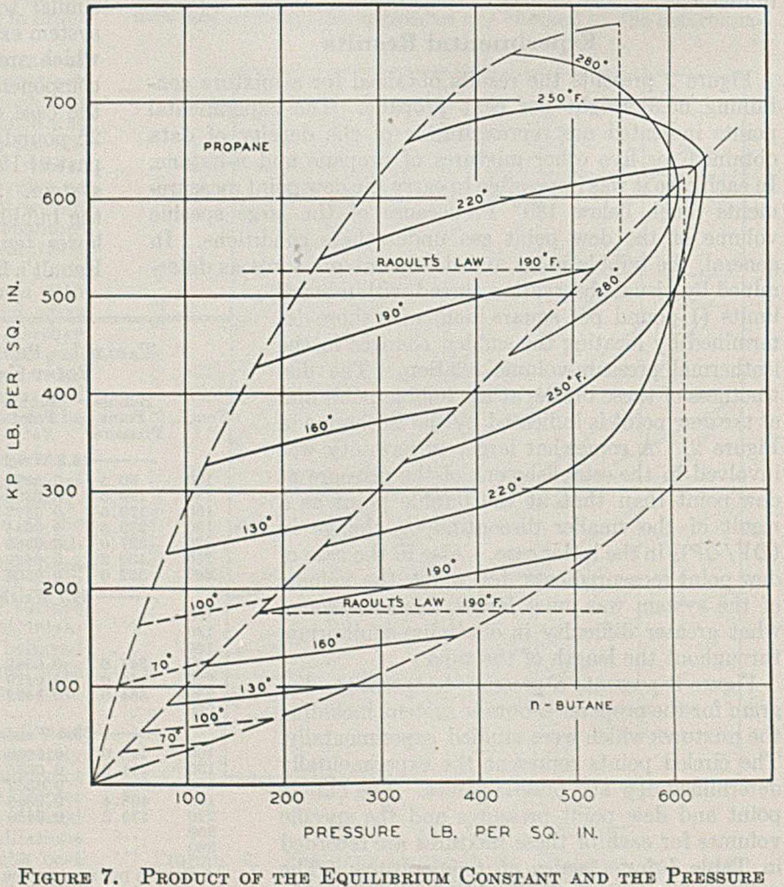

Figure 7. Product of the Equilibrium Constant and the Pressure for Propane and *n*-Butane in the Propane–*n*-Butane System

TABLE III. EQUILIBRIUM CONSTANTS IN THE PROPANE–*n*-BUTANE SYSTEM

Abs. Pressure, Lb./Sq. In.	130° F.	160° F.	190° F.	220° F.	250° F.	280° F.
			Propane			
100	2.40	...	...	...	...	...
150	1.66	2.22	...	...	...	...
200	1.30	1.73	2.17	...	...	...
250	1.07	1.43	1.80	2.16	...	...
300	...	1.23	1.55	1.86	...	...
350	...	1.08	1.38	1.64	1.93	...
400	...	...	1.24	1.47	1.70	...
450	...	...	1.13	1.33	1.53	1.66
500	...	...	1.04	1.22	1.39	1.48
550	...	...	...	1.13	1.25	1.29
600	...	...	...	1.05	1.12	1.08
			n-Butane			
100	0.827	...	...	...	...	...
150	0.587	0.830	...	...	...	...
200	0.465	0.650	0.898	...	...	...
250	0.397	0.542	0.750	0.981	...	...
300	...	0.472	0.652	0.857	...	...
350	...	0.420	0.586	0.768	0.957	...
400	...	...	0.535	0.704	0.880	...
450	...	...	0.498	0.662	0.826	0.987
500	...	...	0.467	0.645	0.796	0.943
550	...	...	...	0.667	0.795	0.925
600	...	...	...	0.798	0.827	0.954

ponents by means of the following relation, in which the subscript k refers to any component and P'' is the vapor pressure of the pure component:

$$K_kP = P''_k \qquad (1)$$

If, on the other hand, the partial volume of the component in the liquid phase is neglected, the product of the fugacity of the component in the gas phase and the equilibrium constant may be evaluated in the following way:

$$K_kf_{kG} = f''_k \qquad (2)$$

It should be remembered, when considering the extent of the deviations indicated above, that the accuracy of the data for this system is not high. It is believed, however, that the measurements were made with sufficient precision to permit their use in establishing the critical behavior and in estimating the phase relations of this system with engineering accuracy.

Acknowledgment

This investigation was conducted as a part of Research Project 37 of the American Petroleum Institute. Cooperation and financial support from that institute are acknowledged. Lloyd R. Zumwalt constructed most of the apparatus described in this paper and carried out a number of the preliminary measurements.

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The System Isopropyl Ether–Isopropanol

Vapor-Liquid Equilibrium

H. C. MILLER[1] AND HARDING BLISS[2]
University of Pennsylvania, Philadelphia, Penna.

AMONG the more important new developments in the chemical utilization of petroleum hydrocarbons is the hydration of propylene to yield isopropanol and isopropyl ether. The interesting solvent properties of both these compounds and the high octane rating of the ether make these materials of particular importance. As is frequently the case, certain fundamental data of engineering utility are missing. The purpose of this paper is to present vapor-liquid equilibrium relations to facilitate the design of separation and purification equipment.

From several methods for measuring the vapor-liquid compositions, the Othmer (*6*) procedure was chosen because of its ease of manipulation, economy of purified chemicals, and general acceptance for this type of work. The still, essentially the same as that described by Othmer, was electrically heated and well lagged to minimize refluxing.

Temperatures of the boiling vapor were read on an Anschütz thermometer, graduated in fifths of a degree centigrade, and calibrated against a National Bureau of Standards certified thermometer. Pressures were controlled and regulated by manual adjustment of the pressure in a 2-liter bottle connected to the vent of the condensate return tube. Small differences between normal barometric and actual atmospheric pressure could be compensated by evacuating or slightly compressing the air in this vessel after smooth and regular boiling had been attained. By this means the pressure was held at 760 ± 0.6 mm. mercury.

The still was charged with about 200 cc. of mixture and heated to boiling. After the air was vented and even boiling attained, the pressure was regulated to 760 mm. No attempt was made to take samples until time for three complete changes of condenser contents had elapsed after the vapor temperature had become constant to 0.05° C. The first portion of samples withdrawn was discarded, and both samples were collected in ice-cooled bottles.

The isopropanol and isopropyl ether used were of the ordi-

[1] Present address, Lago Oil and Transport Company, Aruba, Curaçao.
[2] Present address, Yale University, New Haven, Conn.

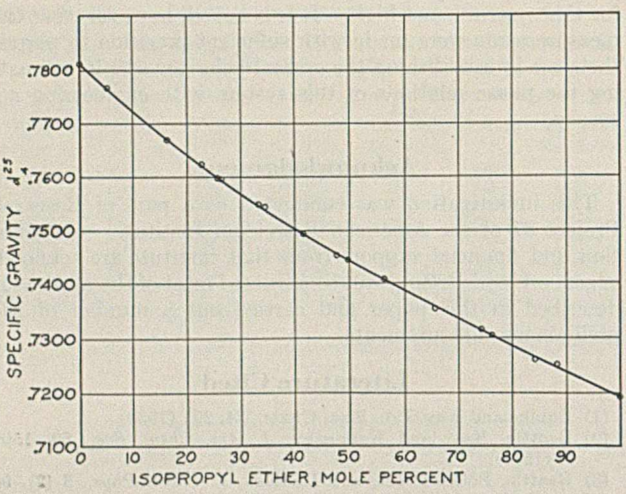

FIGURE 1. SPECIFIC GRAVITY OF ISOPROPYL ETHER–ISOPROPANOL SOLUTIONS

TABLE I. VAPOR-LIQUID EQUILIBRIA OF ISOPROPANOL–ISOPROPYL ETHER SOLUTIONS AT 760 MM.

Ether in Liquid *Mole %*	Ether in Vapor *Mole %*	Vapor Temp. *° C.*	Ether in Liquid *Mole %*	Ether in Vapor *Mole %*	Vapor Temp. *° C.*
0	0	82.3	58.4	69.3	66.77
1.35	6.60	81.06	65.8	72.6	66.33
8.40	30.2	76.02	73.2	75.7	66.20
14.0	37.8	73.98	74.7	76.4	66.18
18.0	43.7	72.48	75.4	76.7	66.18
19.13	45.1	72.78[a]	78.15	78.25	66.17
28.2	54.4	69.93	84.6	82.1	66.31
34.45	57.5	69.90[a]	87.7	84.0	66.56
38.5	62.1	68.18	89.1	84.7	66.33
42.9	62.6	68.02	91.0	86.8	66.57
43.6	64.9	67.79	91.8	88.1	66.77
44.4	64.4	67.87	95.5	91.5	67.09
47.7	65.2	67.56	98.9	96.4	67.73
47.8	65.8	67.53	100.0	100.0	68.5
52.0	66.9	67.19			

[a] Points taken without pressure regulation.

TABLE II. COORDINATES OF THE SMOOTHED CURVE

Ether in Liquid	Ether in Vapor	Ether in Liquid	Ether in Vapor	Ether in Liquid	Ether in Vapor
Mole per cent					
0.0	0.0	34.0	58.2	68.0	73.3
2.0	10.1	36.0	59.6	70.0	74.2
4.0	19.3	38.0	60.8	72.0	75.1
6.0	25.0	40.0	62.0	74.0	76.1
8.0	29.1	42.0	63.1	76.0	77.1
10.0	32.7	44.0	64.0	78.2	78.2
12.0	35.7	46.0	64.8	80.0	79.1
14.0	38.3	48.0	65.6	82.0	80.3
16.0	40.9	50.0	66.3	84.0	81.4
18.0	43.5	52.0	67.0	86.0	82.8
20.0	46.2	54.0	67.7	88.0	84.4
22.0	48.0	56.0	68.4	90.0	86.0
24.0	50.2	58.0	69.1	92.0	87.8
26.0	52.1	60.0	69.8	94.0	89.8
28.0	53.8	62.0	70.6	96.0	91.6
30.0	55.4	64.0	71.6	98.0	94.9
32.0	56.8	66.0	72.4	100.0	100.0

nary commercial grade. The alcohol, boiling originally over a range of 3.5° C. was purified by refluxing with fresh lime, distilling, and carefully fractionating in a vacuum-jacketed, 28-ball Snyder column. Only that fraction boiling at 82.3 ± 0.1° C. was used. Its specific gravity was 0.7810, which agrees exactly with the International Critical Tables (*5*). The ether, originally boiling over a range of 5° C., was purified by drying over sodium and by carefully fractionating. Only that portion boiling at 68.5 ± 0.1° C. was used. Samples separately prepared ranged in specific gravity from 0.7187 to 0.7195 at 25°/4° C. or from 0.7237 to 0.7245 at 20°/4° C., which indicates an accuracy of about 1 per cent, a usual figure for this type of work. The latter range compares as follows with determinations of other investigators:

Sp. Gr., d_4^{20}	B. P. ° *C.*	Citation
0.7260	67.5	(*3*)
0.7258	67.5–69.0	(*4*)
0.7234	68.7	(*7*)
0.725	67.8	(*1*)

Both alcohol and ether tested water-free with anhydrous copper sulfate.

The possible danger due to peroxide formation in this or any ether cannot be overemphasized. The presence of this explosive oxidation product can be detected by adding 1 cc. of a 2 per cent potassium iodide solution to 1 cc. of ether and acidifying (*2*). A brown coloration indicates the presence of the peroxide, which can be removed by steam distilling 200 volumes of ether with 1 volume of 25 per cent sodium hydroxide. The distillate always tested peroxide-free. Storage of the ether over copper powder in dark bottles seemed to decelerate, but not eliminate, peroxide formation.

The purified alcohol and ether were mixed in known proportions and the specific gravities at 25°/4° C. were taken with a 25-cc. pycnometer. The specific gravities and compositions of these isopropanol–isopropyl ether solutions are presented in Figure 1 and the following table:

Isopropyl Ether *Mole %*	Sp. Gr. d_4^{25}	Isopropyl Ether *Mole %*	Sp. Gr. d_4^{25}	Isopropyl Ether *Mole %*	Sp. Gr. d_4^{25}
0	0.7810	33.32	0.7549	65.93	0.7356
5.08	0.7766	34.80	0.7543	74.32	0.7317
16.38	0.7670	41.86	0.7493	76.30	0.7305
22.94	0.7623	47.76	0.7453	84.06	0.7261
25.92	0.7598	49.83	0.7444	88.21	0.7252
26.77	0.7596	56.14	0.7408	100.00	0.7191

The samples, taken from the still and condenser, were analyzed by specific gravity determination and reference to Figure 1. The results are presented in Table I and Figure 2, and the coordinates of the smoothed equilibrium curve are given in Table II. It is apparent that the system has an azeotrope. By graphical interpolation the composition of this azeotrope is seen to be 78.2 mole per cent isopropyl ether. Its boiling point, as determined from a boiling point composition curve, is 66.15 ± 0.05° C.

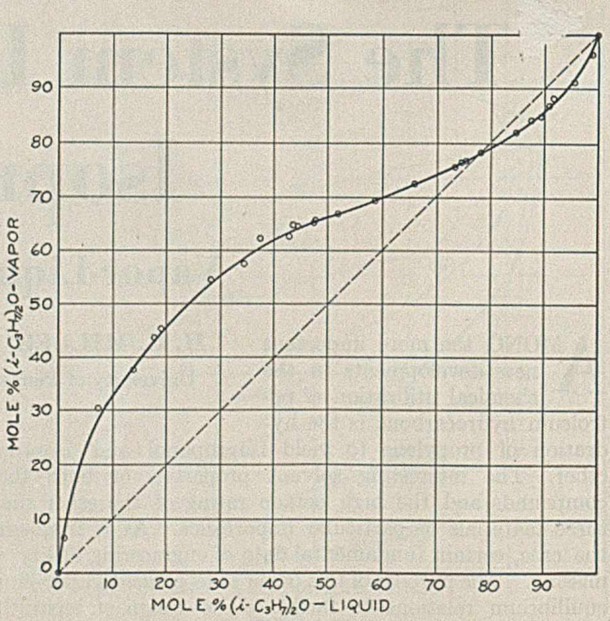

FIGURE 2. VAPOR-LIQUID EQUILIBRIUM FOR ISOPROPYL ETHER–ISOPROPANOL

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Part of a thesis presented by H. C. Miller in June, 1938, to the faculty of the Towne Scientific School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of master of science.

SEPARATION PROCESSES

The Principle of Minimum Dilution in Design of New or Unusual Processes

MERLE RANDALL AND BRUCE LONGTIN
University of California, Berkeley, Calif.

To obtain the highest thermodynamic efficiency in a separation process, those streams which must be mixed should be potentially as nearly at equilibrium as possible. This principle is illustrated by application of graphical methods to the study of cases in which the principle is not adhered to. A number of faulty types of interconnection of separation units frequently found in existing industrial separation processes are pointed out. Application of the principle allows ready detection and elimination of such faulty connections, and permits a process to be easily reduced to the simplest and most effective form.

IN PREVIOUS papers of this series (*3–9*) exact methods of analysis of separation processes were presented, based on the use of the molal property *vs.* mole fraction type diagram, together with methods of transferring the exact results to the more familiar y *vs.* x type diagram. Bošnjaković (*1*) also recently published numerous applications of heat content *vs.* composition diagrams. At present few data are available for construction of the phase diagrams needed in the exact method, particularly for systems in which the heat content is an important factor. The authors are now engaged in collecting and correlating what data are available, and intend to publish it in the form of convenient diagrams.

The methods which have been reviewed and proposed are particularly helpful in a qualitative sense even when a lack of data does not permit them to be used quantitatively. It is possible only to sketch rough outlines of the general features of the necessary diagram where data for a heat content *vs.* mole fraction diagram are lacking. Such a rough sketch will not allow us to determine graphically whether a given equipment operating in a given way will separate a particular raw material into specified products with a specified expenditure of heat. However, it will permit us to decide qualitative, rather than quantitative, questions, such as whether a proposed change in the flow sheet of a process will improve or diminish the separation efficiency.

It is particularly important to have general qualitative principles as guides in attacking new or unfamiliar problems. Without such principles a solution is reached only by groping. The molal property *vs.* mole fraction type diagrams offer considerable assistance in this respect, because of the simplicity with which each condition of material or heat balance governing the behavior of the process is represented by its distinct graphical construction.

In studying a new or unusual process, it is a relatively simple problem to set up the correct design diagram corresponding to a proposed flow sheet. The authors' preferred procedure consists in first setting up the constructions which represent the over-all material balance (i. e., a center of gravity construction for the entering and product streams) and the broader features of the process, and in filling in the details (*4*) subsequently. In determining the general features of the diagram, no attempt is made to have the location of individual points correspond to any particular compositions or stream ratios; these parameters are left free to be chosen after the general layout of the construction has been determined. The details are filled in in an orderly fashion, proceeding from one end of the flow sheet to the other. As the details present themselves, it is easy to decide whether the unit or equipment whose functioning they represent is serving a useful purpose or is really acting to lose the effect gained in some other stage in the process.

Principle of Minimum Dilution

From such studies the authors have been impressed with the importance of the principle of minimum dilution, which

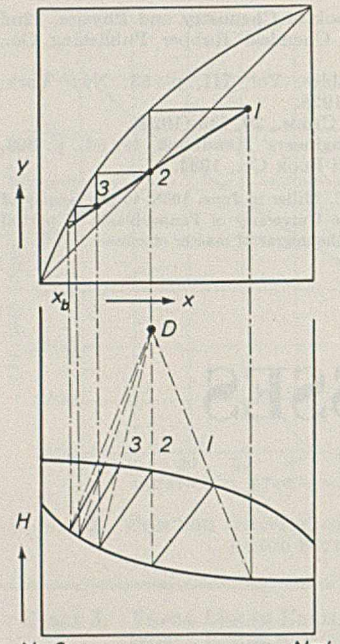

FIGURE 1. LOCATION OF NET FLOW COMPOSITION AND ITS RELATION TO THREE CLASSES OF REFLUXING

in many cases allows a decision as to the best manner of interconnection of units to be made without recourse to either graphical or numerical calculation or to experiment (*10*).

Any separation into purer products, beyond that occurring at equilibrium, must be gained at the expense of some form of energy. From a thermodynamic standpoint a process requires the least expenditure of energy when it is reversible. Any mixing of materials which leads to spontaneous composition changes (such as interdiffusion of two completely miscible liquids of different composition or the changes which bring a liquid and vapor of the same composition to their equilibrium compositions) will be irreversible to an extent depending on the spontaneous change of composition. Some of the energy which was expended in producing the initial separation is lost in such mixing, and must be resupplied in order to recover the lost separation.

In practice, other factors than energy expenditure enter in determining the optimum process. A completely efficient process (thermodynamically) must be infinitely slow and may require overelaborate apparatus. Thus it may be the most extravagant of labor and equipment. As an example, the ordinary fractionating column requires the least expenditure of energy when operating at minimum reflux, but at the same time requires the largest number of plates and hence the most expensive equipment. Again, thermodynamically the fractionating column is essentially inefficient. The mixing of reflux streams with the vapors rising through the column produces irreversibilities which result in a much greater heat expenditure than is required by the reversible process. However, in many cases, economic factors indicate that a fractionating column even with known thermodynamic inefficiencies may be preferable to a thermodynamically more reversible process.

To obtain the highest thermodynamic efficiency, those streams which must be mixed should be potentially as nearly at equilibrium as possible. To be potentially at equilibrium, two completely miscible liquids should have the same composition, temperature, and pressure. As an example, it is known that the best feed conditions obtain when a liquid feed is of as nearly the same composition, temperature, and pressure as the liquid on the plate at which it is entered.

The principle may be given a somewhat more specific though less precise form. In a properly designed process, there are no streams more widely separated than the final products of the process. If such a stream exists, then it must have been irreversibly diluted, with accompanying loss of efficiency at some intermediate stage. As a corollary of this statement, if one of the products of a process undergoes further separation, it is then obvious that there is no place in the process to which the most purified fraction may be returned without dilution and loss of efficiency. It is this form of the principle whose application will be tested by the following examples.

Material Balance as Expressed by y *vs.* x Diagram

From the correspondences between the y *vs.* x and H *vs.* N type diagrams as developed in a previous paper (*5*), each unsaturated phase is represented in the y *vs.* x diagram by a curve or sloping line. Each point on the line represents the composition of a saturated liquid and vapor phase which, when mixed in the proper proportions, will produce the given unsaturated phase. The proportions are given approximately by the slope of the line (with a reversal of sign). Thus a slope of $-{}^3/_4$ requires approximately three moles of liquid to four of vapor; a slope of $+1{}^1/_2$ requires three moles of liquid to a negative two moles of vapor. In the latter case two moles of vapor of the proper composition is to be extracted from three moles of liquid of the corresponding composition in order to obtain the given unsaturated phase.

Point D in the H *vs.* N diagram of Figure 1 represents a superheated vapor. Considered as the net flow point of a stepwise construction for an enriching section, it represents the composition and heat content of the vapor that would be left over as product, if at some point in the section the liquid reflux could be extracted from the rising vapor without loss of heat to a condenser. That there would be residual vapor is indicated in the H *vs.* N diagram by the fact that point D lies nearest the vapor curve and in the y *vs.* x diagram by the fact that the slope of the reflux curve is less than unity. The same superheated vapor is represented in the y *vs.* x diagram by the curve $(\overline{1,\ 3})$ which may be considered as the reflux curve (i. e., operating line) of the construction for the enriching section. The points on the curve were obtained by transferring the liquid and vapor phase mole fractions of the rays through D to the y *vs.* x diagram as x and y coordinates, respectively. In particular, point 2, at which the reflux curve intersects the diagonal line $y = x$, was obtained by transferring the liquid and vapor mole fractions from the vertical line through D (ray labeled 2). Thus the intersection of the reflux curve with the line $y = x$ in general gives the composition of the net flow (e. g., superheated vapor) phase which it represents.

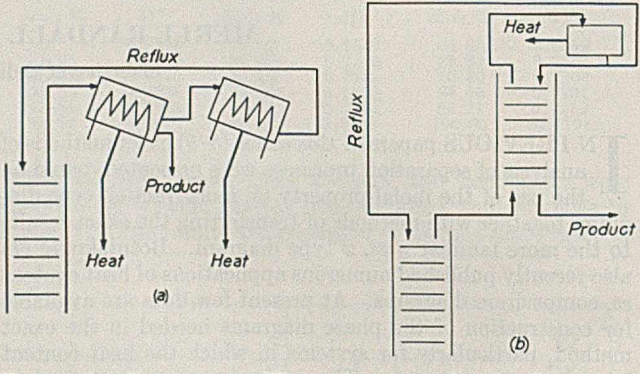

FIGURE 2. CONNECTIONS WHICH RETURN A REFLUX RICHER IN LIGHT COMPONENT THAN VAPOR DELIVERED FROM TOP OF COLUMN

Faulty Connection of Refluxing Equipment

A casual inspection of Figure 1 might lead one to think that the separating efficiency of the plates in an enriching section would be much enhanced if some could operate in the region to the right of point 2, where the reflux curve passes below the line $y = x$; certainly the steps are of longer span. A column section can be made to operate in this region by returning liquid of the proper composition as reflux. The composition of liquid reflux and of the vapor issuing from the top of the section together define a point on the reflux curve (e. g. point 1). If this point is to lie below the line $y = x$, as it must if any of the section is to function in this region, the liquid must be richer in light component than the vapor. This may be accomplished, as in an absorption tower, simply by feeding in a liquid of the required composition. It may also be accomplished by splitting the vapor into an enriched and a stripped fraction in some other equipment. The enriched fraction might then be returned as reflux, ensuring that the column would operate in the manner indicated.

This procedure of returning an enriched fraction of the vapor as reflux should, according to the principle of minimum dilution, result in a loss of separating efficiency. Offhand we have been led to expect the reverse. However, from a consideration of the meaning of the net flow point, D, it is seen that no matter how the required reflux is obtained from the vapor, although the residual product may differ in heat content, it must have a composition corresponding to the composition of the net flow—hence, that of point 2 at which the reflux curve cuts the diagonal, $y = x$. Thus by returning the enriched fraction of the vapor as reflux, not only is this enrichment wasted, but also the enrichment gained in all of the plates operating in the region to the right of point 2.

Figure 2 illustrates two possible interconnections of equipment which return the enriched rather than the stripped fraction of the vapor as reflux. In *a* the vapor is split into fractions by a partial condenser; in *b* it is split by means of a second fractionating column. Other examples might be given in which the vapor stream from the top of a column section is sent to other separating equipment, and finally an enriched rather than a stripped fraction is returned to the first section as reflux. The above considerations show that such an interconnection is to be avoided as wasteful of separating effect, in accordance with the principle of minimum dilution. Similarly, it may be shown that, according with the principle, the returning of a stripped fraction of the liquid from the bottom of a stripping section as the bottom vapor stream is undesirable. In general, the validity of the principle may be demonstrated by qualitative application of the graphical methods.

For purposes of classification there are three ways of returning reflux. The reflux may be of the same composition as the vapor, or it may be an enriched (or a stripped) fraction of the vapor. The composition of vapor and reflux in the three cases is represented, respectively, by points 2, 1, and 3 in the y *vs.* x diagram (and by the corresponding rays in the H *vs.* N diagram) of Figure 1. The corresponding three cases for return of vapor to a stripping section are shown in Figure 3. In both diagrams point 1 represents the undesirable case.

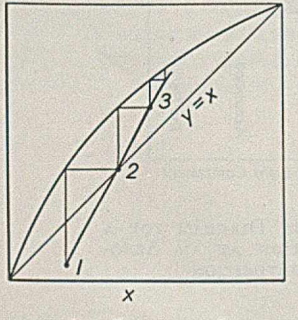

FIGURE 3. DIAGRAM ILLUSTRATING THREE CLASSES OF VAPORIZING EQUIPMENT

Such faulty connection of equipment would not ordinarily be expected in familiar processes which are simple and well understood. However, it is easy to make the mistake of connecting equipment in this fashion when the process is complex or new and unfamiliar. The authors have found examples of faulty interconnection of units in processes which are of commercial importance and in actual use. The point to be emphasized, which is coming to be appreciated in petroleum refining, is that attention must be given to the design of a process as a whole, as well as to the design of individual units. It is entirely possible to design each unit to operate most efficiently without having achieved the most efficient operation of the complete process, as a result of improper interrelationship of the units.

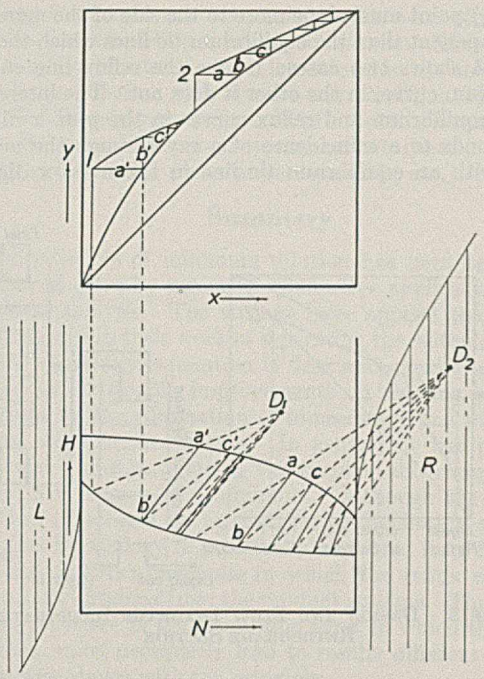

FIGURE 4. DIAGRAM ILLUSTRATING TWO CLASSES OF RETROGRADE PROCESSES

Retrograde Action of a Column Section

Normally the most volatile component concentrates at the top of a fractionating column section. It is possible, however, to operate a column section in such a way that the relative order of the positions at which the various components are found in the section is inverted. Such an operation may be said to be retrograde. Two examples are given by columns operating in the fashion indicated by the two stepwise constructions of Figure 4. Both are characterized by the fact that the stepwise construction lies entirely above the equilibrium curve in the y *vs.* x diagram. A point on the reflux curve represents streams flowing at the same interplate level, while a point on the equilibrium curve represents vapor rising and liquid flowing down from the same plate. Thus, in going down the column the direction of motion through the stepwise construction will be from equilibrium-curve point to reflux-line point along the vertical lines (lines representing liquid), and from reflux line to equilibrium curve along the horizontal lines in the y *vs.* x diagram. When this concept is applied to the construction in which the operating line lies above the equilibrium curve, the composition of streams progresses from left to right through the stepwise construction in going down the column. Thus the more volatile component is found concentrated at the bottom rather than the top of the column.

The necessary condition for retrograde action is that the vapor streams be richer in more volatile component than the liquid streams flowing in the same interlevel by more than an equilibrium separation; i. e., that the reflux line lie above the equilibrium curve in the y *vs.* x diagram. This means that in the H *vs.* N diagram the construction rays through the net flow (D_1) point must slope more to the side of the more volatile component than the equilibrium tie lines which they cut. Figure 4 shows two cases; in one the reflux line cuts the equilibrium curve, in the other it does not. The intersection of the equilibrium and reflux curves in the y *vs.* x diagram corresponds to a coincidence of a ray through the net flow point with an equilibrium tie line in the H *vs.* N diagram.

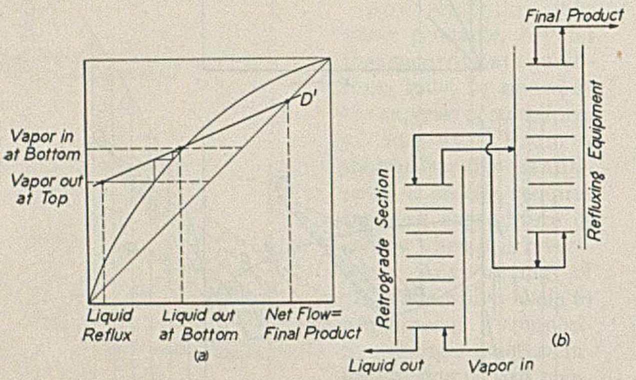

FIGURE 5. DESIGN AND FLOW DIAGRAMS ILLUSTRATING A RETROGRADE SECTION

Hence the second case is represented in the H *vs.* N diagrams by a stepwise construction in which the net flow point (D_2) falls in one of the two regions, L and R, in which it is impossible for a ray to be tangent to either branch of the equilibrium caustic curve (*4*, Figure 2).

In order to obtain retrograde action, it is necessary to return a vapor to the bottom of the section which is richer in light component than the leaving liquid by more than an equilibrium separation. This may be accomplished, if the reflux ratio is greater than unity, by splitting the liquid into two fractions, one of which has the desired composition and the other is poorer in light component. Since the light component is enriched at the bottom of the column in the retrograde case, it is the enriched fraction of the liquid which is being returned as vapor in order to produce retrograde action. This is contrary to the principle whose application is being studied, and hence such retrograde operation should prove to be detrimental to separating efficiency. The retrograde action may also be accomplished by returning a liquid reflux to the top of the column which is poorer in light component by more than an equilibrium separation. If the reflux ratio is less than unity, this reflux may be obtained from the vapor delivered at the top of the column by splitting it into a stripped fraction of the desired composition for reflux, and a residual enriched product fraction. Again, since the more separated product at the top is that richest in heavy component, the procedure used in obtaining retrograde action is contrary to the principle and hence should lead to inefficient separation. It remains to test the principle by means of the graphical construction.

Generally in retrograde action the streams leaving the column section are more nearly of the same composition than the streams entering. Hence the net effect of the retrograde process is to partially mix, rather than separate, the streams fed to it. The process effects a loss rather than a gain in separation and is detrimental rather than useful.

Figure 5*a* represents the compositions of streams in a column operating in retrograde fashion with reflux ratio less than unity. Point D', where the reflux line cuts the diagonal $y = x$, represents the composition of the residue which would remain after the reflux for the section is obtained from the top vapor. The equipment used in obtaining reflux, whatever its nature must be capable of producing the required reflux and this residue from a feed of the same composition as the vapor received from the top of the retrograde section. This refluxing equipment might, for example, be an ordinary continuous-feed fractionating column, connected as shown in Figure 5*b*.

The effect of the retrograde section is to mix the bottom product of this reflux-producing column with less pure material (the vapor fed to the retrograde section) and thus waste part of the separation obtained in the refluxing column. The retrograde section is bucking the action of the refluxing column, where it might be made to aid this action by connecting it in direct rather than retrograde fashion. The argument obviously holds as well for other values of the reflux ratio in the retrograde section.

Retrograde Action in Azeotropic Distillation

The discussion of retrograde action may seem only academic, until it is realized that there is a rather strong tendency to introduce retrograde sections into the flow sheets of new processes whose principles are not too familiar. One reason for the tendency is apparent when we note that the stepwise construction, in the case of a reflux line lying entirely above the equilibrium curve, is not limited as it is in the case of the direct processes. By the use of a retrograde process it would seem that the phenomenon responsible for the condition of "minimum reflux" (in which many plates near the feed stream become ineffective) might be avoided. The plausibility of the idea is even greater in the case of systems in which there is a binary azeotrope.

Figure 6 gives the equilibrium curve for a system which possesses a minimum-boiling mixture corresponding to the azeotropic composition. An important example is that of alcohol-water mixtures. The stepwise construction shown is behaving in a retrograde fashion to the right of the azeotropic composition, since the azeotrope is found near the bottom of this particular portion of the column, whereas the normal tendency is for azeotrope to concentrate at the top. At first glance, we might easily be lead to believe that here is a way to avoid the obnoxious characteristics of the azeotropic mixture. Apparently it is necessary only to connect one section of the column so that it will function in this retrograde fashion; then it will carry the mixture across the azeotropic composition and thus avoid the necessity of special "deazeotropizing" processes.

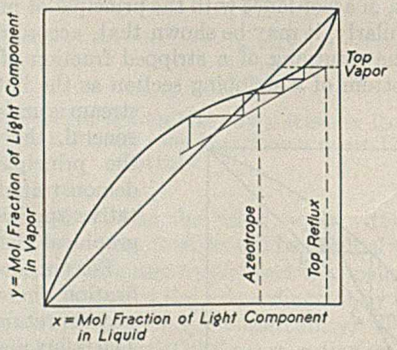

FIGURE 6. DESIGN DIAGRAM FOR A RETROGRADE SECTION AT AN AZEOTROPIC COMPOSITION

That such is not the case may readily be seen from a consideration of material balance. Let it be supposed that the available raw material is not richer in light component than the azeotropic composition. This is the usual case with alcohol and water mixtures. Then the reflux to the top of the retrograde section, which is richer in light component than the azeotrope, must be obtained from the products of the distillation. Since it is the retrograde section which is to be responsible for producing material richer in light component than the azeotrope, it is necessary to obtain the reflux entirely from the vapor delivered by this section, by any convenient means. This requires first that the reflux ratio be less than unity; otherwise there will not be sufficient vapor. This being the case, the reflux line must cut the line $y = x$ to the left of the azeotropic point (Figure 6). Thus the process which will obtain the required reflux from the top vapor must also be capable of yielding a residual top product whose composition lies on the opposite side of the azeotropic composition from that of the reflux. This refluxing process alone would be sufficient to achieve the desired result of crossing the azeotropic composition. The retrograde section, if it can be made to function at all, is unnecessary and hence wasteful. A more thorough investigation of other possible connections utilizing the retrograde section has shown that they cannot be made to function in the desired fashion without the aid of some other process, which is of itself capable of producing the desired result. Since the process must always depend on direct functioning equipment, as long as the reflux streams are obtained from product streams, the presence of a retrograde section can only counteract the effect of some of the direct functioning sections and is therefore detrimental.

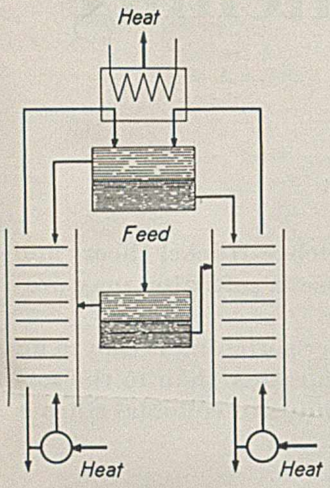

Figure 7. Schematic Diagram of Gay's Process

A particular example is the process proposed by Gay (*2*) for the separation of components in a system possessing both a minimum-boiling mixture and a region of two liquid phases. The flow sheet of the process is similar to that recently proposed by the authors for the same purpose (*7*), as Figure 7 shows. In this process it is possible to have one of the above-feed sections operating in retrograde fashion. This may happen if a feed is entered at too low a level in the columns. In the design diagram Gay avoids this condition by his construction for minimum reflux. In practice this is not sufficient since the actual column may not behave exactly as it was designed (fractional plates are not possible, etc.).

Summary

The principle of minimum dilution has been tested in a number of cases by means of qualitative applications of the graphical analysis. The authors have applied the principle to advantage in their work of separating the isotopic forms of water (where any separation is dear and cannot be wasted, *9*) and in developing improvements on existing separation processes by the elimination of unnecessary and even detrimental steps in the process. In general, it has proved of particular value in reducing the number and complexity of stages in a process to a minimum. Although the principle has been illustrated by application to distillation processes, it applies by analogy in practically unaltered form to extraction and to other processes in which the reflux or recycle streams are obtained from the product streams. The application to processes of the absorption type, in which there is no recycling, must necessarily lead to results different in detail but in accordance with the principle.

Acknowledgment

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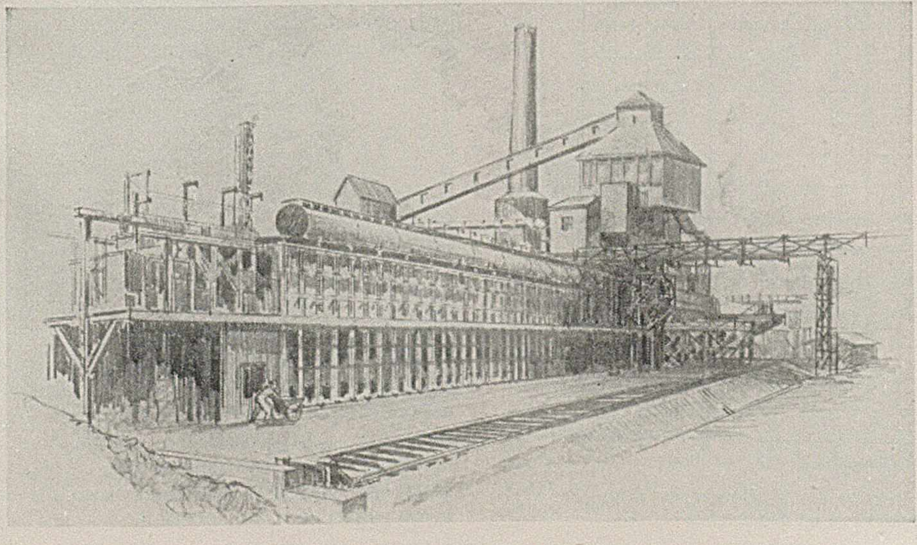


Theoretical Limits of the Lime-Soda Method of Water Softening

T. E. LARSON AND A. M. BUSWELL
Illinois State Water Survey, Urbana, Ill.

Revised calculations involving the activity coefficients of the Debye-Hückel theory and common ion effect show that under specific conditions lime-soda softening may produce a water of hardness as low as 10 to 15 p. p. m.

The beneficial effect of the use of sodium aluminate in water softening is due to an increase in caustic alkalinity and colloidal coagulating action rather than to the formation of insoluble aluminates. The presence of small amounts of colloidal silica is beneficial to coagulation.

SEVERAL reports in the literature (*3*) have indicated exceptionally low residual hardness on auxiliary treatment in softening with sodium aluminate. Although it has been reported (*6*, *10*) that the presence of aluminate induces the precipitation of a highly insoluble magnesium aluminate, no experimental proof was presented to verify this assumption.

A careful consideration of the solubilities of calcium carbonate and magnesium hydroxide will show the variations that may be expected from lime-soda softening, with or without the presence of sodium aluminate.

The solubility products for calcium carbonate and magnesium hydroxide as commonly used give the expected residual hardness as 24.2 p. p. m. (as calcium carbonate).

Using the activity product data of Johnston (*7*) and Kline (*8*) and the activity coefficients derived from the Brønsted-LaMer modification of the Debye-Hückel equation for waters of various ionic strengths (μ), and using sodium sulfate as the typical nonincrusting salt, the following data are indicated (in parts per million):

Na_2SO_4	0	100	500
$\mu^{1/2}$	0.026	0.053	0.106
Ca(as $CaCO_3$)	7.9	8.9	11.4
Mg(as $CaCO_3$)	11.4	12.2	14.1
Total (as $CaCO_3$)	19.3	21.1	25.5

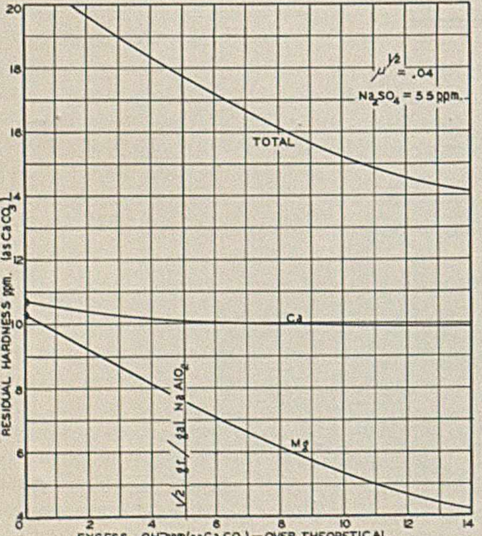


FIGURE 1. EFFECT OF ADDITION OF SODIUM ALUMINATE ON HARDNESS

However, the calcium carbonate hydrolyzes:

$$2CaCO_3 + H_2O \rightleftharpoons 2Ca^{++} + x\,CO^{--} + y\,OH^- + y\,HCO_3^-$$
$$\text{where } x + y = 2$$
$$\text{and } (Ca^{++})_{\text{total}} = (CO_3^{--}) + {}^1/_2(OH^-) + {}^1/_2(HCO_3^-) \qquad (1)$$

Only the CO_3^{--} of the alkalinity present can be used in the solubility product calculations. However, any excess of either y or x will decrease the calcium solubility. Magnesium hydroxide is ionized to give excess hydroxyl ions. It can also be shown that with residual alkalinities less than 100 p. p. m. (as calcium carbonate), the maximum CO_3^{--} concentration is obtained at a pH of 10.4.

Lime-soda softening alone at normal temperatures (15° to 25° C.) should give the following approximate residual hardness (calculated with the mutual effect of presence of excess hydroxyl ion from calcium carbonate and magnesium hydroxide hydrolysis, in parts per million):

$\mu^{1/2}$	0.026	0.106
Ca	10.0	14.8
Mg	10.0	12.6
Total	20.0	27.4

These calculations and data presuppose final equilibrium and cannot be valid otherwise since the constants and equations are all on the basis of final equilibrium. The data, therefore, do not give values to be expected in softening practice but give those that may be approached under proper regulation.

Since the rate of reaction doubles with approximately every 10° C. rise in temperature, and since carbon dioxide is expelled and leaves excess hydroxide as the soluble calcium hydroxide, precipitation and coagulation should be more complete at elevated temperature. This is the basis for hot water softening. As the result of such treatment the values given will be less for magnesium and may be more for calcium.

Should a compound such as sodium aluminate be added to the extent of 0.5 gram per gallon, complete hydrolysis to aluminum hydroxide should give excess hydroxyl ion to the extent of 5 p. p. m. (as calcium carbonate), which should reduce the calcium plus magnesium hardness by 3.4 p. p. m. (Figure 1). Actual tests showed that the hardness reduction by addition of sodium aluminate were greater than calculated values for excess hydroxyl ion, particularly for magnesium.

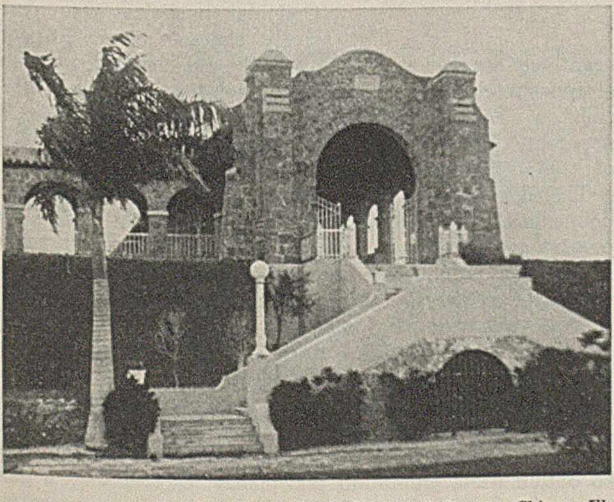
Clark and Price (*5*) gave four reasons why low final hardness due to the formation of very insoluble magnesium aluminate is probably untrue. To these may be added the fact that if this were so, magnesium aluminate would be the first to precipitate, leaving the excess magnesium to obey the solubility or "activity" product equation for magnesium hydroxide, since the magnesium concentration is always greater than the aluminate concentration.

SAMPLES of magnesium chloride, $^2/_3$ e. p. m. (equivalents per million equivalents of water) or 33 p. p. m. (as calcium carbonate) samples were treated with varying amounts of sodium aluminate (92 per cent). The results of analyses (gravimetric) showed that the magnesium was precipitated not according to the aluminate concentration but according to the hydroxyl-ion concentration. The aluminate precipitated was far less than that which would be expected to be removed per equivalent of magnesium removed.

Samples of tap water (hardness 275 p. p. m., alkalinity 340 p. p. m., total mineral content 365 p. p. m.) were treated with sulfuric acid to give a noncarbonate water. These and unaltered 2-liter samples were thoroughly aerated to remove carbon dioxide and treated in 3.5-liter battery jars with varying amounts (not greatly different from theoretical requirements) of lime and soda ash or lime alone.

Since tests showed that calcium carbonate did not form or settle out as readily as magnesium hydroxide unless sufficient stirring was employed, a 2-hour stirring period and a 1-hour settling period were used in all tests. Samples were collected from the supernatant liquor and analyzed according to Standard Methods of Water Analysis (*1*) without filtration.

Tests *C* and *D* (Table I, Figure 2), typical of eight series, show the effect of the addition of 0.5 grain per gallon of sodium aluminate. In these tests, as in the others, the effect of the presence of hydroxyl ion (due to hydrolysis of sodium aluminate) is clearly evident. The residual calcium as well as magnesium is decreased. The decrease is more than can be accounted for by calculation, which shows that the action of aluminate and the hydrous alumina aid in coagulating the colloidal magnesium hydroxide and calcium carbonate. The residual hardness was in no case less than the theoretical limit calculated for final equilibrium.



Courtesy, Alvord, Burdick & Howson, Chicago, Ill.

ENTRANCE TO THE OPERATING GALLERY OF THE MIAMI, FLA., SOFTENING PLANT WITH A CAPACITY OF 40 MILLION GALLONS A DAY

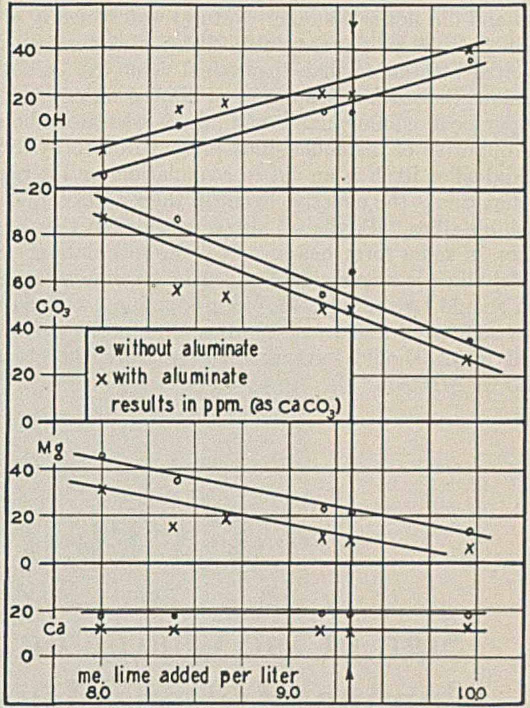


FIGURE 2. EFFECT OF ADDING 0.5 GRAIN PER GALLON OF SODIUM ALUMINATE

TABLE I. EFFECT OF ADDING 0.5 GRAIN PER GALLON OF SODIUM ALUMINATE

Test	M. E.[a] Added/Liter CaO $NaCO_3$	M. E.[a] Added/Liter $NaAlO_2$	Residual P. P. M./Liter (as $CaCO_3$) OH	CO_2	Ca	Mg	Total
			C. 2-Hour Stirring				
Original soln.	9.32[b]	...	−345.0	...	155.0	121.0	276.0
1	8.00	...	− 14.1	94.6	16.1	45.3	61.4
2	8.00	0.10[c]	− 12.1	98.8	14.1	47.1	61.2
3	9.33	...	13.1	64.5	17.2	21.6	48.8
4	8.00	0.10	− 3.0	86.6	10.4	31.4	41.8
5	9.33	0.10	20.2	48.4	9.9	9.0	18.9
6	8.66	0.10	17.2	54.4	12.5	18.0	30.5
			D. 4-Hour Stirring				
1	8.40	0.10	14.1	56.4	9.9	15.3	25.2
2	8.40	...	7.0	86.6	17.2	35.1	52.3
3	9.18	0.10	21.2	48.4	10.4	11.3	21.7
4	9.18	...	13.1	54.4	17.2	23.4	40.6
5	9.96	0.10	40.3	26.2	11.5	5.8	17.3
6	9.96	...	36.2	36.2	16.7	13.5	30.2

[a] Milliequivalents.
[b] Theoretical requirement.
[c] NaOH equivalent to $NaAlO_2$

SINCE sodium aluminate has been found very effective in the removal of large quantities of soluble silica (*4*, *11*), it was decided to investigate the possible effect of soluble silica in water softening.

Synthetic samples of tap water were made with controlled amounts of silica present. Experiments indicated that the presence of some silica (6 p. p. m.) even with high excess hydroxyl-ion concentration and aluminate was necessary for good coagulation. Also if high silica (30 p. p. m.) was present but no sodium aluminate, the solution remained very turbid and did not settle out. Natural waters nearly always contain 5 to 20 p. p. m. soluble silica; therefore from the tests cited little more than theoretical value can be derived. Also, since the stock solution was of diluted water glass from a 40 per cent commercial brand, there was also about an equal quantity of insoluble silica present due to hydrolysis. Colloidal silica itself is an aid to coagulation, and it is probable that this is the effective agent in these tests rather than the soluble silica. Baylis (*2*) also reported that the presence of silica in some form has an effect on coagulation. Since colloidal silica is negatively charged in alkaline solution, its action should be similar to colloidal alumina. On the addition of sodium aluminate anhydrous aluminosilicate may be formed which should have action similar to the clays described by Mattson (*9*).

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WATER SOFTENING

Sign of the Charge on Colloidal Particles of Hydrous Alumina, Hydrous Magnesium, and Calcium Carbonate

T. E. LARSON AND A. M. BUSWELL
Illinois State Water Survey, Urbana, Ill.

Colloidal hydrous alumina is negatively charged above, and positively charged below, a pH of 8.2. As the pH changes on aging, a flocculation zone is approached in which basic aluminum sulfate of variable composition constitutes the solid phase. Colloidal calcium carbonate is shown to be negatively charged and magnesium hydroxide positively charged throughout the pH range of water softening.

THE relation between electrical charge and certain coagulation effects met with in water purification is not clear in several instances. This is partly due to the earlier notion that hydrous alumina was positively charged throughout the pH range encountered and partly due to a lack of information concerning the charge on other precipitating substances.

Various optimum pH zones of coagulation for alum floc have been reported in the literature (*1*, *2*, *3*, *8*, *9*). Investigations have shown that these zones are dependent to a certain extent upon the type and concentration of ions in the water to be coagulated (*2*, *8*, *9*). The purpose of this paper is to present data on the charge on colloidal calcium carbonate and magnesium hydroxide, and to indicate the change undergone by hydrous alumina in connection with coagulation and softening.

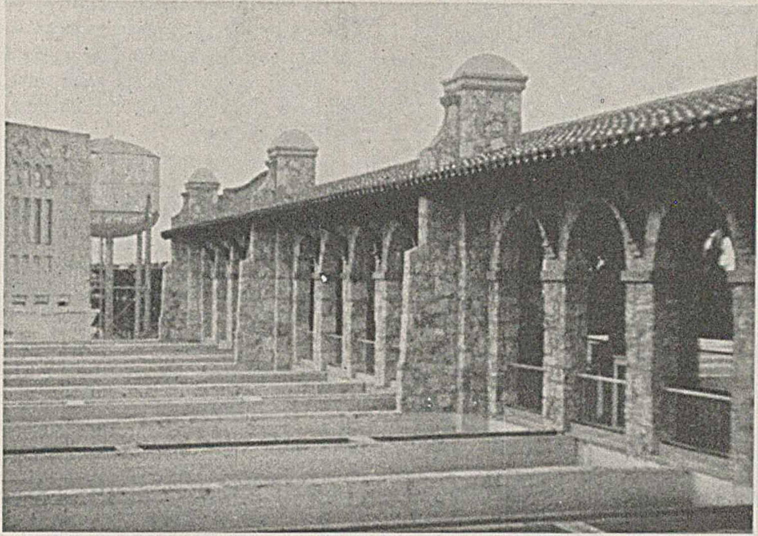
Electrophoresis determinations were made on hydrous alumina at various pH values by means of the ultramicroscope with the cylindrical cell of Mattson (*5*). Corrections for light beam deviation (*4*) were used to obtain focus at the correct depth. The pH was determined potentiometrically with a glass electrode.

The hydrous alumina was prepared by adding aluminum chloride and aluminum sulfate, respectively, to various concentrations of sodium hydroxide. Continued stirring showed a steady change in the pH of the solution. When aluminum chloride was used, if the initial pH on addition of the coagulant was greater than 8.2 the colloidal particles were negatively charged and the pH decreased with time. If the initial pH was less than 8.2, the particles were of positive charge and the pH increased with time.

When aluminum sulfate was used, the behavior was similar to that of aluminum chloride when the initial pH was greater than 8.2. When the initial pH was less than 8.2, an increase with stirring was noted, but if the final pH became as great as 7.6 to 8.2, flocculation occurred. Colloidal particles were positively charged below 7.6 and negatively charged above 8.2. As the pH changed, particles of opposite charge appeared in the solution, and when flocculation occurred, particles of either charge were equally apparent. Typical data are shown in Figure 1 for 2 grains of $Al_2SO_4.16H_2O$ per gallon.

The fact that aluminum hydroxide is not the only compound in the solid phase when polyvalent negative ions are present accounts for the variation in isoelectric point when other than monovalent ions are present. Miller (*8*) has shown the existence of a basic aluminum sulfate of composition varying with pH (or hydroxyl-ion concentration), and aluminum concentration. Each of these compositions of basic aluminum sulfates should have a particular isoelectric point, which explains the zone of precipitation found when sulfate is present. Mattson (*6*) checked Miller's work with phosphate present and varied the phosphate concentration to obtain basic aluminum phosphates, each having a particular isoelectric pH for the particular phosphate concentration within the zone of insolubility. Likewise aluminosilicates were shown to have isoelectric points varying with the relative concentration of aluminum and silicate present (*7*).

Magnesium hydroxide was found to be positively charged at all pH values as high as 12, beyond which no determinations were considered necessary. Calcium carbonate was found to have a negative charge in the presence of calcium bicarbonate as well as in the presence of calcium hydroxide.



Courtesy, Alvord, Burdick & Howson, Chicago, Ill.

The Mild Climate at Miami Makes It Practicable to Omit the Customary Building over the Filters of the Softening Plant

The relatively slow approach to equilibrium is shown by the change of pH with prolonged stirring, which is substantially equivalent to aging. Proper mixing and sufficient detention period are primary prerequisites for efficient softening and coagulation. The resulting formations of precipitates of variable composition of mixtures of various insoluble compounds are significant in many phases of water treatment. Although no definite stoichiometric relations can be shown, it is seen that color, turbidity, and bacteria removal are all dependent on pH of flocculation of the agent which, in turn, is dependent on the relative concentration of polyvalent ions present. Each particular water should have a particular isoelectric pH for each concentration of aluminum added, and this pH will also vary according to whether the aluminum is added as potassium alum, filter alum, aluminum chloride, or sodium aluminate. This pH will depend slightly on the form and amount of colloidal matter (color, turbidity, and bacteria) and more definitely on the highly charged, greater concentrations of polyvalent ions such as sulfate, carbonate, silicate, and iron.

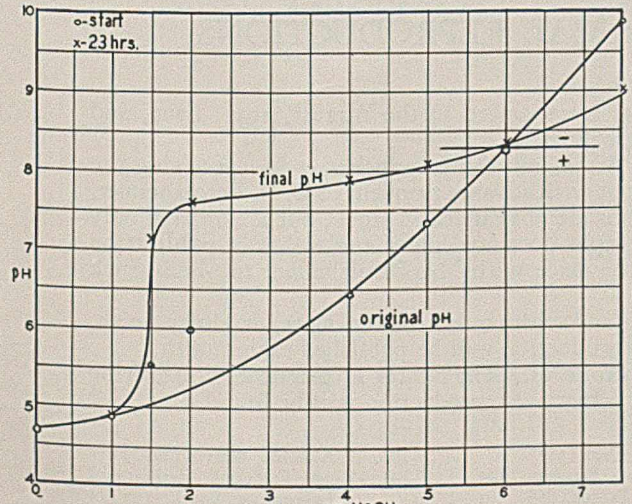


Figure 1. Data for Aluminum Sulfate

Likewise, the addition of an aluminum floc in treatment should not be so effective as the addition of aluminum in solution or in the solid or colloidal state since in that event, two consecutive reactions must take place instead of one. These steps are solutions of ions combined with aluminum to maintain equilibrium with those in solution, and then adsorption of ions from solution to maintain another solid-to-solution equilibrium. This does not mean that the use of a floc would be totally ineffective, whether it be freshly prepared or obtained from a previous coagulation.

With reference to water softening where the pH is high, most of the aluminum should exist as soluble aluminate. In the presence of considerable excess magnesium hydroxide (positively charged), definite adsorption of and coagulation by the negatively charged aluminate ions and alumina particles should take place. Colloidal particles are coagulated by oppositely charged particles as well as by ions, and the resulting hydrous oxides act as catalysts or reservoirs for hydrogen and hydroxyl ions adjacent to the magnesium and aluminum hydroxides as the relatively slow formation of calcium carbonate takes place and thereby hastens the approach to equilibrium.

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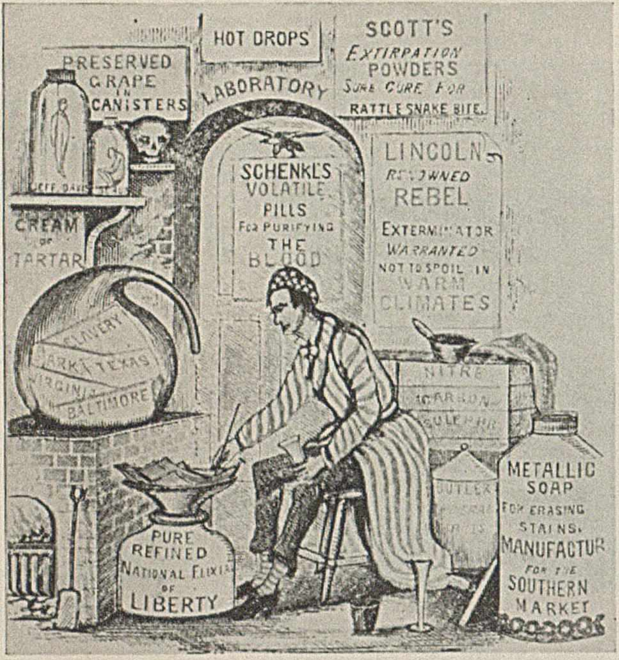
CHEMICAL PATRIOTIC ENVELOPE



The use of illustrations, cartoons, and caricatures for patriotic and propaganda purposes goes back to the 18th Century. It was vigorously utilized in the English campaign against Napoleon.

It again became active in 1840 when the British Post Office issued the first postage stamps and stamped envelopes. The latter, known as "Mulready envelopes" because the original was made by William Mulready, were not popular and were soon caricatured extensively.

In the United States the use of pictures on envelopes was soon adopted by the temperance societies and the anti-slavery party. By 1852 this use had assumed large proportions.

But it remained for the great wave of patriotism which followed Lincoln's Emancipation Proclamation to produce an avalanche of patriotic envelopes.

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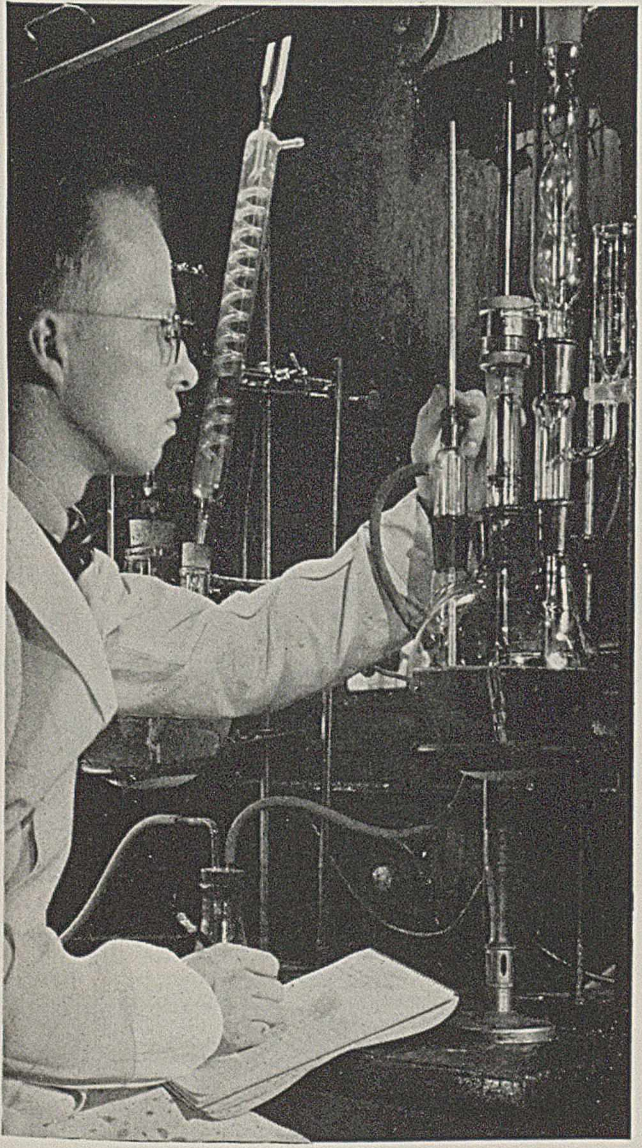

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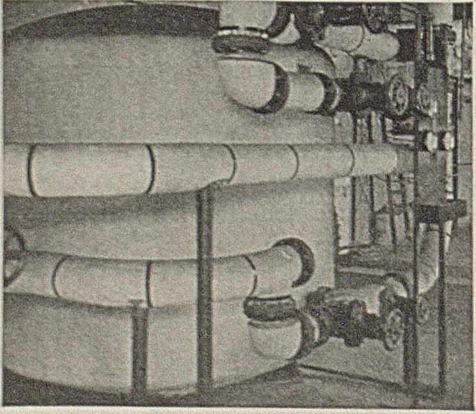

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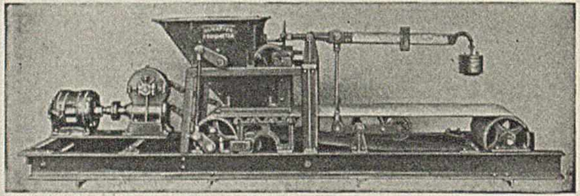

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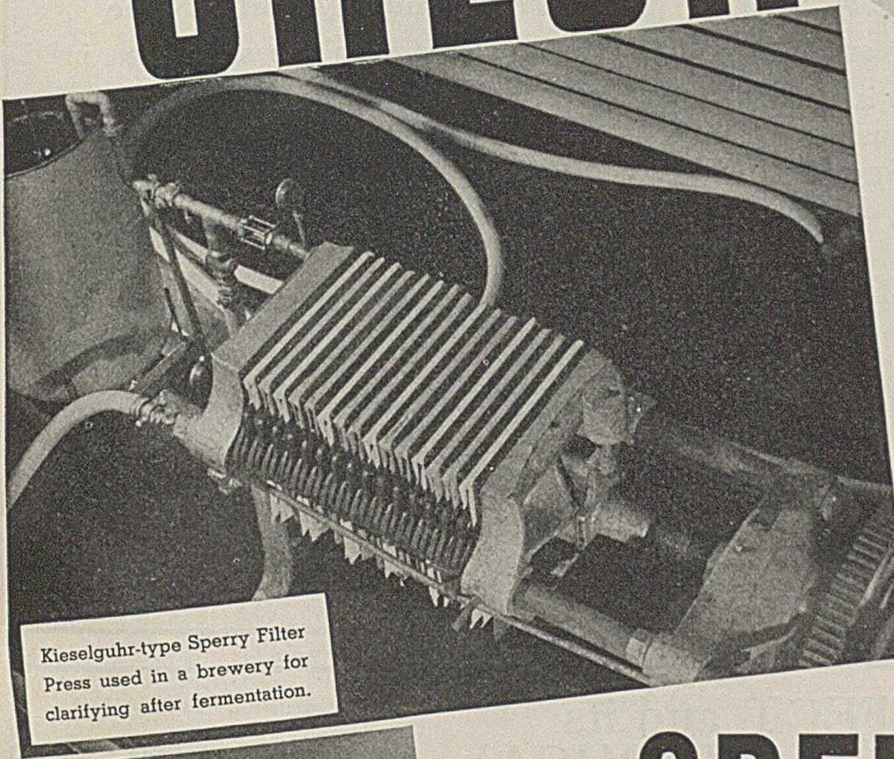

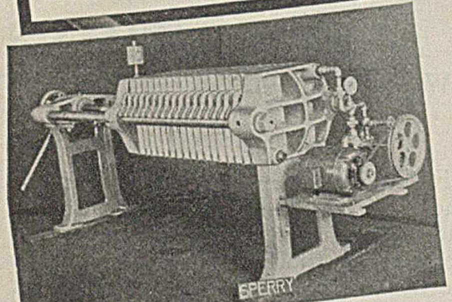
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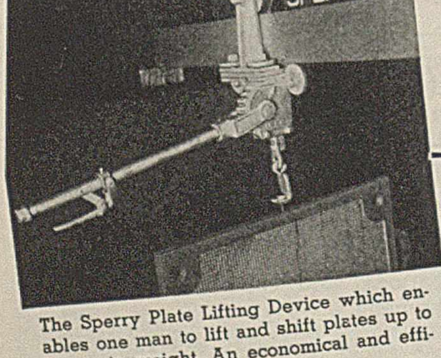
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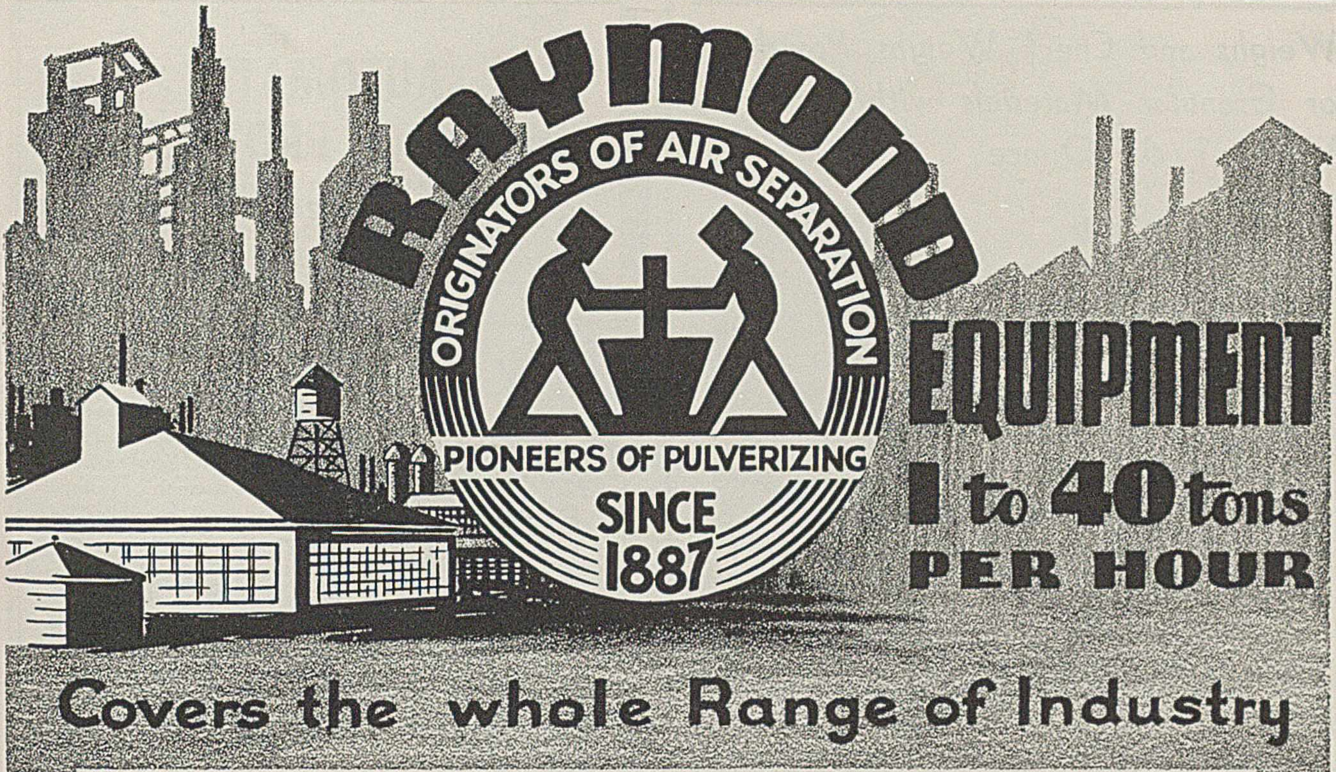

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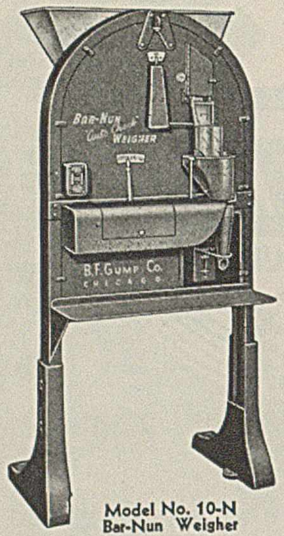
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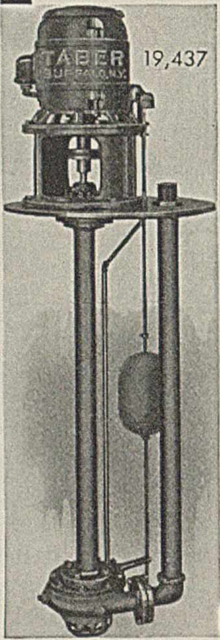
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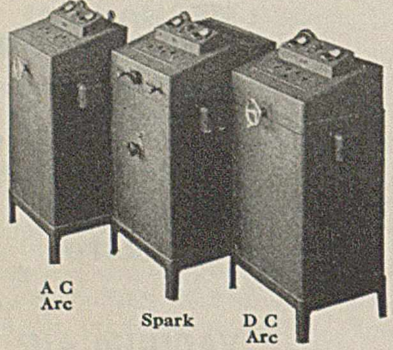
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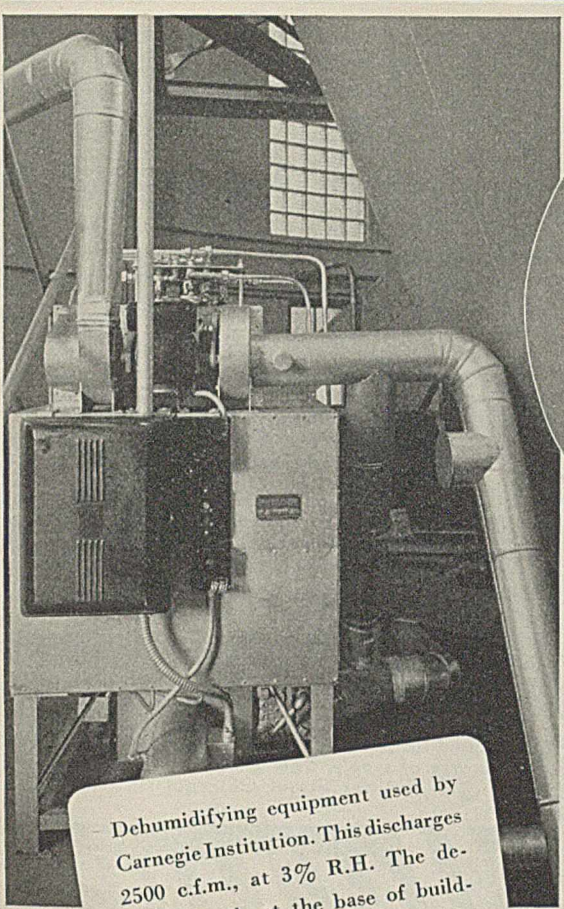

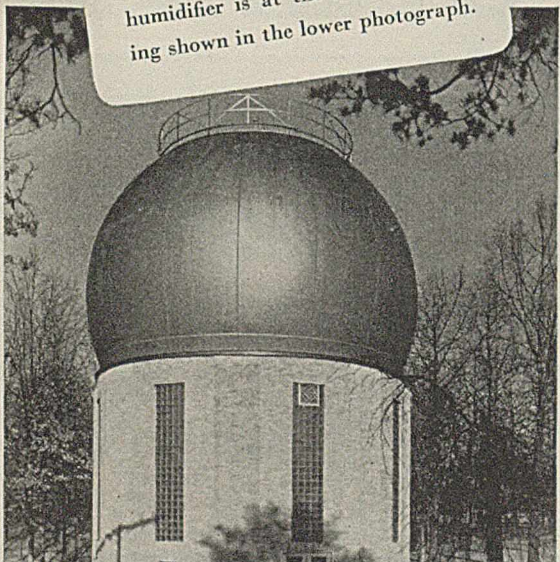

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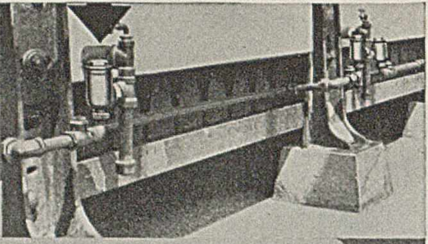

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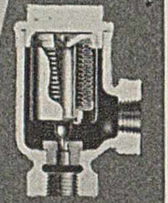

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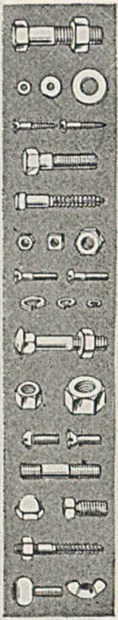

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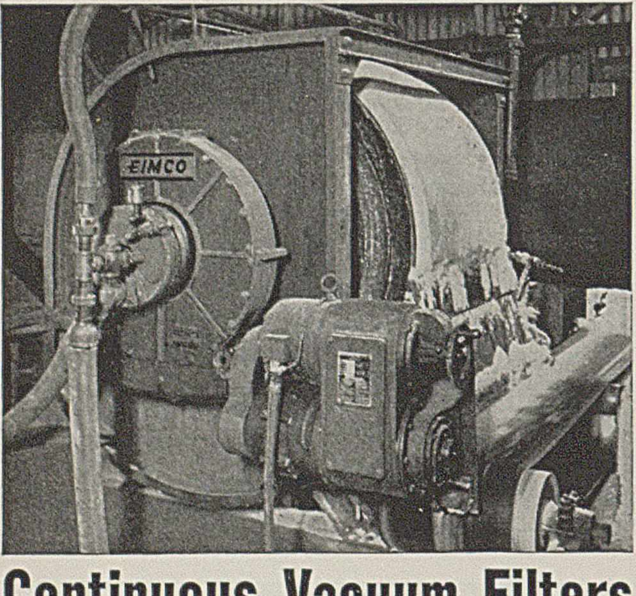

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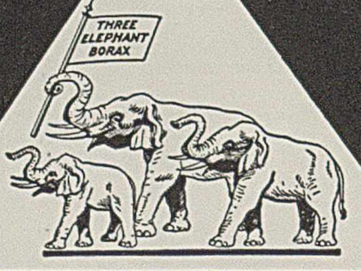

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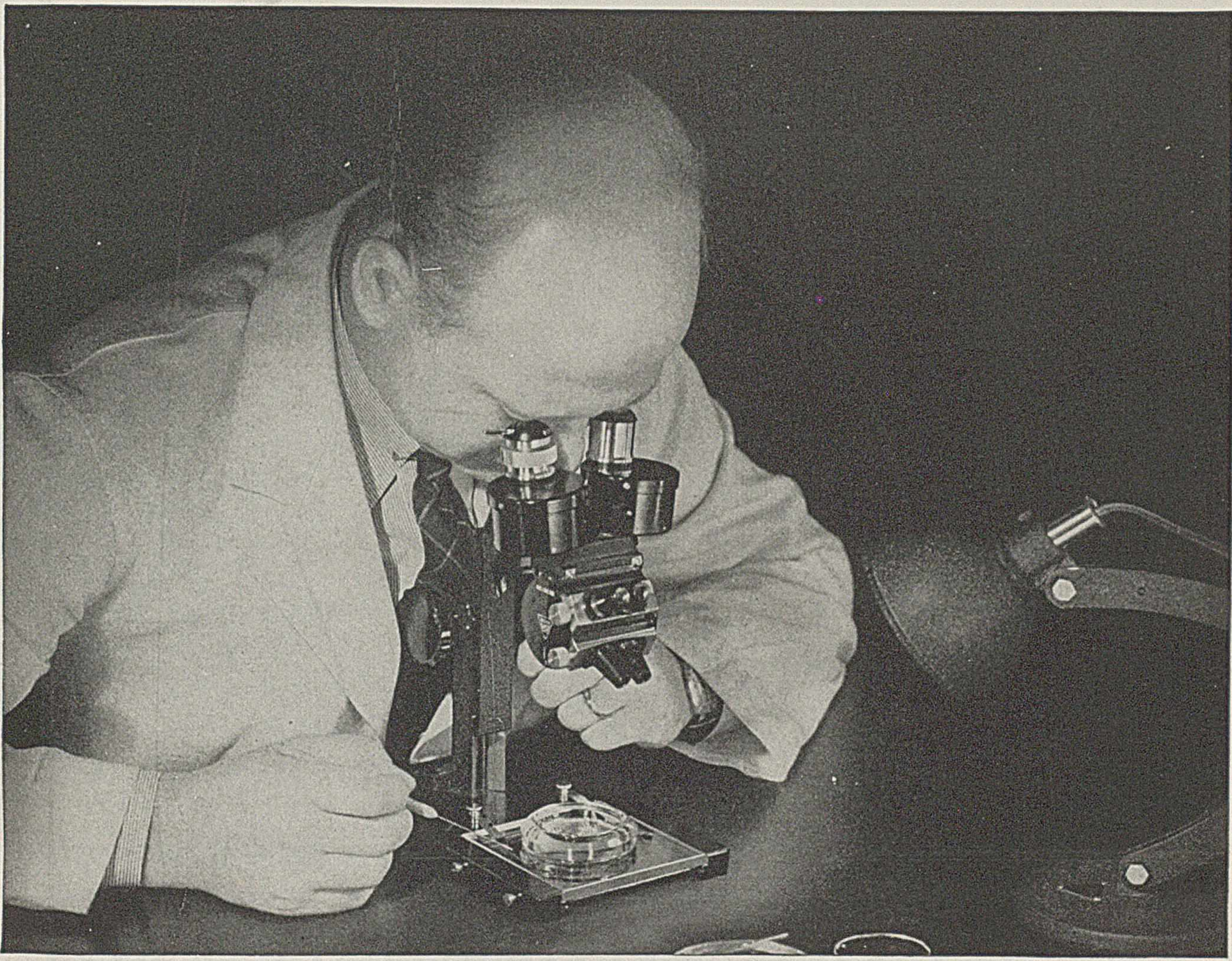

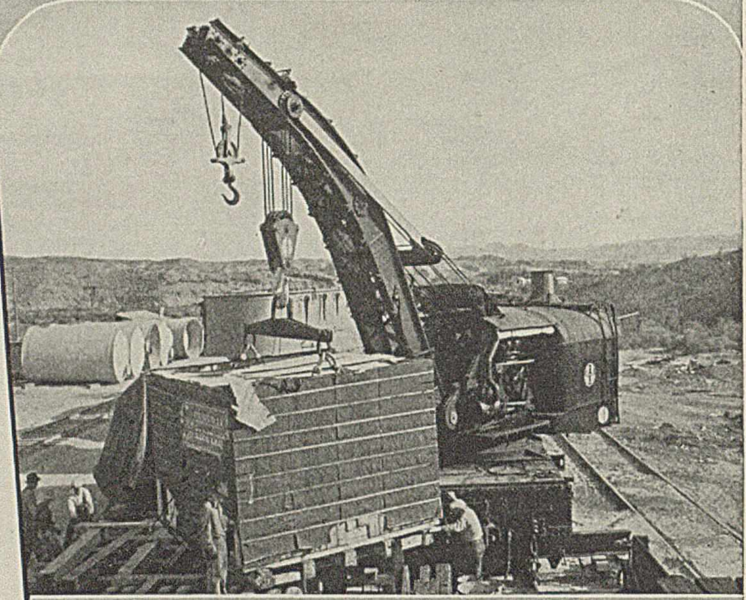

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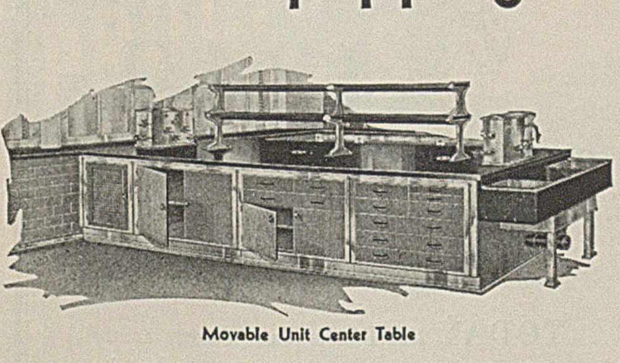
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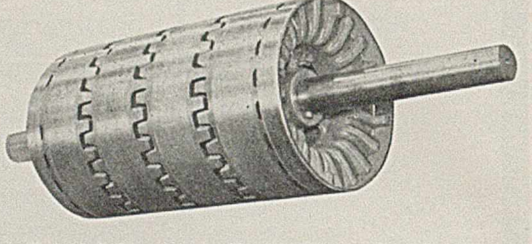

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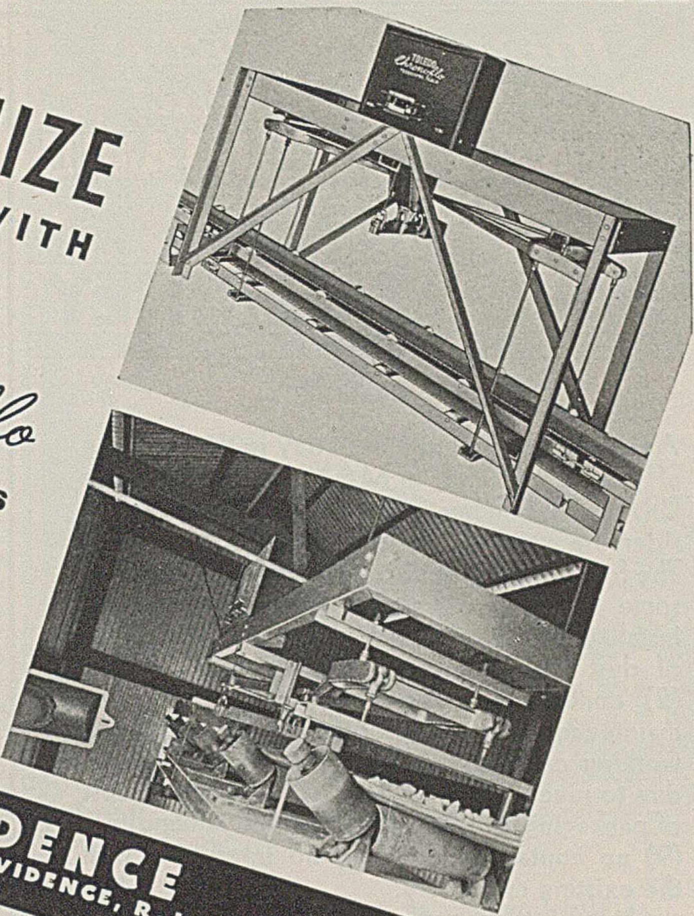

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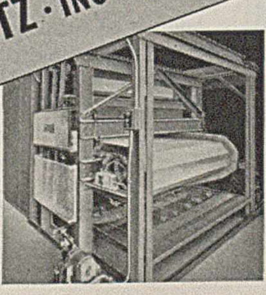

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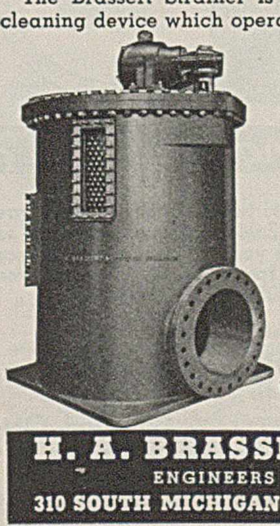

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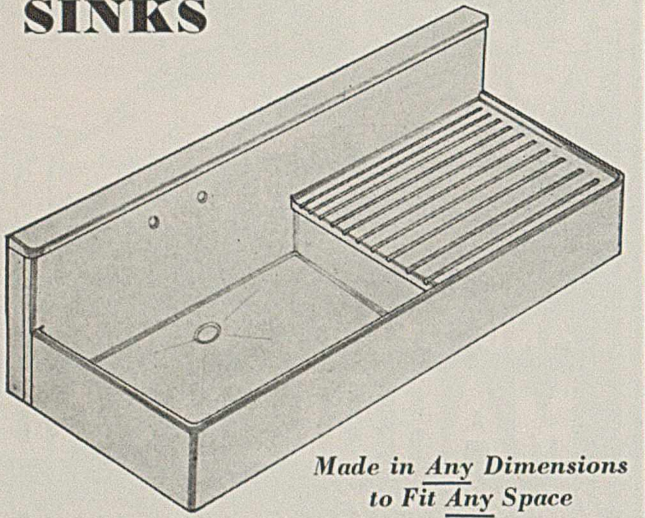


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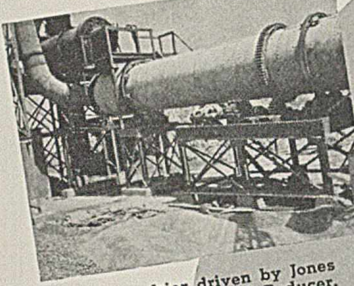

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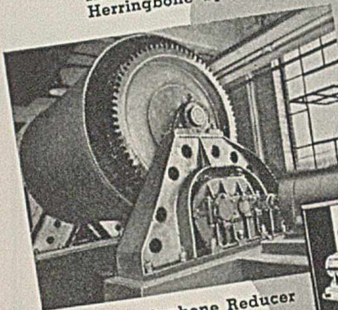

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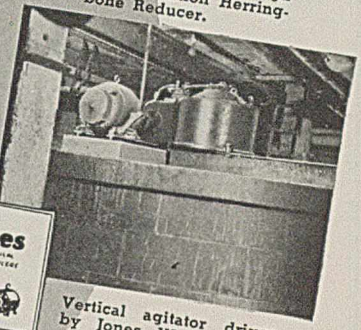

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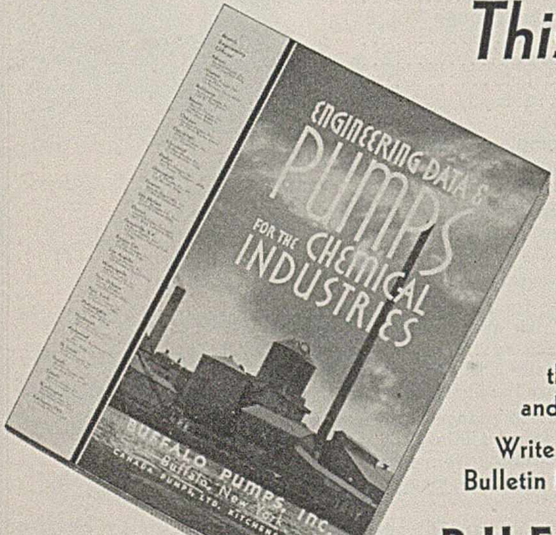

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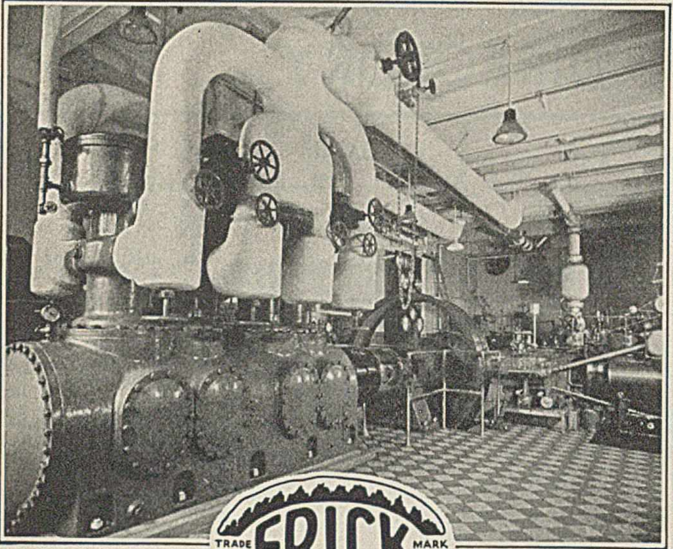

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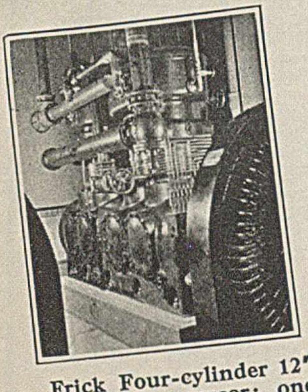

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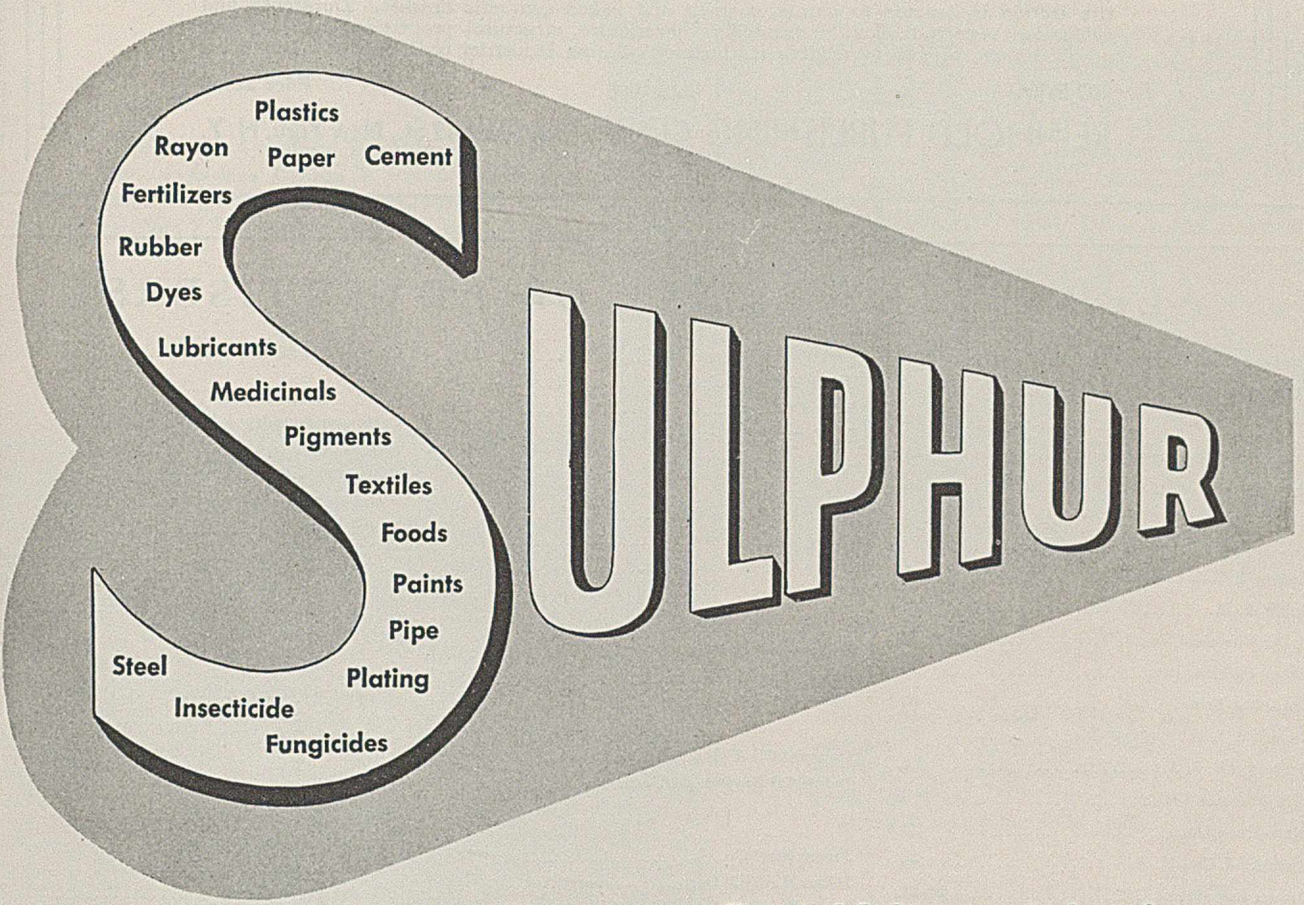
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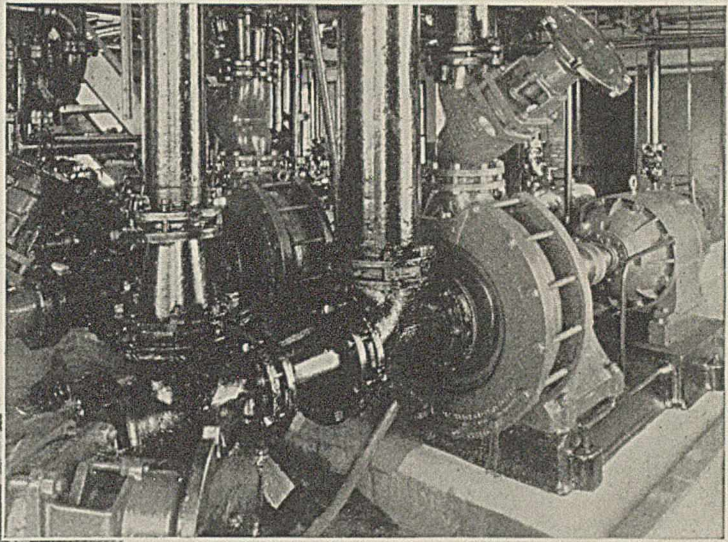

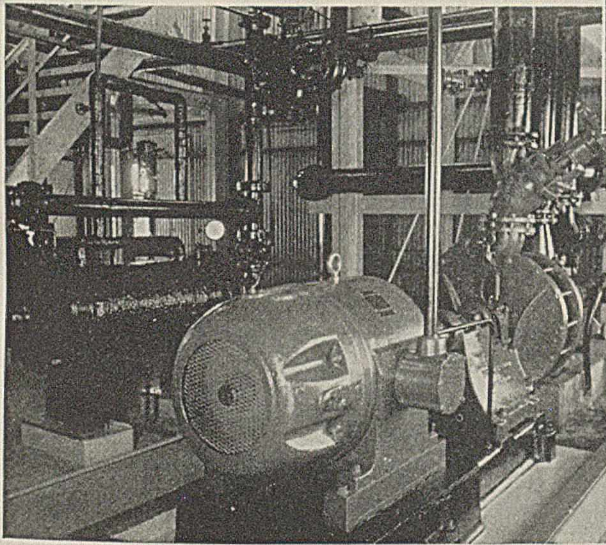

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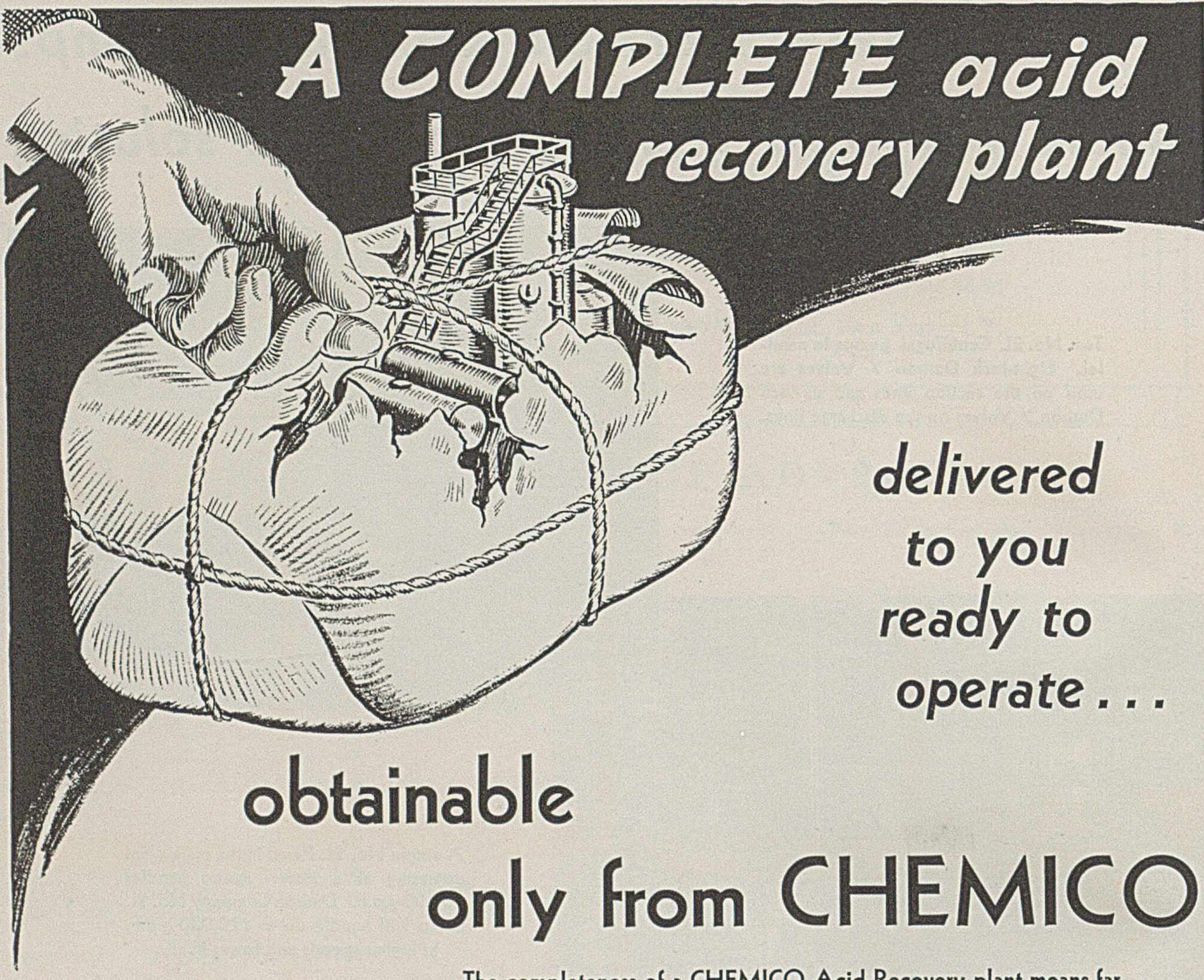

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CHEMICO completeness begins with a thorough analysis of individual plant requirements by experienced acid technologists. Then follows the correct selection of proven processes, or, if necessary, the origination of required processes fully tested by pilot plant operation. Many of the processes and much of the equipment in CHEMICO plants are patented and exclusive, and provide results not otherwise obtainable. And finally, after skillful design and erection of buildings and installation of equipment have been accomplished, CHEMICO completeness further includes initial operation of the plant and thorough training of the operating crew before delivery.

CHEMICO completeness, backed by 25 years of specialized experience and extensive resources, supplemented by a guarantee of design, material, workmanship, and performance, and proven by installations all over the world, has made CHEMICO the recognized headquarters for acid recovery processes and plants. Inquiries are invited, with the assurance that all information will be held strictly confidential.

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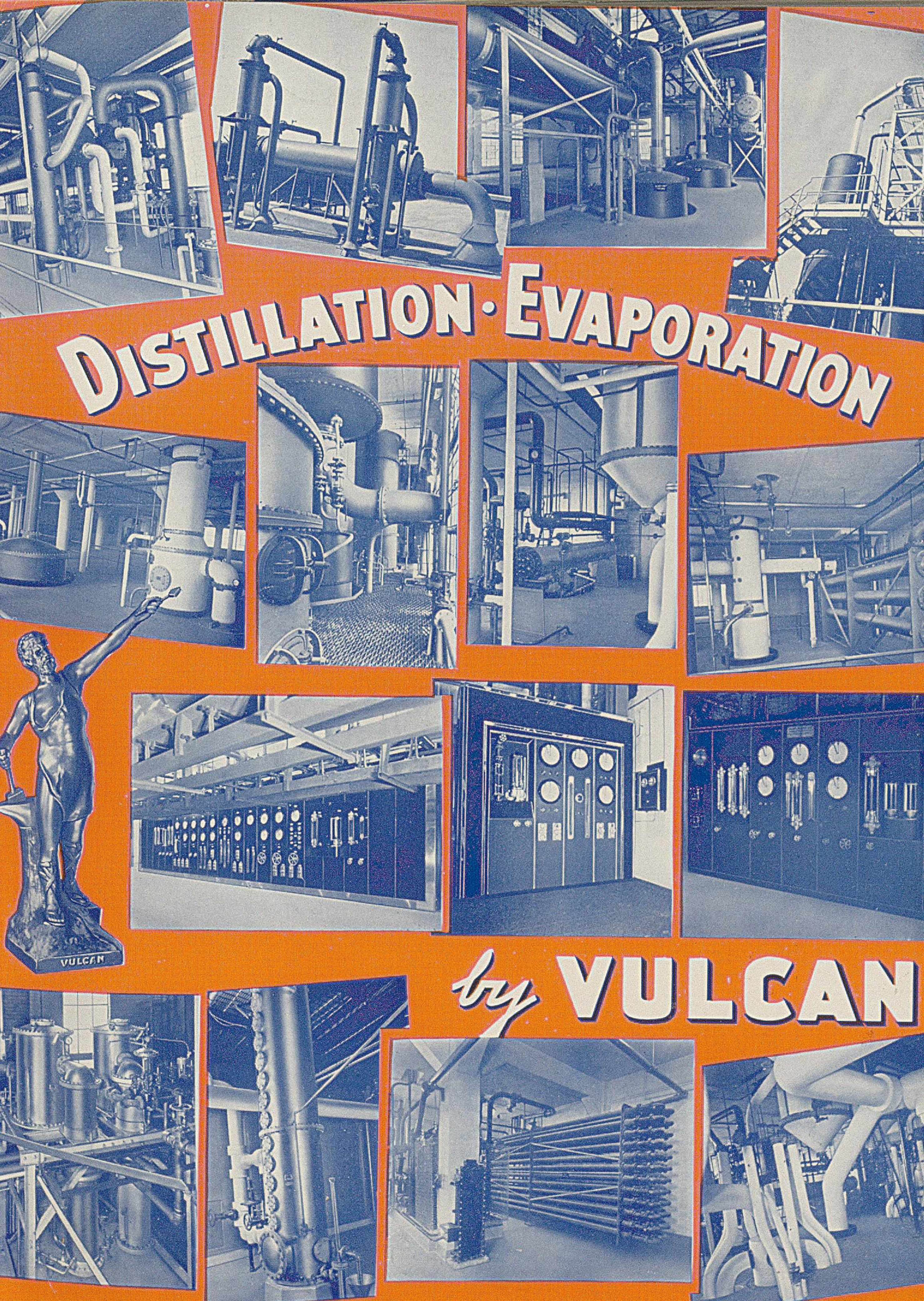
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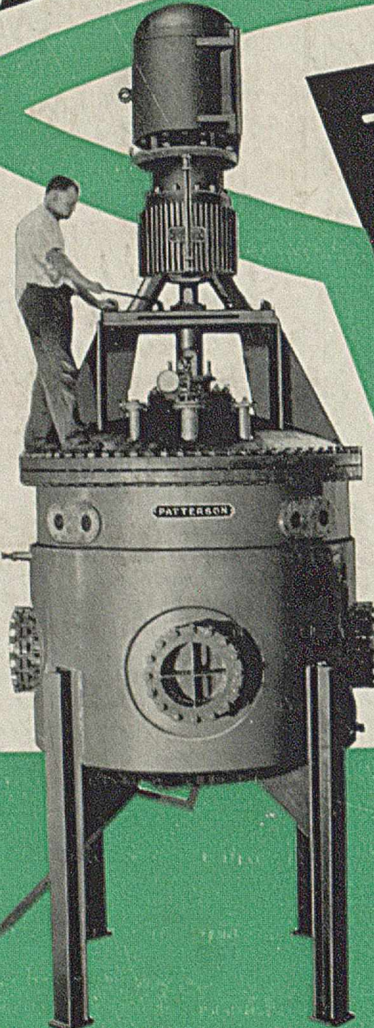

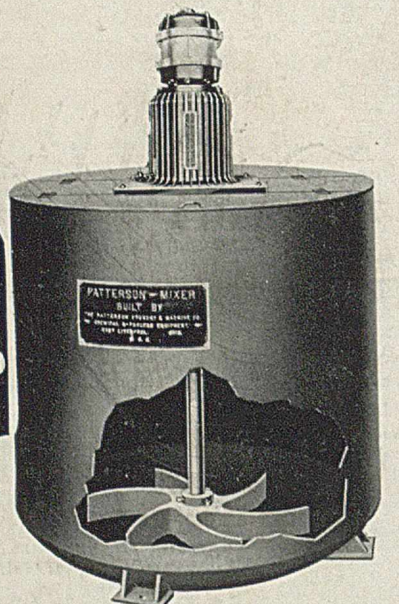

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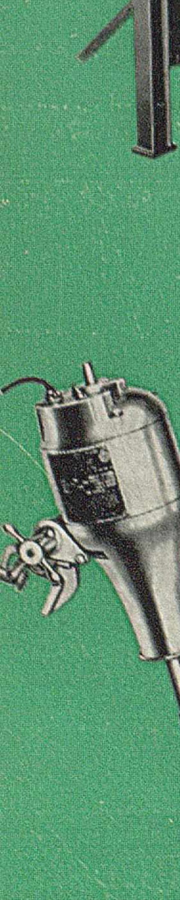

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